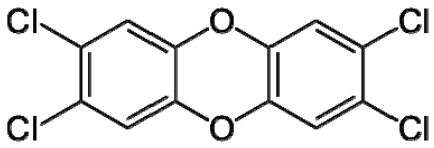
BACWA Guidance Document

Part I: Sampling and Analysis Planning

for

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS By Method 1613 Revision B (October 1994)



March 1, 2010

Foreword

The BACWA Laboratory Committee was tasked with preparing a sample collection and data review guidance document to be used in support of Dioxin/Furans testing by EPA Method 1613, High Resolution-Gas Chromatography/Mass Spectrometry (Revision B).

The sampling guidance has been developed at two levels. It encompasses both the actual plant-level sampling procedures and how to develop a Sampling Plan. Data quality objectives serve as a foundation for the overall program of handling Dioxin/Furan testing. This guidance has used sources from private laboratories, consultants, and government agencies related to sampling procedures and sampling plans for Dioxin/Furan testing. This guide is also intended to be a training tool for staff who collect samples from wastewater treatment plants. Part I of the guidance document discusses basic sampling plan development, establishing data quality objectives, options for what quality control samples to collect, and best-available practices to assure the highest level of sample integrity for Dioxin/Furan sampling. An example template for Dioxin/Furans sampling is included in Part I to aid BACWA members in advancing their own procedures.

The BACWA Laboratory Committee was also tasked with developing guidance for performing data quality assessment once a laboratory report is received. The additional section, (Part II), is based on revised "Attachment G" requirements from the California Regional Water Quality Control Board, San Francisco Bay Region, March 2010. Part II provides guidance for performing data review of Method 1613 Dioxin/Furan laboratory reports. This includes guidance for calculating Dioxin-TEQ based on "Attachment G", discussion regarding commonly used terms for Dioxin/Furans testing, case study presentations to illustrate issues when reviewing Dioxin/Furan data, instructions for handling contract laboratories, and how to work with data requiring qualification or rejection. Part II includes an Excel spreadsheet for manually calculating Dioxin-TEQ and a template checklist for Dioxin/Furans data review.

The BACWA Laboratory Committee is indebted to many hard-working volunteers from public wastewater treatment plant laboratories and private laboratory staff who collectively contributed to the development of this guidance document. Without their time, effort, and expertise, this guidance document would never have been realized. The BACWA Laboratory Committee would like to extend its appreciation to the following agencies and private laboratories:

Frontier Analytical Laboratory
Vista Analytical Laboratory
Maxxam Analytics
TestAmerica, Inc
City of Benicia
East Bay Municipal Utility District (EBMUD)
City of Sunnyvale

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1.0. Background Information for Dioxin/Furans Testing

1. 1 Regulatory Requirements for Dioxin/Furans Monitoring in Wastewater Treatment Plant Effluent

The EPA's Water Quality Objective (WQO) for Dioxin, as established in the California Toxics Rule (CTR) is a Dioxin-TEQ of 0.014 pg/L for the protection of human health. The State Implementation Plan (SIP) requires a limit for 2,3,7,8-TCDD, if a limit is necessary, based on reasonable potential and requires monitoring for 3 years by all major NPDES dischargers for the other 16 Dioxin and Furan compounds. Reasonable Potential Analysis (RPA) is based on comparing the Maximum Effluent Concentration from a given discharger to the WQO of 0.014 pg/L Dioxin-TEQ. The Federal Register Notice from May 18, 2000 details the California Toxics Rule and Chapter 5 of California's State Implementation Plan.

1.2 Chemical Structure of Dioxin and Dioxin-Like Compounds

Dioxin and "Dioxins-like" compounds refer to structurally similar chemicals, including some polychlorinated biphenyls (PCBs). They have the ability to alter the pattern of growth and differentiation of a number of cellular targets by initiating a series of biochemical and biological events, resulting in the potential for a spectrum of cancer and non-cancer responses in animals and humans.

Several hundred of these toxic compounds exist and are members of three closely related families: the polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and certain polychlorinated biphenyls (PCBs). Sometimes the term Dioxin is used to refer to the most heavily studied, and one of the most toxic Dioxins which is 2,3,7,8-tetrachlorodibenzo-p-Dioxin (2,3,7,8-TCDD).

A polychlorinated dibenzodioxin (PCDD) is two benzene rings joined together by two oxygen atoms (Figure 1). In Method 1613, the same compound is referred to as a "CDD" (Chlorinated Dibenzo-p-Dioxin). A polychlorinated dibenzo-furan (PCDF) is similar but has only one oxygen atom (Figure 2). In Method 1613, the same compound is referred to as a "CDF" (Chlorinated Dibenzofuran). In the California State Implementation Plan (SIP), the terminology of CDD and CDF is used to refer to the two families of chemicals (chlorodibenzo-p-dioxins [Dioxins] and chlorodibenzo-p-furans [Furans]). This Guidance document will refer to these families of chemicals as Dioxin/Furans.

