DIOXIN IN THE BAY ENVIRONMENT—A REVIEW OF THE ENVIRONMENTAL CONCERNS, REGULATORY HISTORY, CURRENT STATUS, AND POSSIBLE REGULATORY OPTIONS

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INTRODUCTION

Staff is seeking direction from the Board on appropriate actions to address the dioxin problem in the Bay. This report provides general background information about dioxins[1], staff's current understanding of the problem, and options for actions to address the problem.

This report summarizes much of the information that has previously been presented to the Board. One of the more significant events was a public workshop held by the Board on May 7, 1997, to receive technical information from experts recognized nationally in the field of dioxin policy and research. Following are several highlights from the workshop:

- There is general agreement that 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD) is a highly toxic compound that can produce a variety of health effects in humans. Possible health effects include chloracne, developmental and reproductive effects, carcinogenesis, and immunosuppression. Formal criteria have not been adopted for other congeners, although a scheme for evaluating mixtures of congeners in comparison to the toxicity of 2,3,7,8-TCDD has been developed.

- Background or ambient levels of dioxins present in the environment are found at levels at or above those associated with human health concerns and potentially other organisms.

- U.S. EPA data show that dioxin releases to the environment have declined significantly in the last 15 years. Lake sediment cores collected by the U.S. EPA at various locations throughout the United States indicate that the concentration of dioxins in the environment appears to be decreasing. Additional data are required to see if this trend is significant and is continuing.

- Data on dioxins are relatively scarce because the analysis is very specialized and expensive.

- Human body-burden of dioxins in the United States is approaching the level where health affects may be observed. The primary pathway for dioxin exposure to humans is through dietary intake, not drinking water. For most of the population of the United States, this means that more than 90% of the dioxin exposure is from the consumption of meat and dairy products. This may not be representative for segments of the population that are dependent upon alternative sources of protein (i.e. subsistence fisher people).

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[1] There is group of compounds (coplanar polychlorinated biphenyls or PCBs) which are sometimes included in discussion of "dioxin" issues. These coplanar PCBs cause similar toxicities as dioxins, but their sources are different. Therefore, this paper addresses options for dioxins only.

There are a total of 210 different compounds of dioxins and furans each with chlorine atoms at different locations on the structure. Those with chlorine atoms at the 2, 3, 7, and 8 positions are highly toxic, and there are seventeen of these compounds. They are called congeners of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin.

The most toxic of the group is 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD). This is also the most studied of the congeners. Generally, as the number of chlorine atoms increases, the toxicity decreases. Toxic effects include tumor promotion, wasting syndrome (loss of body mass), alteration of immune responses, and reproductive and developmental deficits.

Dioxins are very persistent in the environment. As the number of chlorine atoms increases, the persistence also increases. The only significant breakdown process for dioxins is degradation by sunlight or gaseous dioxins. Unfortunately, most of the dioxins in the environment are not in the gaseous phase, but are adsorbed on particles or dissolved in fatty tissue of organisms where the breakdown process is minimal.

What is TEQ?

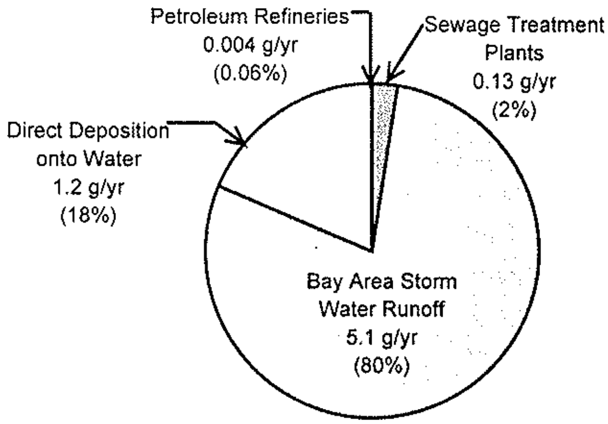
Toxicity Equivalent or TEQ is a method that the U.S. EPA and other government agencies around the world have adopted to assess the toxicity of mixtures of dioxins and furans found in the environment. It is a weighted sum of the concentrations of the seventeen congeners using Toxicity Factors that reflect the toxicity of each congener relative to 2,3,7,8-TCDD (see Appendix A for additional discussion). The idea is to generate a single number to allow comparison of the toxicity of various mixtures of congeners at different concentrations. There is not total agreement regarding the toxicity of some congeners. Some scientists believe that certain congeners are less toxic than represented by the toxicity factors and others believe that these same compounds are more toxic than represented.

