Permit Strategies for Dioxins in Bay Area Municipal Wastewater Treatment Plants

Introduction

In early 2008, the San Francisco Estuary Institute (SFEI) convened a panel of national experts to provide an unbiased review and analysis of factual information currently available for dioxins as it pertains to San Francisco Bay. For this discussion, "dioxins" refers to the compound 2,3,7,8-TCDD and a group of chemical compounds that share certain chemical structures and biological characteristics. These compounds include the chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and certain polychlorinated biphenyls (PCBs). The panel of experts met in Oakland, California, on February 22, 2008, at the Institute. Representatives of (and stakeholders from) the San Francisco Bay Regional Water Quality Control Board, the US Environmental Protection Agency, the Bay Area Clean Water Agencies (BACWA) and others with expertise in the field, were present to observe the panel and did engage with them in a limited way to ask questions and respond to their questions,. Subsequently, the panel held numerous conference calls and agreed to address questions posed by the Institute in both short- and long-term contexts. For the short term, the panel agreed on recommendations that could help alleviate some of the dioxins-related regulatory difficulties faced by municipal wastewater treatment plants. For the long-term, they agreed that the problems faced by the dischargers are best addressed by regional solutions for the dioxins contamination problems in the Bay.

Nationally, the panel of experts pointed out, *The Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States: The Year 2000 Update* (External Review Draft, March 2005; EPA/600/P-03/002A) includes an inventory of contemporary releases from known sources of dioxins in the United States. Only preliminary estimates were available for municipal wastewater discharges but they accounted for only 0.2% of the total estimated releases in the United States for 2000. Releases to air, accounted for 98.6% of the 2000 total. Prior to this report, a 1998 report on dioxins in San Francisco Bay by Regional Water Board staff indicated that municipal and industrial wastewater treatment plants contributed 2% of dioxin to San Francisco Bay. The USEPA Region 9 website points out that this information is based on preliminary data and that source categories nationally and in the Bay Area that are not well characterized. In any event, it is clear that publicly-owned treatment works (POTWs) contribute a very small percentage of the dioxins inputs to San Francisco Bay.

The San Francisco Estuary Institute prepared a report titled, *Dioxins in San Francisco Bay: Conceptual Model/Impairment Assessment* in January 2005, which included an evaluation of the current level of impairment of dioxins and furans in San Francisco Bay. The Institute determined that dioxins and furans in San Francisco Bay are mostly produced as byproducts of combustion of various materials and as contaminant byproducts of chlorinated-chemical processes, such as syntheses of organochlorine pesticides, pulp bleaching, and manufacture of polyvinyl chloride (PVC). In the past, specific "point-source" emissions from facilities such as

incinerators and smelters were estimated to be the largest sources of dioxins. However, currently it is believed that most of those large point sources have been controlled. More disperse sources, such as yard burning and vehicle emissions remain at levels similar to those in the past, and they are now expected to contribute more dioxins than the point sources.

Suspected scant sources of dioxins in municipal wastewater include laundry gray water, human waste, food waste, storm water inflow, shower water, bleached toilet paper and industrial sources. The ability to control the low levels of dioxins present in treated municipal effluent through either source control or additional treatment is uncertain. Pollution prevention for dioxins is challenging given the ubiquitous nature of these compounds in the above mentioned sources and the extremely low concentrations at which these compounds are present in wastewater (typically four to five orders of magnitude lower than detectable levels of mercury and other constituents of concern). Analytical limitations hinder the ability to use monitoring as an element of a pollution prevention program. Sample contamination and analytical anomalies in effluent samples also limit quantitative approaches to pollution prevention. Regional and source- specific measures represent the best approach to pollution prevention for dioxins in the San Francisco Bay region.

It is therefore apparent that municipal wastewater treatment plants are not a significant source of dioxins to San Francisco Bay, and in any event there is significant uncertainty regarding the contribution from POTWs. This fact makes it even more important to use the best science and understanding currently available to develop a permitting and compliance strategy for dioxins in San Francisco Bay.

