San Francisco Bay Regional Water Quality Control Board

Sent Via Email

December 31, 2013

To: Attached Mailing List

Subject: Sampling Analysis and Reporting Protocols Using EPA Method 1668C for Final Order No. R2-2012-0096, NPDES Permit No. CA0038849

This letter requires that dischargers regulated by Order No. R2-2012-0096 follow the attached *POTW PCBs Sampling, Analysis, & Reporting Protocols Using EPA Method 1668C*, prepared by the Bay Area Clean Water Agencies, in collaboration with the Regional Water Board, when conducting sampling, analysis, and reporting of PCBs with EPA Method 1668C. These protocols update the May 2011 version. There are two significant changes: (1) enhanced requirements for laboratories conducting PCBs analysis to reduce the potential for contamination, and (2) reduced number of qualifiers for PCBs results to simplify reporting.

As indicated in the attached protocols, method blanks, which otherwise met the criteria listed in EPA Method 1668C, contained background levels that affected the sum of PCBs reported to the Water Board since the PCBs Watershed permit became effective in April 2011. To ensure that the Water Board receives representative data, the attached protocols include additional requirements for laboratories performing PCBs analysis to reduce the potential for background contamination. Also, to simplify reporting requirements, we reduced the number of qualifiers for reporting PCBs data. Dischargers shall follow these reporting protocols effective immediately.

If you have any questions regarding this letter, please contact Robert Schlipf at (510) 622-2478 or email him at rschlipf@waterboards.ca.gov.

Sincerely,

Bill Johnson

Bill Johnson
Acting Chief, NPDES Wastewater Division

Attachment: Sampling Analysis and Reporting Protocols

DECEMBER 9, 2013

BAY AREA CLEAN WATER AGENCIES

POTW PCBs Sampling, Analysis & Reporting Protocols Using EPA Method 1668C

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SUMMARY

On December 12, 2012, the San Francisco Bay Regional Water Quality Control Board (Regional Water Board) adopted Order No. R2-2012-0096, *Waste Discharge Requirements for PCBs From Municipal and Industrial Wastewater Discharges to San Francisco Bay, NPDES Permit No. CA0038849*. The order supersedes order No. R2-2011-0012 and continues to implement the waste load allocations (WLAs) and implementation requirements of the polychlorinated biphenyls Total Maximum Daily Load (PCBs TMDL) that was adopted February 13, 2008. The Order includes requirements for monitoring and reporting of PCBs using both the approved EPA Method 608, and proposed EPA Method 1668C by Publicly Owned Treatment Works (POTWs). The following Sampling, Analysis & Reporting Protocols (Protocols) were prepared to provide a guidance document for POTWs and laboratories when generating data using EPA Method 1668C. They are intended to serve as a supplement to the official EPA Method 1668C instructions (USEPA, 2010), which, at this time, have not been confirmed as final nor promulgated as a rule by the USEPA. Protocols for analysis and reporting using EPA Method 608 are not discussed in this document.

BACKGROUND

The February 2008 San Francisco Bay Basin Plan Amendment for the PCBs TMDL included a WLA for municipal wastewater dischargers of 2.0 kg/yr (kilograms per year). The estimated aggregate loading from municipal dischargers based on 2003 flow data is 2.3 kg/yr, but the final load for municipal wastewater dischargers was promulgated at 2.0 kg/yr by the Regional Water Board to incorporate expected reductions. The TMDL also splits the 2.0 kg/yr into individual POTW waste load allocations by dividing each POTW's flow rate by a group flow rate (grouped according to secondary and advanced-secondary treatment) and multiplying that value by the total POTW aggregate waste load allocation. The proposed individual and group allocations in Order No R2-2011-0012 were developed from available PCB effluent concentration data for nine POTWs as presented in the PCBs TMDL Project Report (RWQCB, 2004). The data were collected using EPA Method 1668A from five POTWs with secondary treatment and four POTWs with advanced secondary treatment. A total of nine samples were collected over a three month period in 2000-2001 to characterize PCB effluent levels for secondary treatment and a total of fourteen samples were collected over a nine-month period to characterize PCB effluent levels for advanced secondary treatment in 1999-2000. No data was available to characterize effluent quality from the remaining 30 facilities that received WLAs in the February 2008 TMDL.

Order No R2-2012-0096 includes the same performance-based limits for PCB's as Order No R2-2011-0012. As in Order No R2-2011-0012, the limits are based on data for 40 congeners that are representative surrogates for PCBs that are causing impairment (**Table 1**). These 40 congeners are the same ones that formed the basis for the impairment and were monitored in the Regional Monitoring program using USEPA method 1668A.