Where Do Dioxins Come From and Where Do They End Up?

Dioxins are not deliberately manufactured. Rather, they are unintentional byproducts of combustion and incineration. They are also byproducts generated from some chemical processes such as chlorine bleaching of wood pulp and paper, and chlorinated pesticide and chemical manufacturing. The primary source of dioxins from discharges directly to water is from pulp and paper mills.

The bulk of dioxins releases are to air, but much of this ultimately ends up in aquatic sediments. Sunlight degrades gaseous dioxins, but most dioxins quickly adsorb onto particles, thus inhibiting degradation. These dioxins eventually deposit on soil and surface water bodies. Storm water runoff carrying soil particles add dioxins to surface water systems. Additionally, because of dioxins'

Discharges to S.F. Bay



The following discussion explains our current understanding of the sources to each of the above categories of dioxin discharges.

For the largest categories of direct deposition and storm water runoff, we believe the sources are air emissions from disperse sources or from reservoir sources. Reservoir sources are historic releases that are still in the environment because of the persistence of dioxins. We suspect this because the concentrations and characteristics were similar throughout the region (SFBRWQCB 1997), independent of industrial activity. The current significant sources are on- and off-road mobile sources, and residential wood combustion (BAAQMD 1996). Dioxin is also present from historic discharges. These may include over 20 medical waste incinerators and other combustion sources that operated historically in the Bay Area. Currently, there are two sewage sludge incinerators (Central Contra Costa County Sanitary District and Palo Alto's sewage treatment plant) and one medical waste incinerator (Integrated Environmental Systems in Oakland) in the Bay Area.

For the sewage treatment plants, the sources may also be diffuse. Possible sources are laundry gray-water, storm water inflow, shower water, human waste, bleached toilet paper, food waste, and industrial sources. Of these, the predominant one appears to be laundry gray-water (EIP 1997). Dioxins in gray-water may come from pentachlorophenol treated cotton from overseas, chloranil-based dyes in the fabric, fabric bleaching, soil and human skin.

For the industrial category, the only documented source of dioxins in the Bay Area is from petroleum refineries. The specific source is the wash waters from catalyst regeneration of reformers. Further studies have shown that the refineries' treatment systems remove these dioxins to below detection limits prior to discharge (Tosco Corporation 1997). These studies also suggest that the dioxins that remain in the discharge are primarily due to storm water runoff from areas

Regional Board Regulatory History

The Regional Board began adopting dioxin limits in NPDES permits for point source discharges in 1992. The legal basis for inclusion of limits for dioxins in these permits is the narrative standard in the Basin Plan. The narrative prohibition, "All conservative toxic and deleterious substances, above those levels which can be achieved by a program acceptable to the Regional Board, to waters of the Basin" is the standard that is applied. The development of actual effluent limitations followed the procedure specified in the Basin Plan. This included the best professional judgment of Board staff that there was reasonable potential for exceedances of standards. Since there was concern regarding potential water quality problems in the receiving waters, staff acted in a protective manner, and included limits for dioxins. These water quality based effluent limits were developed based on available technical information.

The limits vary from facility to facility based on best professional judgment. However, the primary question in each case was whether to establish dioxin limits for 2,3,7,8-TCDD only or to establish a TEQ based limit for all of the dioxin congeners. In 1992, U.S. EPA had established criteria for 2,3,7,8-TCDD and the criteria document included a discussion of the use of toxicity equivalence factors and TEQ. However, U.S. EPA declined to promulgate TEQ standards in its 1992 National Toxic Rule. The California Ocean Plan, and the now invalid Enclosed Bays and Estuaries Plan established by the California State Water Resources Control Board, included TEQ limits for dioxin.

The first discharges regulated by the Regional Board were petroleum refineries. Catalytic reformers used as part of the oil refining process are a source of dioxins documented in the literature. Currently, all the refineries in the Bay Area have a limit of 0.14 picogram per liter (pg/l)[2] as TEQ. Only the Tosco Avon facility has violated this limit. The Pacific Refinery also recently violated its dioxin limit. Under the terms of the Cease and Desist Order issued by this Board in 1995, Tosco has further characterized dioxins in their discharge. Based on the data, staff has come to several conclusions:

- The mass of dioxins discharged from the Tosco Avon facility is less than the mass that would be discharged from a catchment area of approximate equal size anywhere in the Bay Area. This is based on estimates of average aerial deposition of dioxin and transport by storm water to surface water.