Regulation of Dioxins Using Bioaccumulation Equivalency Factors (BEFs)

The California Toxics Rule (CTR) establishes a numeric water quality criterion for 2,3,7,8-TCDD of 1.4×10^{-8} µg/L for the protection of human health. In the preamble to the CTR, USEPA stated its support for the regulation of other dioxin and dioxin-like compounds using toxicity equivalence quotients (TEQs). For California waters, USEPA stated specifically, "*if the discharge of dioxin or dioxin-like compounds has reasonable potential to cause or contribute to a violation of a narrative criterion, numeric WQBELs for dioxin or dioxin-like compounds should be included in NPDES permits and should be expressed using a TEQ scheme.*" [65 Fed. Reg. 31682, 31695 (2000)] This procedure, most recently developed by the World Health Organization (WHO), uses a set of toxicity equivalency factors (TEFs) to convert the concentration of congeners of dioxins and furans into an equivalent concentration of 2,3,7,8-TCDD. Apart from regulation of 2,3,7,8-TCDD, implementation of the TEQ approach in San Francisco Bay is based on the application of best professional judgment using best available information in the interpretation of the narrative water quality objective for bioaccumulative substances contained in the Basin Plan.

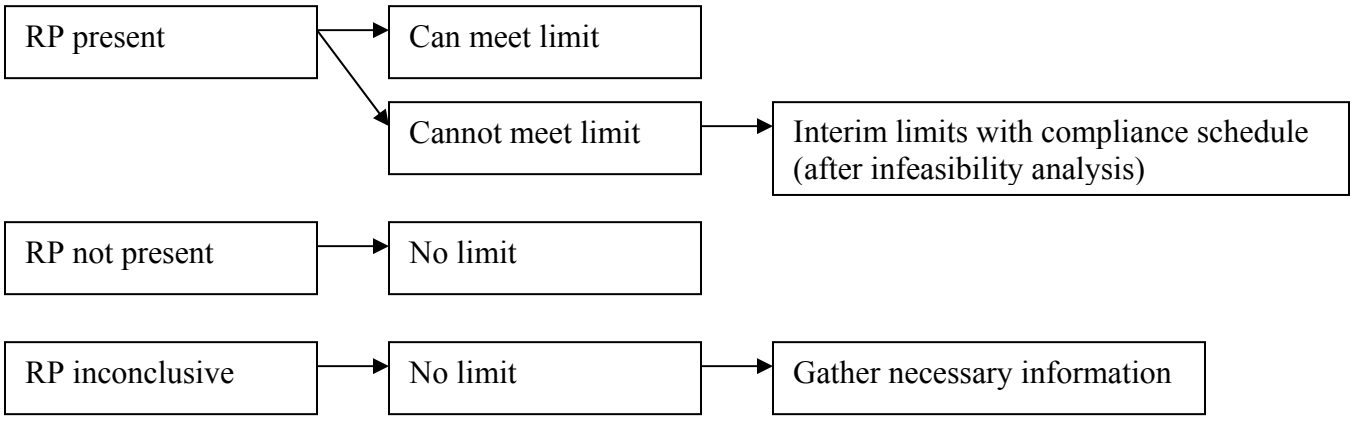
USEPA's more recent assessment of dioxin uptake by biological systems has shown that each dioxin congener's assimilation is individually definable. These bioaccumulation factors, when converted to a 2,3,7,8 -TCDD equivalency, are referred to as bioaccumulation equivalency factors, or BEFs. BEFs account for the biological uptake from the water column of the various dioxin congeners and correct the TEQ-based water quality objectives that would otherwise suggest complete and equal biological assimilation of each dioxin congener. USEPA supports

the modification of TEFs using BEFs for dioxin-TEQ. Specifically, USEPA has stated, "*TEFs and BEFs shall be used when calculating a 2,3,7,8-TCDD toxicity equivalence concentration when implementing both human health noncancer and cancer criteria.*" [40 CFR, Part 132, Appendix F]

Permitting Strategy

Because the dioxin-TEQ permitting and compliance strategy currently being implemented creates a number of short-term and long-term compliance issues for Bay Area publicly-owned treatment works (POTWs), this document includes a permitting strategy whereby effluent and receiving water dioxins concentration data are modified using both TEFs and BEFs for computation of a Toxicity Equivalent Quotient (TEQ) prior to comparing the observed data with the CTR water quality criterion for 2,3,7,8-TCDD as listed in the California Toxics Rule for the reasonable potential analysis.