OBJECTIVE

The objective of these Protocols is to produce and report data that represent as closely as possible actual concentrations of PCBs in POTW effluent. This objective will be achieved, in part, by using established methods for sample collection and laboratory analysis, accepted QA/QC procedures, and consistent reporting practices. The ability to meet this objective will be accomplished by evaluating the resulting laboratory measurements in terms of reporting limits, precision, accuracy, representativeness, comparability, and completeness.

Table 1. List of 40 PCB Congeners Causing Impairment in the Bay

PCB 008	PCB 066	PCB 118	PCB 170
PCB 018	PCB 070	PCB 128	PCB 174
PCB 028	PCB 074	PCB 132	PCB 177
PCB 031	PCB 087	PCB 138	PCB 180
PCB 033	PCB 095	PCB 141	PCB 183
PCB 044	PCB 097	PCB 149	PCB 187
PCB 049	PCB 099	PCB 151	PCB 194
PCB 052	PCB 101	PCB 153	PCB 195
PCB 056	PCB 105	PCB 156	PCB 201
PCB 060	PCB 110	PCB 158	PCB 203

SOURCE: Table F-14 in Order No. R2-2012-0096

IMPORTANCE OF COLLECTING ADDITIONAL DATA

A larger dataset obtained from EPA Method 1668C analyses from all POTWs may allow the Regional Water Board to assess variability in PCB monitoring data due to different treatment processes, diurnal patterns, flow changes (dry weather versus wet weather), and other factors. This variability will be useful in recalculating WLAs and/or incorporating uncertainty factors when translating WLAs into NPDES permit limits.

SAMPLING PROTOCOLS

The following protocols must be followed when collecting, holding, and transporting PCBs samples for analysis using EPA Method 1668C. The sample locations and sampling frequency are specified for POTWs in Order No. R2-2012-0096. Samples shall be collected at the locations indicated as compliance monitoring points in the individual POTW NPDES permits (often, but not always, EFF-001).

Sample Collection

Samples shall be collected as 1-liter (L) grab samples in appropriate pre-cleaned amber glass containers following applicable clean sampling techniques from EPA Method 1669 (U.S. EPA, 1996). The following procedures should be used to reduce the likelihood of sample contamination:

- Wear clean, powder-free gloves
- Minimize time bottle is open
- Don't set lid down
- Don't allow rainwater to drip into bottle
- Don't touch inside of bottle/lid

Care shall also be taken to keep bottles dust-free prior to sample collection. At a minimum, three (3) 1-L grab samples shall be collected at each sampling location. One of the grab samples should be sent to the analytical laboratory and two (2) should be refrigerated and retained at the POTW until the analysis is completed and the data are accepted for reporting to the Regional Water Board. The extra sample retained at the POTW will be sent to the laboratory, analyzed and reported in the event of a batch QC failure or the first grab sample being lost.

Sample Handling

If residual chlorine is present, add 80 mg of sodium thiosulfate to each 1-L sample. Samples must be kept in the dark at less than or equal to 6ºC from the time of collection until receipt at the laboratory. Sample bottles, shipping instructions, chain of custody templates, and billing information will be provided by the analytical laboratory. If the sample will be frozen, allow room for expansion. EPA Method 1668C allows samples to be held for up to 1 year prior to extraction if stored in the dark at less than or equal to 6ºC.

Sampling Frequency

The effluent monitoring requirements for POTWs using proposed EPA Method 1668C are shown in **Table 2** (excerpted from Table E-2 in Order No. R2-2012-0096). Major dischargers are required to sample more than once per year to ensure collection of samples during the wet and dry seasons. Minor dischargers may collect a sample anytime during the calendar year. All dischargers must follow Attachment G requirements (adopted as Order No. R2-2010-0054 and attached to NPDES permits) to collect effluent samples on days that are coincident with influent sampling and during periods of day-time maximum peak effluent flows.

Table 2. PCBs Monitoring Requirements for POTWs

Parameter	Units	Sample Type	Minimum Sampling Frequency
Total PCBs [1] (as Aroclors)	µg/L	Grab	Semi-annually for Major Dischargers
			Annually for Minor Dischargers
PCBs [2] (as congeners)	pg/L	Grab	Quarterly for Major Dischargers with Design Flow > 5.0 mgd
			Semi-annually for Major Dischargers with Design Flow[3] < 5.0 mgd
			Annually for Minor Dischargers, except as otherwise indicated below
			Once every Five Years for Marin County (Paradise Cove) Sanitary District No. 5, City of St. Helena, and Crockett Community Services District (Port Costa)

Unit: µg/L = micrograms per liter; pg/L = picograms per liter

Grab Samples: If allowed in the Pretreatment and Biosolids Monitoring Requirements of the Dischargers' individual NPDES permits, grab samples shall be collected coincident with composite samples collected for the analysis of other regulated parameters.