The chemical structure for 2,3,7,8-Terachoro-p-dioxin is shown in (Figure 3) where the substitution of chlorine at 2, 3, 7, and 8 are illustrated on the ring structure:

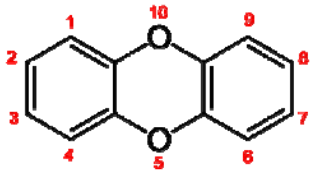


Figure 1:
Polychlorinated Dibenzo-p-dioxin ring structure

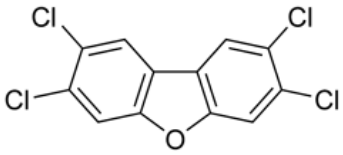


Figure 2:
2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF)

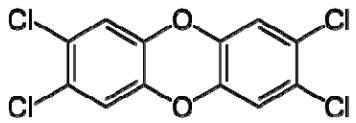


Figure 3.
2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

1.3 Sources of Dioxins and Dioxin-Like Compounds

Understanding the potential sources of Dioxin/Furans is very important for designing a meaningful "Sampling and Analysis Plan" which will ensure accurate conclusions from the analytical testing. Dioxin/Furans are not created intentionally, but are produced inadvertently by a number of human activities and natural processes. Dioxin/Furans are released into the air from combustion processes such as commercial or municipal waste incineration and from burning fuels (i.e. wood, coal, or oil). Dioxin/Furans can also be formed when household trash is burned and during forest fires. Chlorine bleaching of pulp and paper, certain types of chemical manufacturing and other industrial processes all can create small quantities of Dioxin/Furans. Cigarette smoke also contains small amounts of Dioxin/Furans. Even if all human-generated Dioxin/Furans could somehow be eliminated, low levels of naturally produced Dioxin/Furans would still be introduced into the environment.

When released into the air, some Dioxin/Furans may be transported long distances. Because of this, Dioxin/Furans are found worldwide. When Dioxin/Furans are discharged into water, they tend to adhere to and settle with sediments where they can be further transported or ingested by fish and other aquatic organisms. Dioxin/Furans are broken down in the environment very slowly and, when deposited on plants, can be bio-accumulated through the food chain by animals and aquatic organisms. In animals, Dioxin/Furans tend to accumulate in the fat tissue. It is currently unknown what the natural background level of Dioxin/Furans is in the environment. The ambient background levels of Dioxin/Furans are assumed to consist primarily of man-made sources. The uncontrolled burning of residential waste and accidental fires at landfills are thought to be among the largest sources of Dioxin/Furans in the environment in the U.S. Municipal sources are a very small contributor of the Dioxin/Furans load to the SF Bay, and the likely dominant sources are from current and historical air emissions.

Interferences co-extracted from samples will vary from source to source, depending on the diversity of the site being sampled. The most common interferences include chlorinated biphenyls, methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. The laboratory will apply cleanup steps to reduce or eliminate these interferences which allow reliable determination of the Dioxin/Furans. If these interferences are known to be present in significant quantities in a sample, it is always advisable to alert the laboratory.

Interviews with the private laboratories who volunteered to support the development of this Guidance document stated that there are very little interferences of concern for typical wastewater final effluents. The exception would be if an Agency sends a mid-process sample that has not been subject to all of the treatment steps of a final effluent. The Chain of Custody (COC) submitted by the Agency should clearly indicate if this is the case so that the contract laboratory can be prepared for any additional cleanup steps not normally applied to 'typical' wastewater effluent samples.

2.0 Considerations for Establishing an Effective "Sampling and Analysis Plan"

For permit compliance, a "Sampling and Analysis Plan" with established Data Quality Objectives (DQO's) is necessary to ensure that the accuracy and precision of the data generated are known. Having detailed procedures for sampling helps assure the integrity of the wastewater sample. Having an established set of quality control (QC) checks with data quality objectives (DQO's) helps ensure that the data reviewer develops the correct conclusions from the testing effort. All phases of assuring compliance rely on the provision of accurate, precise, comparable, and complete analytical data which is accomplished by having a detailed "Sampling and Analysis Plan" with DQO's.

2.1 Quality Control (QC) Check Program Overview

The following summary (Table 1) details the various quality control checks that should be considered for incorporation into a comprehensive "Sampling and Analysis Plan". By developing a comprehensive set of QC checks and carefully evaluating QC data generated by the laboratory, all data generated will be of known quality.

Table 1

<table>
<tr><th>Dioxin/Furans
QC Parameters</th><th>Laboratory-Related QC</th><th>Sample and Collection
QC</th></tr>
<tr><td rowspan="2">Negative Controls

Assures there is no background contamination affecting sample results</td><td rowspan="2">Method Blank</td><td>Equipment Blank</td></tr>
<tr><td>Field Blank</td></tr>
<tr><td>Positive Control-Accuracy

(%Recovery)

Assures results are accurate</td><td>Laboratory Control Sample-

Batch Level QC Verification

(For Method 1613, this is the OPR check)</td><td>Matrix Spike-

For Method 1613, labeled isotopes are spiked in each wastewater sample as an indication of matrix effects.