It is envisioned that the following decision tree would be used for the permitting approach:



Additional Considerations

Two additional approaches for dioxin effluent limits should be considered in the development of a regulatory approach for dioxin in the San Francisco Bay Area. First, since dioxin is a constituent which has impacts that develop over long periods of time, the annual average of effluent data should be considered for use in the development of reasonable potential, and for compliance.

Second, due to the variability of dioxin data and potential for contamination of samples, if an "outlier" is observed in the data, the discharger should be able to "retest" a data point. It would be desirable to have a provision allowing this approach directly in the permit. In addition, Regional Water Board staff should examine the specific data set for the Discharger to determine whether the data is believed to be representative of dioxin-TEQ concentrations in effluent. Where the data set is deemed not to be representative, the permit should include a monitoring requirement and provision for reopener if reasonable potential is determined using the representative data set.

Interim mass limits, if applicable, were computed from the Minimum Levels. Language for source control and special studies in provisions was modeled after language in the mercury watershed permit, and contains deadlines as applicable.

Permit Language

Basic Fact Sheet Language

X. Dioxin-TEQ

(a) *WQC*. 40 CFR 122.44(d) provides that, where Reasonable Potential exists for a pollutant that does not have a numeric water quality criterion or objective, such as for a narrative water quality objective, WQBELs may be established by using a calculated numeric water quality criterion supplemented with other relevant information. WQBELs may take the form of mass limits, water column concentration-based limits, or a non-numeric program of source control and best management practices established under a schedule of compliance. The assessment of the need for dioxin-TEQ WQBELs in this Order is based on interpretation of the Basin Plan's narrative WQO for bioaccumulative substances using the CTR's numeric WQO for 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) and other relevant scientific information, including USEPA guidance, as described below. Numeric criteria for dioxin-TEQ are not established in the CTR. The Basin Plan narrative WQO for bioaccumulative substances states:

> *Many pollutants can accumulate on particulates, in sediments, or bioaccumulate in fish and other aquatic organisms. Controllable water quality factors shall not cause a detrimental increase in concentrations of toxic substances found in bottom sediments or aquatic life. Effects on aquatic organisms, wildlife, and human health will be considered.*

Because it is the consensus of the scientific community that dioxins associate with particulates, accumulate in sediments, and bioaccumulate in the fatty tissue of fish and other organisms, it is proper to consider the Basin Plan's narrative bioaccumulation WQO in the regulation of these pollutants. Elevated levels of dioxins in fish tissue in San Francisco Bay demonstrate that the narrative bioaccumulation WQO is not being met. USEPA has therefore included all segments of the San Francisco Bay in the current 303(d) listing as impaired by dioxins. In consideration of the applicability of the narrative WQO for bioaccumulative substances to WQBELs for dioxin-TEQ in wastewater effluent, a key factor is whether these constituents are controllable. As stated above, available information indicates that the ability to control these constituents through wastewater treatment or source control is unknown and uncertain. Additionally, it is well understood that wastewater effluent is a small source of dioxins in the regional context. This information has been considered by the Regional Water Board in its exercise of best professional judgment in the regulation of dioxin TEQs.

The CTR establishes a numeric WQO for 2,3,7,8-TCDD of 1.4×10^{-8} µg/L for the protection of human health, when aquatic organisms are consumed. When the CTR was promulgated, USEPA stated its support of the regulation of other dioxin and dioxin-like compounds using toxicity equivalencies (TEQs) in NPDES permits. For California waters, USEPA recommended, "if the discharge of dioxin or dioxin-like compounds has reasonable potential to cause or contribute to a violation of a narrative criterion, numeric WQBELs for dioxin or dioxin-like compounds should be included in NPDES permits and should be expressed using a TEQ scheme." [65 Fed. Reg. 31682, 31695 (2000)] This

procedure, developed by the World Health Organization (WHO) in 1998, uses a set of toxicity equivalency factors (TEFs) to convert the concentration of any congener of dioxin or furan into an equivalent concentration of 2,3,7,8-TCDD.