[1] Aroclor Monitoring: Dischargers shall use USEPA Method 608 for this monitoring. These data will be used for assessing compliance with the limits in Tables 6B and 7B of Order No. R2-2012-0096. Non-detected and/or estimated values shall be treated as zeros in the calculation of Total PCBs.

[2] Congener Monitoring: This monitoring is for informational purposes. Dischargers shall use USEPA Proposed Method 1668C and report the results for each of the 40 congeners that contribute to the Bay's impairment and congeners that co-elute with the 40 congeners. For congeners that co-elute with the 40 congeners, Dischargers shall report the sum of these co-eluting congeners. A summation for total PCBs is not required.

[3] Design Flow: The design flows for each facility are included in Tables F-1A and F-1B of the Fact Sheet.

ANALYTICAL LABORATORIES

All samples shall be analyzed using proposed EPA Method 1668C (April 2010 version) to provide consistent concentration information for the 40 PCB congeners and their co-elutions. Each laboratory must demonstrate annually its capability to analyze the required 40 congeners and co-elutions at the method-specified minimum levels (MLs, Table 2 of EPA 1668C) by following the procedure described in USEPA 1668C Section 17.6.1.4.1.

Between 2011 and 2013 method blanks, which otherwise met criteria listed in EPA 1668C and the 2011 PCB Reporting Guideline, contained background levels that affected the sum of PCBs reported by POTWs. In an effort to ensure quality data is reported for all POTW's, the following guidelines are adopted to prevent laboratory contamination from skewing analytical results. Any analytical laboratory that wishes to analyze and report PCB congener's data for Region 2 must demonstrate that their laboratory background levels do not adversely affect the analytical results. This shall be done by documenting and statistically determining if laboratory background levels that

are found in laboratory method blanks are acceptable. In order to achieve this, for each congener, the value of two standard deviations above the average (mean) level in minimum of 10 blanks must be at or below 75% of the corresponding method-specified ML. The sample-specific detection limit (SSDL) of the corresponding congener shall be used as numerical value in the following calculations when the congener is not detected as specified by the method.

$$AVE_{MB,10} + 2*SD_{MB,\ 10} < 0.75 * ML$$

$AVE_{MB,10}$ = Average (mean) of 10 or more method blanks.
$SD_{MB,\ 10}$ = Standard deviation of 10 or more method blanks.
ML = Corresponding ML for the congener

Quality Assurance/Quality Control

Quality assurance and quality control (QA/QC) samples are required in conjunction with POTW samples to verify data quality. With each batch of 20 or fewer samples, the laboratory will analyze method-required QA/QC samples of method blanks and spike blanks. Matrix spikes may be analyzed based on sample availability.

Method required batch controls are as follows:

- Method Blank—as batch contamination monitoring.
- Spike Blank—as sample preparation recovery assessment.
- Mid-Calibration Range Standards performed at the start and every 12 hours of instrument operation—as calibration verification.

Additional required batch controls are as follows:

- Method Blank—If any of the 40 congeners of interest are present in the method blank at greater than 20 pg/L, the batch is invalidated.
- Mid-Calibration Range calibration verification performed at the end of the run.

REPORTING

As specified in Order No. R2-2012-0096:

> *Each Discharger subject to PCBs effluent limitations of this Order shall submit PCBs monitoring data collected in its regular monthly or quarterly Self-Monitoring Reports (SMR) required in that Discharger's individual permit. These PCB data shall include detection limits, reporting levels, estimated values, or quantified values for the 40 congeners that contribute to water quality impairment plus co-elutes (66 congeners in total, see Table F-14), using USEPA Method 1668C as well as total PCBs (as Aroclors) using USEPA Method 608.*

The following information is provided to generate a standard spreadsheet format for use by analytical laboratories, ensuring EPA Method 1668C data are reported consistently, and in a manner compatible with the California Integrated Water Quality System (CIWQS) Electronic Self-Monitoring Report module (eSMR2).

General requirements for data reporting and acceptability:

1. The Minimum Level of Quantitation reported for each congener for this analysis shall be the published Method MLs (Table 2, EPA1668C). The laboratory analyzing the samples must have on file data demonstrating a lower calibration limit that is equal to or less than the published Method ML. Laboratories may revise the lower calibration limits based on final published values when EPA Method 1668C is fully approved and promulgated.

2. The Method Detection Limit (MDL) reported for each of the congeners for this analysis shall be established by the laboratory using the MDL protocol described in 40 CFR 136 Appendix B. The MDLs reported by the laboratory shall meet the criteria set in EPA Method 1668C. The laboratory shall demonstrate capability by achieving MDLs below method-specified MDLs. The MDL is based on analysis of low-level replicates of clean matrix (deionized water).