Agencies can request that unlabeled Dioxin/Furans be spiked in their sample</td></tr>
<tr><td rowspan="2">Positive Control-Precision

(Relative Percent Difference or RPD)

Assures results are precise</td><td rowspan="2">Laboratory Control Sample (OPR Check)

The precision data for the laboratory comes from it control charting OPR results from each batch over time.</td><td>Replicate Samples-

Calculate limits from historical data at own wastewater treatment plant</td></tr>
<tr><td>Matrix Spike, Matrix Spike Duplicate-

Calculate limits from historical data at own wastewater treatment plant</td></tr>
</table>

***A double blind check sample is prepared by a Performance Testing vendor. It is reagent water spiked with Dioxin/Furans and made to look like a real sample. The vendor will provide a certificate for acceptable performance so the laboratory's results can be evaluated.**

2.2 Sampling Considerations

The two prime objectives of the sampling effort are to maintain the physical/chemical composition of the sample and to prevent contamination. To meet these objectives, there must be a measure of control over all sample-handling procedures including sample container selection, materials which come in contact with the sample, and transport to the laboratory.

There are several aspects to meeting these two sampling-related objectives:

- Selecting the proper container
- Selection of materials which come in contact with the sample during collection
- Using the correct preservation strategy
- Establishing standard operating procedures for sample collection
- Assuring that the sampling team are trained to apply the procedures correctly
- Implementing reliable sample shipping methods

In support of assuring all of these aspects are correctly executed, QC checks generated during sampling are strongly recommended (i.e. Equipment Blanks, Field Blanks) to provide assurance that positive detects for Dioxin/Furans are not from contamination.

One additional consideration is collecting homogenous samples for replicates. With respect to wastewater sampling, the greatest source of variability comes from fluctuation in total solids. This is because Dioxins/Furans tend to concentrate in organic phases which are the 'solids' in wastewater samples. Samples whose percent solids levels vary significantly between replicates will have less agreement between replicates. The timing for collecting sample replicates should be within 'minutes' to reduce the impact of this factor. Typical wastewater effluents do not present problems when processing due to solids levels, which are generally 5% or less. However, variability in solids levels between replicates should be a concern when assessing sample replicate data.

Selection of the sampling point and sampling equipment are also important. The most likely source of field-related contamination is from re-use of sampling equipment and containers (grab samplers, tubing, buckets, bottles, etc). The issue relates to build up of organic materials in the re-used containers and Dioxins/Furans concentrating into an organic layer. Sampling from a dedicated port may also be subject to organic build-up and may lead to false positive detections as Dioxins/Furans may accumulate over time in the port. Some Agencies have developed strategies of sampling the effluent to avoid this potential problem, One example is the use of a portable peristaltic pump with new silicon tubing and pre-cleaned bottles with Teflon™-lined caps for each sampling event. More details on collection will be presented in Section 3.0.

2.2.1 Containers

The required containers for Discrete or Composite Sampling is summarized below:

a. Sample bottles and caps
b. Liquid samples (waters, sludges and similar materials containing 5% solids or less) - Use a sample bottle made of amber glass, 1.1 L minimum volume, with a screw cap.
c. If amber bottles are not available, samples shall be protected from light.
d. Bottle caps—Threaded to fit sample bottles. Caps shall be lined with fluoropolymer (i.e. Teflon™).

Interviews with the contract laboratories concurred that pre-cleaned 1.1 L bottles with Teflon™ lined caps from reputable vendors do not present problems with background contamination. While Method 1613 states a cleaning protocol in Section 6.1.1.5, less handling of the "pre-cleaned" sampling containers and bottle caps is preferable based on guidance from Dioxin/Furan testing laboratories. It is strongly suggested to never re-use sampling containers or equipment even if using the cleaning protocol. Based on interviews with the contract laboratories, re-used equipment is the most likely source of problems. Using 'pre-cleaned' bottles or new materials in contact with samples (composite sampler liners, bottles, silicon tubing, Teflon™ tubing, etc) each time is the most cost-effective approach in the long-run.

2.2.2 Compositing Equipment

Agencies who use an automatic or manual compositing system need to incorporate glass containers that are pre-cleaned by a reputable vendor. Only new glass or new fluoropolymer tubing (i.e. Teflon™) shall be used. If the composite sampler uses a peristaltic pump, a minimum length of new, compressible silicone rubber tubing may be used in the pump once. Before use, any tubing (silicone, Teflon™, etc) may be thoroughly rinsed with analytical grade methanol, followed by repeated rinsing with reagent water to minimize sample contamination. Based on a review of Method 1613 and interviews, new Teflon™ or silicon tubing are acceptable materials for use in sampling equipment.