USEPA's comprehensive assessment of dioxin uptake by biological systems has shown that the assimilation of dioxin congeners from the water column into organisms is individually definable. These individual factors for specific congeners, when converted to a 2,3,7,8- TCDD equivalency, are referred to as bioaccumulation equivalency factors or BEFs. BEFs account for the biological uptake from the water column of the various dioxin congeners and properly adjust the TEQ-based water quality objectives that would otherwise suggest complete and equal biological assimilation of each dioxin congener. USEPA supports the modification of TEFs using BEFs for dioxin-TEQ. Specifically, USEPA has stated, "TEFs and BEFs shall be used when calculating a 2,3,7,8-TCDD toxicity equivalence concentration when implementing both human health noncancer and cancer criteria." [40 CFR, Part 132, Appendix F] The applicable TEFs and BEFs are shown in Table F-X, below.

Table F-X. Dioxin/Furan TEF and BEF Values

Dioxin/Furan Congener	Toxicity Equivalency Factor (TEF)	Bioaccumulation Equivalency Factor (BEF)
2,3,7,8-TCDD	1.0	1.0
1,2,3,7,8-PeCDD	0.5	0.9
1,2,3,4,7,8-HxCDD	0.1	0.3
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.05
OCDD	0.001	0.01
2,3,7,8-TCDF	0.1	0.8
1,2,3,7,8-PeCDF	0.05	0.2
2,3,4,7,8-PeCDF	0.5	1.6
1,2,3,4,7,8-HxCDF	0.1	0.08
1,2,3,6,7,8-HxCDF	0.1	0.2
2,3,4,6,7,8-HxCDF	0.1	0.7
1,2,3,7,8,9-HxCDF	0.1	0.6
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.4
OCDF	0.001	0.02

The following formula demonstrates the mathematical relationship of TEQ to BEFs to TEFs:

$$TEQ = \Sigma ((C)_x * (TEF)_x * (BEF)_x)$$

where:

TEQ = Toxicity equivalent quotient
$(C)_x$ = concentration of congener *x*
$(TEF)_x$ = TCDD toxicity equivalency factor for congener *x*
$(BEF)_x$ = TCDD bioaccumulation equivalency factor for congener *x*

In the absence of site-specific BEFs, USEPA supports applying the BEFs calculated using national bioaccumulation factors. This is justified by the favorable comparison of BEFs calculated in other aquatic systems to those calculated for the general BEFs. USEPA stated specifically, "In the absence of site-specific data, EPA believes that national bioaccumulation factors are broadly applicable to sites throughout the United States and can be applied to achieve an acceptable degree of accuracy when estimating bioaccumulation potential at most sites." In addition, USEPA indicated that BEFs calculated from data obtained for multiple ecosystems confirms that the small potential differences in bioaccumulation mean that these BEFs are predictive of bioaccumulation differences for dioxins and furans in fish for ecosystems throughout the U.S. [Methodology for Deriving Ambient Water Quality Criteria for Protection of Human Health, Draft Technical Support Document, Volume 3, Development of Site-Specific Bioaccumulation Factors, pp. 1-5, 5-28]

To determine if the discharge of dioxins or for the Discharger has reasonable potential to cause or contribute to a violation of the Basin Plan's narrative bioaccumulation WQO, Regional Water Board staff used TEF and BEF values, in combination, as shown above, to express the measured concentrations of 17 dioxin congeners in effluent and background samples as equivalent to 2,3,7,8-TCDD. These "equivalent" concentrations were then compared to the CTR numeric criterion for 2,3,7,8-TCDD (1.4×10^{-8} µg/L). Compliance with the dioxin-TEQ requirement will be based upon the sum of detected congener TEFs modified by their respective BEFs.

Although the 1998 WHO scheme includes TEFs for dioxin-like PCBs, they are not included in this Order's version of the TEF procedure. The CTR has established a specific water quality standard for dioxin-like PCBs, and they are included in the analysis of total PCBs.