- The catalytic reformer does not appear to be a significant source of dioxins in the waste stream. This conclusion is based on comparison of the mass

[2] 1 pg/l is approximately 1 part per quadrillion or ppq. One ppq is 1/1000ths of a part per trillion or ppt. One ppt is 1/1000ths of a part per billion or ppb.

determining compliance with an effluent limit set based on the criteria for 2,3,7,8-TCDD or for any of the other congeners.

Currently, we assume a value of zero when a congener is below detection. Different conventions can be used such as assuming the value is at the limit of detection, or one half the detection limit. These are all commonly acceptable approaches for studies. However, for permit compliance determination, we believe using zero is the most defensible approach at this time.

Methods are available to improve analytical sensitivity. These involve concentrating a larger volume of the sample onto a solid absorbent and extracting the dioxins from the absorbent before analysis. Researchers have used these methods successfully on relatively clean environmental samples, but these methods have not been used on effluent samples which may be considerably more complex chemically. Data validation would be necessary before using these methods for compliance determination.

Current detection limits have already shown that dioxins are a widespread problem. Improved detection limits are not likely to change our overall understanding of the problem, but it will be useful for assuring permit compliance.

ACTIONS TAKEN OR IN PROGRESS

In addition to the regulatory action taken on discharges from petroleum refineries and sewage treatment plants, we have taken steps in response to the health advisory on consumption of fish from the Bay. Warning signs, in multiple languages, are posted at fishing piers throughout the Bay Area. We helped prepare and distribute brochures describing preparation methods for seafood that will minimize exposure to contaminants. We are also working in conjunction with other State and Federal agencies to prepare an educational program regarding consumption of seafood from the Bay.

Staff has played a large part in collecting data from storm water and some specific industrial discharges to help try to understand the problem. Staff has analyzed this data and data from treatment plants within the Region. A study of air deposition of a number of compounds, including dioxins, was included in the Regional Monitoring Program, but is not yet complete. This study will include the deployment of specialized sampling equipment to provide more accurate measurements of the rate of air deposition of selected compounds, including dioxins.

Additional fish tissue has been collected and is undergoing chemical analysis. Future studies will also include shellfish and crabs. It is probable that tissue

Options

The remainder of this section contains different options for Board consideration. The actions are summarized in two categories: actions to improve understanding of the problem, and actions that might reduce discharge to the Bay. Following each option is a short discussion of the action's purpose or possible effects, and the positive and negative points.

There is possibly a third category of action that might assist with risk reduction and risk management for exposed populations. One example is to educate and assist people on alternative food sources. These types of actions would require participation by numerous other agencies involved in human health protection and improvement.

Several presumptions are embedded in the options outlined below: the Regional Board does not have the ability to change the criteria adopted by U.S. EPA; and the Regional Board must include limits in NPDES permits for pollutants that have a reasonable potential to exceed water quality criteria.

A. Actions to improve understanding of the problem

1a. Action – Implement a dioxin limit for just 2,3,7,8-TCDD for all point source dischargers, such as petroleum refineries and sewage treatment plants. Require these dischargers to continue monitoring for all other dioxin and furan congeners. If detected levels expressed as TEQ are greater than the permit limit for 2,3,7,8-TCDD, require the discharger to conduct source audits.

Purpose – The monitoring aspect of this action will confirm and refine staff's current assessment with respect to the importance of local wastewater discharge sources relative to observed environmental levels. This will result in elimination of effluent limits for the other sixteen congeners of dioxins and furans in NPDES permits. Based on current data, assuming non-detects are zero, all point sources would be in compliance with a limit for 2,3,7,8-TCDD.

Positive – This is similar to the approach proposed in the draft Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays and Estuaries of California so no new policy would have to be established by the Board. Also, if lower detection limits methods are developed, the source audits would allow identification of actual sources that could be controlled.