Should cleaning be incorporated into the Agency's "Sampling and Analysis Plan", the methanol used for cleaning a composite sampler must meet the following specifications: distillated in glass, pesticide quality, and lot-certified to be free of interferences. It is recommended that the lot-certificates be retained should further review by the Agency be required to eliminate the cleaning step as a source of positive detections for Dioxin/Furans.

2.2.3 Reagent Water for Equipment Cleaning, Equipment Blanks, and Field Blanks

Typical water purification systems used by Agencies for their in-house testing are not known to contribute to background contamination of Dioxin/Furans. The purchase of ultra pure water from major vendors for equipment cleaning, equipment blanks, and field blanks is also not known to result in false positives from its use.

2.2.4 Preservation, Storage, and Holding Times

Samples are to be collected in amber glass containers following conventional sampling practices which are detailed in the "*Standard Practice for Sampling Water,"* ASTM Annual Book of Standards, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980. Aqueous samples that flow freely are collected in refrigerated bottles using automatic sampling equipment per Method 1613.

Agencies are to use instructions from the Methods Update Rule (MUR), March 2007 (40 CFR part 136) for Preservation, Storage, and Holding Times. The MUR supersedes instructions provided in Method 1613, Section 8.0 which are slightly different.

- The acceptable temperature range for storing samples under the MUR for Dioxin/Furan testing is ≤6°C.
- If samples contain residual chlorine, add 0.008% sodium thiosulfate to de-chlorinate the sample.
- The holding time for adding de-chlorinating agent is less than 15 minutes.
- After receipt by the contract laboratory, it will check the pH of the sample and adjust the pH to <9 prior to extraction.

Contract laboratories do expect that Agencies will send samples that have been de-chlorinated within 15 minutes of sampling. If residual chlorine is present, the laboratory will provide that information in the final report to the Agency.

2.2.5 Negative Controls

Because of the ability of Dioxin/Furans to become airborne from combustion processes (i.e. incineration, fires, cigarette smoke) and to accumulate in organic matrices, there is a significant probability that low level detections of Dioxin/Furans may be field- or laboratory-related and not actually in the effluent tested. This, coupled with testing requirements in the low part-per-quadrillion (pg/L) detection range, makes the need for a rigorous Quality Control (QC) strategy necessary for sorting variables if positive detections are reported.

Equipment and Field Blank information may help the Agency determine if positive detects are related to the field sampling effort. If the water or preservative become suspect, a "Reagent Water with Preservative" QC check should be considered. If this QC check is planned, Agencies will need to devise a system to use the same lot of bottles/preservatives/reagent water for the Equipment Blank and Field Blank. However, based on discussions with Dioxin/Furan testing laboratories, reagent water and de-chlorination reagents are not usually a problem.

The "Sampling and Analysis Plan" is recommended to discuss detailed procedures for the collection of both Equipment Blanks and Field Blanks. These quality control checks can be used to objectively rule out background contamination from sampling. The following definitions for these QC measures are summarized below:

a. Equipment Blank-A sample of analyte-free water which has been used to rinse common sampling equipment to check the effectiveness of the decontamination procedures or verify that new materials in contact with samples do not contribute Dioxin/Furans.

b. Field Blank-This blank is prepared during sampling by filling a clean container with analyte-free reagent water in such a way that ambient sources of Dioxin/Furans may be detected.

These QC checks should be retained by the Agency under the storage conditions specified in Table II (MUR) and only analyzed if there are positive detects in the samples.

Should there be unexpected positive detections for Dioxin/Furans, the contract laboratory should be able to eliminate itself as a source of contamination by providing its Method Blank and instrument level background checks upon request. The combination of Equipment Blanks, Field Blanks, and the laboratory's background checks can be used to identify if the positive detection is field-related, laboratory-related, or sample-related. More information regarding laboratory-related QC checks are detailed in Part II.

2.2.6 Positive Controls

2.2.6.1 Accuracy Determination from Samples (Matrix Spike)

Dioxin/Furans testing by Method 1613 does present differences in terminology and approaches for evaluating the effect of the matrix on Dioxin/Furan results. In traditional environmental testing, target analytes are spiked into an aliquot of a sample which is known as a Matrix Spike (MS). After adjusting for background levels of target analytes in a sample, accuracy from the matrix is determined.

For Method 1613, 15 isotopically labeled analogues of the 2,3,7,8-substituted Dioxin/Furans are added to each wastewater sample. These isotopically labeled analogues are added before extraction and are used to represent the performance of each corresponding unlabeled 2,3,7,8-substitured Dioxin/Furan in the sample. When the laboratory reports a positive result for the corresponding Dioxin/Furan, it is adjusted for the performance of the isotopically labeled analogue. This technique is known as Isotope Dilution which is fully discussed in Part II of this Guidance under Section 1.1.7.

While not directed by Method 1613, an Agency can instruct its laboratory to spike its own wastewater sample with unlabeled target analytes in accordance with the Agency's own "Sampling and Analysis Plan". However, use of isotopically labeled analogues of the 2,3,7,8-substituted Dioxin/Furans makes the MS QC check unnecessary. Should the Agency still desire the MS QC check, one additional liter of sample is submitted above the two liters required for testing from one location.