Additional Fact Sheet Language if Reasonable Potential is Found (language would be significantly simpler if there is no RP)

(b) **RPA Results.** The Discharger collected effluent data for dioxin congeners from *XXX* through *XXX*; the maximum effluent concentration of dioxin-TEQ was *XXXX* µg/L. Because the maximum annual average effluent concentration exceeds the most stringent applicable WQO of 1.4×10^{-8} µg/L, there is reasonable potential for the discharge to cause or contribute to exceedances of applicable WQO . For this analysis, samples taken over a one year period were averaged and compared to the CTR criterion for 2,3,7,8-TCDD. Annual average concentrations have been employed because the time period of concern for this bioaccumulative pollutant is long term, on the order of years or decades.

(c) **Dioxin-TEQ WQBELs.** Final WQBELs for dioxin-TEQ shall be annual average mass-based limits. A mass-based annual average WQBEL for dioxin TEQs of XXX grams per year has been calculated from the CTR objective for 2,3,7,8-TCDD at the permitted average dry weather effluent flow rate. Compliance with this limit will be based on actual flows and dioxin TEQ values calculated using the TEF and BEF values discussed previously. This limit will remain in place until the dioxin TMDL is completed and a WLA for the discharge is established.

(d) **Feasibility of Compliance [only where noncompliance with final WQBELs is determined].** During *XXX* through *XXX*, the Discharger's annual mass discharge of effluent concentrations for dioxin-TEQ, as modified by BEFs, were in the range of 0 to *XXXX* grams per year(*X* samples). The Discharger submitted a Feasibility Analysis asserting that the Discharger cannot immediately comply with these WQBELs due to the uncertainty and variability of these effluent data. Due to the nature of these pollutants, Regional Water Board staff concurs with the Discharger's assertion. This Order contains a compliance schedule based on the Basin Plan to allow time for the Discharger to comply with these effluent limits based on new interpretation of a narrative objective. These final effluent limits will become effective on ten years and one day from the effective date of this permit. The Regional Water Board may amend these limits based on new information or a TMDL for dioxins.

(e) **Interim Effluent Limit.** Since it is infeasible for the Discharger to comply with the final WQBELs for dioxin-TEQ, this Order establishes an interim mass limit based on the MLs of all congeners and their respective TEFs and BEFs, or based on actual performance data, whichever is higher. The sum of each congener's ML times its respective TEF and BEF times its annual average effluent flow volume is XXX grams per year and is established as an annual average interim limit. [Note: The preceding sentence must be changed to "The observed mean annual dioxins mass loading plus three standard deviations is established as the annual average interim effluent limit" where such a value exceeds the ML-based limit]}This interim limit will remain in effect until 10 years from the effective date of this permit.

(f) **Antibacksliding/antidegradation.** The previous permit did not include a dioxin-TEQ effluent limit; therefore, antibacksliding and antidegradation requirements are satisfied. .[Must be revised for permits that included a previous dioxin TEQ effluent limit]

Draft Effluent Limitations and Discharge Specifications:

B. Final Effluent Limitations for Toxic Substances

The Discharger shall comply with the following toxic pollutant effluent limits, as described in the attached MRP (**Attachment E**):

Table 7. Effluent Limitations for Toxics Substances

Parameter	Units	Effluent Limitations [1], [2]				
		Average Monthly	Average Weekly	Maximum Daily	Average annual	
Copper (example)	µg/L	XX	---	XX	---	---
Cyanide (example)	µg/L	XX	---	XX	---	---
Dioxin-TEQ [5]	grams per year		---		XXX---	---
Total Ammonia (example)	mg/L as Nitrogen	XX	---	XX	---	---

Footnotes for Table 7:

[1] a. All analyses shall be performed using current USEPA methods, or equivalent methods approved in writing by the Executive Officer.
b. Limitations apply to the average concentration of all samples collected during the averaging period (daily = 24-hour period; monthly = calendar month; annual = calendar year).
c. All metal limitations are expressed as total recoverable metal.