3. Sample-specific detection limit (SSDL) for each congener shall be reported when there is a non-detect. When a congener is detected in a sample, the result will be reported and, if the result is below the method-specified ML, the result is not quantifiable and will be qualified with a 'DNQ'. The SSDL is calculated by the instrument processing method based on the noise level in the vicinity of the target peak in sample extracts containing real matrix.

4. The current reporting format is by submitting .pdf documents. In the future, guidelines shall be provided for CIWQS reporting.

Qualifiers allowed in reporting are defined in Table 3. The ND and DNQ qualifiers take precedence over all other qualifiers. ND must be reported when a value is less than the SSDL. DNQ must be reported when a congener is detected, but is less than the method-specified ML.

Table 3. EPA Method 1668C Qualifiers Defined in CIWQS and Applied by Analytical Laboratory

Qualifiers	CIWQS Field	Qualifier Description
ND	Qualifier	The analyte was not detected in the sample at the sample-specific detection limit (SSDL).
DNQ	Qualifier	The reported result is an estimate. The concentration is greater than the sample-specific detection limit (SSDL) but is less than the method-specified ML.
C	Comment, Qualifier	Coelution reported in the comment field for the lowest numerically designated congener in a coelution, and in the qualifier field for the other congeners in the coelution.
Cxxx	Comment	Co-elutes with the indicated congener. Concentration is reported under the lowest numerically designated congener. 'xxx' denotes the congener number for the lowest numerically designated congener in the co-elution.
M	QA Code	Estimated maximum possible concentration (EMPC). [1]
D	QA Code	Dilution data. Result obtained from the analysis of a dilution.
B	QA Code	Congener is present in the method blank.

NOTE: If the analytical laboratory wishes to qualify data where the qualifier is not available for entry in CIWQS, the information should either be translated into one of the mandatory CIWQS qualifiers or submitted in a separate report to the discharger. This is not a comprehensive list of all possible qualifiers. Additional qualifiers may be used by the laboratory.

[1] Estimated maximum possible concentration -- EMPC is calculated when responses of S/N≥2.5 are observed for both the quantitation ions and all identification criteria are met except the ion abundance ratio criteria. In this instance, the quantitation ion with the least area is used as a starting point. The theoretical ion abundance ratio is then applied to determine the amount of the second quantitation ion area to be used to calculate the EPMC.

5. For co-eluting congeners of interest (i.e., included in the Table F-15 of Order No. R2-2012-0096), results shall be reported on the line of the lowest numeric congener with a "C" in the comment field. For the higher numeric congeners that are part of this co-elution, results shall be reported as null with "C" entered in the qualifier field and Cxxx in the comment field.

   Examples:

In reporting PCBs 056/060 in CIWQS, **both** co-eluters are congeners of interest so the following convention shall be used:

Parameter	Qualifier	Result	MDL	ML	RL	QA Code	Comment
PCB 056	DNQ	10	7.77	50		D	C
PCB 060	C						C056

At this time, C is not yet available as a CIWQS Qualifier but will be requested via the Regional Board once electronic reporting is required for PCB congeners.

In reporting PCB 021/033, where PCB 021 is not part of the list of 40 congeners causing impairment, **only one** co-eluter (PCB 033) is a congener of interest so the following convention shall be used:

Parameter	Qualifier	Result	MDL	ML	RL	QA Code	Comment
PCB 033		10	7.77	50		D	C021

6. Results shall be reported without blank-correction.

7. Concentrations shall be reported in pg/L.

8. Consistent with Attachment G of NPDES permits, data should not be reported by an agency if data have been invalidated based on QA/QC results and analysis. If data are invalidated, it is recommended that documentation be prepared and filed internally to explain the process and reasons for invalidation. If data quality is discovered to be insufficient after the data have been reported to the Regional Water Board, the data invalidation procedure indicated in Attachment G should be followed.

PCBs Concentrations and Use of Qualified Data

PCBs shall be reported as individual congener concentrations with assigned qualifiers. A summation of individual congeners to produce a "Total PCBs" value is not required at this time. To maintain consistency with Total PCB reporting requirements (Table 2):

- Data qualified with DNQ or ND should be set to "0" for the purpose of performing summation.
- Data qualified with B, M, or D should be summed using the reported concentration.

Congener Naming Convention

Analytical laboratories and dischargers shall report PCBs congener results using the "Congener Number" (e.g., PCB 008) as specified in Table 1 of EPA Method 1668C, available on-line at:
http://water.epa.gov/scitech/methods/cwa/upload/M1668C_11June10-PCB_Congeners.pdf.

To ensure consistent recordkeeping and reporting formats, each congener shall be identified using the acronym "PCB" following by the three digit congener number as in PCB XXX (e.g., PCB 008, PCB 028, PCB 118).

REFERENCES

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