2.2.6.2 Precision Determination from Samples (Matrix Spike Duplicate or Sample Duplicate)

Determination of precision from sample measurements can be accomplished through the use of a Matrix Spike Duplicate (MSD) or analysis of the same sample in duplicate (Duplicate Sample).

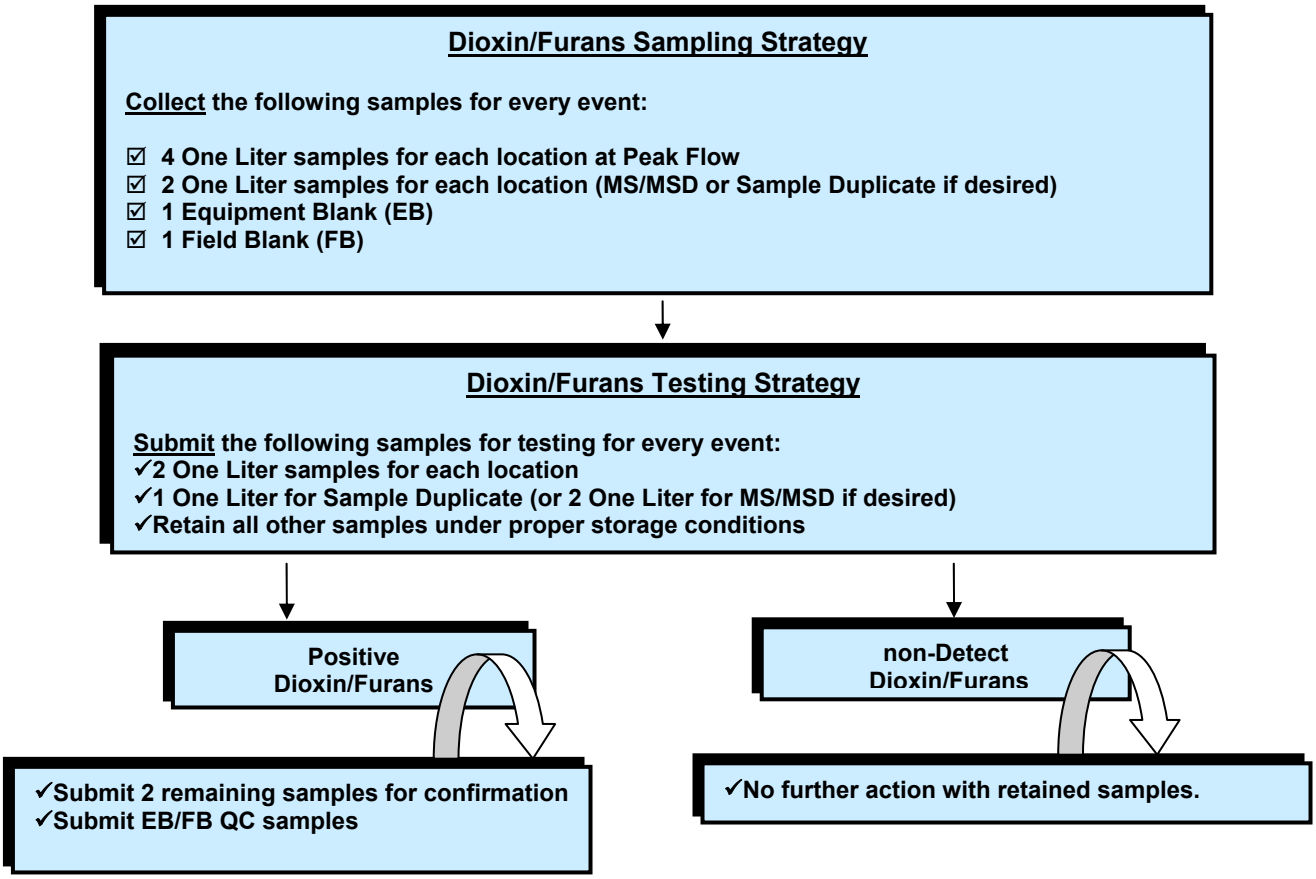
As with the matrix spike, the use of isotopically labeled analogues of Dioxin/Furans for an MSD makes this QC check unnecessary. Should the Agency still desire an MS/MSD using unlabelled Dioxin/Furans as part of its own "Sampling and Analysis Plan", the laboratory will require two additional liters above the two liters needed for testing from one location.

If precision is determined from a Duplicate Sample, one additional liter is required above the two liters needed for testing from one location.