[2] A daily maximum or average monthly value for a given constituent shall be considered noncompliant with the effluent limitations only if it exceeds the effluent limitation and the Reporting Level for that constituent. As outlined in Section 2.4.5 of the SIP, the table below indicates the Minimum Level (ML) upon which the Reporting Level is based for compliance determination purposes. A Minimum Level is the concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point. The ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration

standard analyzed by a specific analytical procedure, assuming that all the method specified sample weights, volumes, and processing steps have been followed.

Table 8. Minimum Levels for Pollutants with Effluent Limitations

Parameter	Minimum Level	Units
2,3,7,8-TCDD	5	pg/L
1,2,3,7,8-PeCDD	25	pg/L
1,2,3,4,7,8-HxCDD	25	pg/L
1,2,3,6,7,8-HxCDD	25	pg/L
1,2,3,7,8,9-HxCDD	25	pg/L
1,2,3,4,6,7,8-HpCDD	25	pg/L
OCDD	50	pg/L
2,3,7,8-TCDF	5	pg/L
1,2,3,7,8-PeCDF	25	pg/L
2,3,4,7,8-PeCDF	25	pg/L
1,2,3,4,7,8-HxCDF	25	pg/L
1,2,3,6,7,8-HxCDF	25	pg/L
1,2,3,7,8,9-HxCDF	25	pg/L
2,3,4,6,7,8-HxCDF	25	pg/L
1,2,3,4,6,7,8-HpCDF	25	pg/L
1,2,3,4,7,8,9-HpCDF	25	pg/L
OCDF	50	pg/L

[5] Dioxin-TEQ: Final effluent limits for dioxin-TEQ shall become effective on *XXXXX* [10 years and 1 day from effective date of permit]. The Regional Water Board may amend these final effluent limitations prior to this date in accordance with TMDLs that become effective subsequent to the effective date of this Order. Qualified data shall not be used to determine compliance with this final effluent limit.

C. Interim Effluent Limits

The Discharger shall comply with the interim limit shown in Table 9, with compliance measured at Monitoring Location EFF-001 as described in the attached MRP (**Attachment E**). The interim limit for dioxin-TEQ shall remain in effect until *XXXX* (ten years from permit effective date). Starting *XXXX* [ten years plus 1 day from permit effective date], for dioxin-TEQ, the final effluent limits in Table 7 shall become effective.

Table 9. Interim Effluent Limitations for Dioxin-TEQ

Pollutant	Annual Average Effluent Limit (grams per year)
Dioxin-TEQ	XXX

Draft Language for Provisions Section of Permit

X. Dioxins Monitoring, Source Control, and Special Studies

The Discharger, either individually or as part of a group, shall develop, implement, and document cost-effective pretreatment/pollution prevention reduction strategies for dioxins in accordance with the following:

a. The Discharger shall identify and document, individually or as a group, a uniform protocol for sampling and analysis for dioxins in effluent and receiving waters in the San Francisco Bay region. This work effort shall be reported on in the Discharger's annual Self-Monitoring Report which is submitted after the one year anniversary of the permit effective date.

b. The Discharger shall participate individually, or in a regional study, to establish regional methodologies for pollution prevention programs for dioxins in wastewater treatment and shall implement elements of such a program in its service area, as appropriate. A menu of dioxins source control activities shall be developed within one year of the permit effective date, and reported in the Discharger's annual Self-Monitoring Report which is submitted after one year anniversary of the permit effective date.

c. The Discharger shall participate in regional efforts to perform effluent and ambient monitoring, fish tissue monitoring, source identification, linkage analysis and other steps contributing to the development of a TMDL for dioxins.

Draft Language for the Monitoring and Reporting Program:

Section IV. A., footnote to Effluent Monitoring at E-001 Table (normally Table E-4):

[11] Dioxin-TEQ. Chlorinated dibenzodioxins and chlorinated dibenzofurans shall be analyzed using the latest version of USEPA Method 1613; the analysis shall be capable of achieving the MLs listed previously in this Order. Alternative methods of analysis must be approved by the Executive Officer. In addition to reporting results for each of the 17 congeners, the dioxin-TEQ shall be calculated and reported using 1998 USEPA Toxicity Equivalency Factors (TEFs), as modified by BEFs (see Fact Sheet for explanation of BEF), for dioxin and furan congeners.