2.2.7 Suggested Sampling and Testing Strategies

In support of a "Sampling and Analysis Plan" that takes a quality system approach to Dioxin/Furan testing, not all of the QC samples need to be submitted to the contracted laboratory initially. In order to manage cost, the following strategy summarized in Table 2 may be considered for submitting samples:

Table 2



Due to the stability of Dioxin/Furans, an Agency may hold its retained samples depending on the outcome of the initial testing round for up to 1 year, as long as, all preservation and storage requirements specified in Table II of the MUR are followed. The Agency is advised to document that its storage conditions for retained samples met the requirements of Table II during extended periods resulting from re-testing. Should

Dioxin/Furans be detected, the Agency can initiate analysis of its retained samples and Equipment Blank/Field Blank QC samples to aid in assessing the source of positive detections.

2.2.8 Additional 'Sampling Related' Recommendations

Some Agencies have implemented the use of "Clean Hands/Dirty Hands" sampling procedures for Dioxin/Furans testing to avoid false positives in their effluents. This document provides examples of applying the "Clean Hands/Dirty Hands" protocol for Dioxin/Furans sampling.

In general, wastewater effluent samples do not have problems with background contamination, as long as, pre-cleaned containers and new sampling tools (Teflon™ tubing, silicone tubing, buckets, grab samplers, bailers, liners, etc) are used. The more likely source of background contamination detected in equipment or field blanks comes from re-used equipment (i.e. bailers, dedicated sampling ports), smoking during sampling, smokers performing sampling, high levels of dust, or idling combustion engines (trucks, generators, etc) in proximity to sampling.

As a precaution, Agency's should instruct the sampling staff to note the presence of traffic-related combustion sources in the event that sampling occurs in a highly urban area surrounded by freeways. Dioxin/Furans congener patterns are distinct if their source is from combustion. Any detections in the Agency's QC or samples should be checked for congener patterns related to combustion if suspected.

2.3 Establishing Data Quality Objectives (DQO's)

It is recommended that an Agency establish DQO's for its QC checks to assure all data generated are of known quality. Table 3 below represents example DQO's for an Agency's QC checks. The Agency can modify this table to specify its own DQO's established in its "Sampling and Analysis Plan".

Table 3.

QC Check	Suggested Data Quality Objectives (DQO's)
Equipment Blank	**Less than ML stated in Table A, "Attachment G"**
Field Blank	**Less than ML stated in Table A, "Attachment G"**
Sample Matrix Performance-For EPA Method 1613, labeled Dioxin/Furans are spiked in each wastewater sample as an indication of matrix effects.	**Individual samples must meet %Recoveries from Table 7 or Table 7A of Method 1613.** **Qualify results exceeding these limits**
MS/MSD-An Agency may request the laboratory spike with unlabeled Dioxin/Furans list and chart ongoing results for every 20 samples	**%Recovery = ±50%** **RPD = 50%** **Qualify results exceeding these limits**
Replicate Samples-Calculate limits from historical data at own wastewater treatment plant or use starting limit provided in this guidance	**RPD = 30% if results are >5X the ML** **RPD = 50% if results are <5X the ML** **Qualify results exceeding these limits**

The contract laboratory must meet all requirements for EPA Method 1613 and qualify any data not meeting the specifications. Please review Appendix 4, Part II of this Guidance document for Laboratory DQO's.

When selecting a contract laboratory for performing testing, the agreement between the Agency and laboratory should state that analysis is performed using EPA Method 1613 and that the laboratory should hold California Department of Public Health accreditation (CA DPH ELAP) for Method 1613. Additional instructions for the contract laboratory from an Agency are recommended under Part II, Section 3.0 of this guidance document.

3.0 Best Practices for Sampling Dioxin/Furans

Several Agencies were interviewed and focus points provided below from their best practices to minimize field contamination when sampling. This section is broken down into best practices for composite sampling, grab sampling, and "Clean Hands-Dirty Hand" procedures.

3.1 Composite Sampling – For Dioxin/Furans sampling, Agencies are recommended to use an automatic composite sampler that is clean and contains new flexible Teflon™ pump tubing for each sampling event for Dioxin/Furans. The sample collection container used in the automated sampler must have adequate capacity for all planned analysis. The sample collection container must meet the specifications detailed in Part I, Section 2.2.1 a-d.

If a sample is to be collected for a discharge of 12 hours or less, the frequency of sample collection should be at shorter intervals and a high volume to help assure a representative sample of adequate volume.

3.2 Grab Sampling - A grab sample is defined as an individual sample collected "all in one motion". Grab samples represent the conditions that exist at the moment the sample is collected and do not necessarily represent conditions at any other time. For surface grab samples, it is best not to use sample containers containing pre-measured amounts of preservatives as they can be diluted out during the collection process. For samples requiring de-chlorination, add preservative within 15 minutes of collection. Where practical, use the actual sample container submitted to the laboratory for collecting samples. This procedure eliminates the possibility of contaminating the sample with an intermediate collection container and not being able to track it as a source.

a. Direct Container-When collecting a grab sample directly into the container, follow these steps:

1. Submerge the container, neck first.
2. Invert the bottle so the neck is upright and pointing into the flow (if applicable).
3. Return the filled container quickly to the surface.
4. Pour out a few mL of sample. This procedure allows for addition of sodium thiosulfate to de-chlorinate the sample (if required) and for sample expansion.
5. Secure the cap onto the container and label.

b. Pole-If sample containers are attached to a pole via a clamp, submerge the sample container and follow steps 3.2.a.3 to 3.2.a.5 above

c. Peristaltic Pump-Dioxin/Furans may also be collected using a battery operated peristaltic pump and flexible silicon tubing (i.e. ISCO Accuwell 150 Portable Peristaltic Pump).

Example:

Clamps are cinched down to prevent wobbling of the tubing during sample collection.

1. When using a peristaltic pump, new tubing is to be used with each sampling event (i.e. Nalgene Flexible Silicon Tubing that is platinum-cured is acceptable for Dioxin/Furans).

Example:

Fresh silicon tubing is used for each sampling event. Used tubing can be re-used after cleaning for other semi-volatile sampling.

2. Collect a Field Blank to determine if any positive detections for Dioxins/Furans may have come from the environment. Make sure to transfer the reagent water at the site. Pour the reagent water container high enough above the top of the Field Blank container to allow for potential ambient levels of Dioxin/Furans to be collected.

Example:

Transfer the reagent water to allow air to be trapped during pouring to the Field Blank container.

3. Prepare the Equipment Blank by circulating reagent water through the peristaltic pump's tubing into the same Equipment Blank container.

Example:

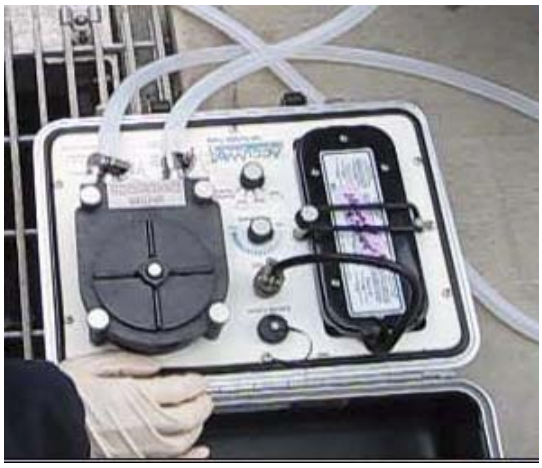
Reagent water is circulated from the original container through the tubing back into the original container to create an Equipment Blank.

4. The tubing is placed to a depth 6 – 12 inches below water surface, where possible.

Example:

Suspend the flexible tubing through a PVC conduit to assure the depth is 6-12 inches below the water surface. Loose tubing will skip on the surface of the flow with no weight to hold it under water. A suitable weight can be used.

5. Pump several tubing volumes of sample through the system to acclimate the tubing.



6. Fill the desired number of sample bottles via the discharge tubing being careful not to remove the inlet tubing from the water.

d. Dedicated Sampling Port Procedure-This is a sampling procedure where no pumping equipment is used. A dedicated sampling point with a representative continuous flow is used to sample for Dioxin/Furans.

This is an example of a continuous flow sampling port to collect wastewater effluent for Dioxins/furans testing. Assemble the following containers:

√Use all new, pre-cleaned, 1.1 L amber sample containers.

√Assemble (5) five empty 1.1L ambers and (1) one 1.1L amber filled with Ultrapure water.

1. Collect a Field Blank to determine if any positive detections for Dioxins/Furans may have come from the environment. See Section 3.2.c.2 for instructions to collect the Field Blank.

2. An Equipment Blank is not prepared for this sampling procedure from a tap since all materials are new and have not been exposed to previous sampling events.

3. Sampling staff must be very careful to not touch the sampling port with the bottle to avoid contamination.

Example:

Tilting the container without touching any surface in the continuous stream is the technique used to collect samples from a dedicated sampling port.

3.3 "Clean Hands/Dirty Hands" Protocol-Some Agencies may wish to use the "Clean Hands/Dirty Hands" sampling protocol when sampling for Dioxins/Furans. This procedure is identical to that used for low level mercury sampling. The "Clean Hands/Dirty Hands" procedure can be used for both the peristaltic pump sampling procedure, as well as, from a dedicated port. As an example below, how to use the "Clean Hands/Dirty Hands" procedure is illustrated from a dedicated tap.

Designate one member of the sampling team as "clean hands" and the other as "dirty hands". "Clean hands" is responsible for all operations involving contact with the sample and/or sample bottle. "Dirty hands" is responsible for all other activities that do not involve direct contact with the sample or sample bottle. The proper collection of a sample requires a great deal of coordination between "clean hands" and "dirty hands". Each sampler must know and understand his role.

The sampling team puts on a clean pair of gloves. All sampling personnel must wear clean, powder-free gloves at all times. Furthermore, when personnel come in contact with equipment that has not been pre-cleaned, they must stop and put on a new pair of clean gloves. "Dirty hands" personnel must help "clean hands" personnel to put on a clean pair of gloves whenever needed.

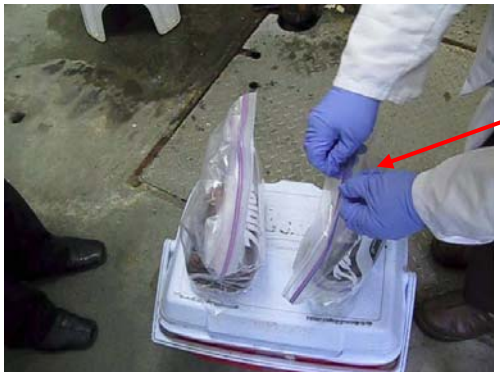
√Use all new, pre-cleaned, 1.1 L amber sample containers.

√Assemble (6) six empty 1.1L ambers and (1) one 1.1L amber filled with Ultrapure water.

√All containers listed above are double bagged.

√Have 2-4 sets of clean laboratory gloves available and 2 staff for this procedure.

1. "Dirty Hands" opens the outer bag with the clean 1 L ambers for the Dioxin/Furan sampling event.



Example:

"Dirty Hands" is responsible for handling the outer bag during sampling

2. “Clean Hands” opens the inner bag to remove the clean 1 L ambers for Dioxin sampling. “Clean hands” removes the cap, while holding the cap upside down.

Example:

“Clean Hands” is responsible for handling the inner bag and the 1 L amber during sampling

3. “Clean Hands” holds the sample container during collection. “Clean Hands” must be very careful to assure the 1 L amber does not touch any surfaces to prevent contamination and to hold the cap down in the other hand.

Example:

Tilting the container in the continuous stream is the technique used to collect samples from a dedicated tap during “Clean Hands/Dirty Hands” procedures.

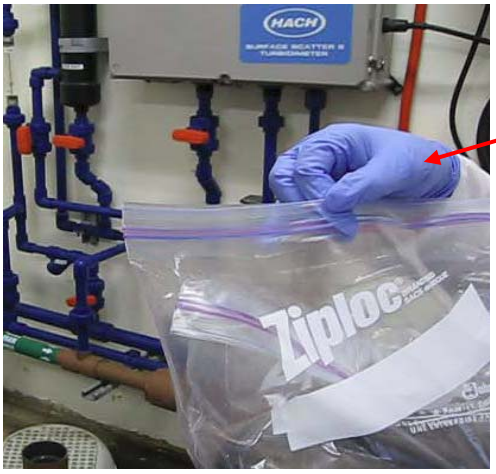
4. “Dirty Hands” reopens the outer plastic bag and “Clean Hands” opens the inside bag, places the 1 L bottle inside, and zips the bag. “Dirty hands” zips the outer bag.

Example:

“Clean Hands” seals the inner bag

“Dirty Hands” holds the outer bag

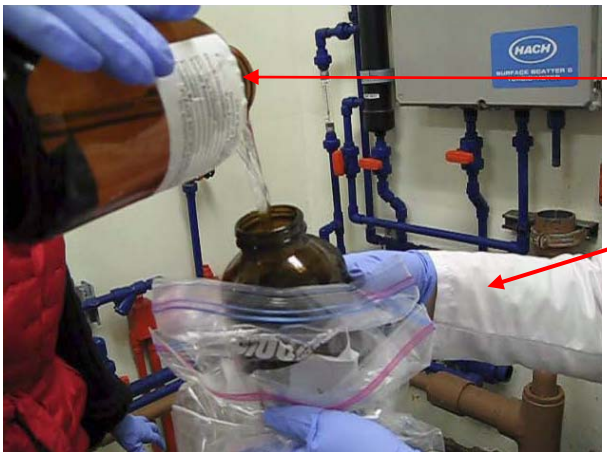
5. “Dirty Hands” closes the outer bag.



Example:

“Dirty Hands”

6. “Clean Hands” pours the Field Blank and “Dirty Hands” holds the outer bag.



Example:

“Clean Hands” is very careful to allow about 4 inches above the Field Blank bottle when pouring in Reagent Water to expose the sample to the air:

“Dirty Hands” holds the outer bag.

Appendix 1: References

1. Federal Register Notice, May 18, 2000. California Toxics Rule (40 CFR Part 131, CTR 2000).
2. Chapter 5, California State Water Resources Board, State Implementation Plan, Section V, Analysis of Issues & Alternatives, California SIP.
3. Standard Practices for Sampling Water, ASTM Annual Book of Standard, ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.
4. Method 1613, Revision B, 1994, Section 8.0.
5. Methods Update Rule, March 12, 2007, Table II, Page 11238.
6. Florida Department of Environmental Protection, SOP FS 2400 (Wastewater Sampling, March 31, 2008), and SOP FS 8200 (Clean Sampling for Ultra-trace Metals in Surface Water, March 31, 2008).

Appendix 2: SOP Template for Dioxin/Furans Sampling – Separate Word 2003 Document

Please see the separate Word 2003 Template for a Dioxin/Furan sampling procedure that accompanies this Guidance document