Negative – This action will provide additional information on potentially less than 5% of the total dioxins currently discharged into the Bay. This may have large monetary impacts on publicly owned treatment works because dioxins analyses are expensive and currently available in only five commercial current detection limits is the fear that there are discharges occurring above the effluent limit that go undetected. This concern is minimized if the dioxin sources are controlled at the source and not simply diluted by other wastewaters to the point where it is below the detection limit.

Negative: In addition to those listed for 1a, it is possible that some generation sources will not be regulated. This can happen if an incomplete literature search is conducted or because some sources are not currently documented in the literature. Also, there are currently no guidelines or consensus regarding reasonable source control measures.

1d. Action -- No new action. Continue to impose dioxins limits as TEQ in permits as they come up for reissuance or new issuance. Continue to enforce permit limit violations and required source audits for these violations.

Purpose - This option fully utilizes the regulatory authority of the Board under the current permitting program.

Positive - The Board would not need to set a new policy.

Negative - Similar to 1a, source audits would be economically burdensome for many dischargers. Additionally, based on current data, about 9 out of 25 dischargers would be unable to consistently comply with the limit as TEQ. The Board has enforced against one of these dischargers and may enforce against another in the near future. Because permit exceedances may be caused by diffuse sources, compliance with the limit would required substantial upgrading of the end-of-pipe treatment systems for removal of solids, possibly costing on the order of $10's of million per facility. Control of these discharges would impact less than 5% of the dioxins load to the Bay. Another draw back is additional Board staff resources that would be diverted from other problems to pursue enforcement items.

2. Action – Require all storm water runoff and non-point source discharges to monitor for dioxins.

Purpose - Based on current data and staff interpretation of that data, the primary source of dioxins is mobile and stationary combustion sources. While the absolute magnitude of this contribution may be questioned, staff believes that regardless of the total, this source still represents the primary ongoing source of dioxins to surface water. This occurs both as direct deposition from air and through secondary transport of dioxin attached to material, such as sediment, that enters surface water as runoff. As with most diffuse sources, this is very difficult to control. The purpose of this action would be to more accurately quantify the contribution of dioxins to the Bay from secondary sources.

would have an extremely high consumption rate. Archived blood or tissue samples may already exist.

Negative – Sample collection from live organisms would require a special permit. Sample collection would require special equipment and expertise. The translation of the data to human receptors may be problematic.

5. Action: Establish a regional reasonable potential analysis to assess which category of discharge is having the most significant impact on dioxins in the Bay. This would be performed based on currently available data.

   Purpose: This would provide the legal vehicle for deleting dioxins limits from point source discharge permits which account for less than 5% of the total dioxin input to the Bay. This option would allow regional board staff to devote resources on options involving only storm water runoff discharges. These options include further monitoring and working with CalEPA to address the cross-media problem of dioxins.

   Positive: Devotes resources on the area that has the most impact to the Bay.

   Negative: The Board will have only indirect authority over any source reductions that are needed.

B. Actions to limit dioxin discharge to the environment

1. Action – Request that Cal/EPA direct its agencies to assess dioxin as a cross-media issue to identify sources of dioxin, the best potential control strategies, and impacts to public health and aquatic life.

   Purpose - This would help to identify sources that eventually enter storm water from the air and would provide better discrimination for potentially controllable sources.

   Positive – This would involve all of the appropriate agencies in identifying sources and formulating a cost effective control strategy. It would foster a cross media approach and help agency personnel to focus on the root causes of the problem.

   Negative – Resources for agency staffing and any contract dollars needed may be limited.

2. Action – Require treatment of all storm water to remove dioxin. This would probably require sediment removal from all storm water outfalls.

Appendix A

Dioxin Toxicity Equivalence

As stated above, 2,3,7,8-TCDD is the most widely studied of the forms of dioxin. This is also the most toxic of the dioxin compounds. Consequently, standards for the discharge to water have been established for 2,3,7,8-TCDD. Standards have not been established for the other congeners. The use of toxicity equivalence factors (TEFs) to calculate a TEQ is one method to assess the toxicity of mixtures of dioxins and furans.

Toxicologists establish a TEF for each congener. For many of the congeners, the TEFs are often based on very limited toxicological data. The establishment of these TEFs is a source of open debate within the toxicology community. The U.S. EPA and the World Health Organization have each adopted this approach for risk assessment, though each organization uses different TEF values for some congeners. The key point is that most of the controversy surrounds the TEFs for OCDD and HpCDD. These congeners are the most commonly detected and usually detected at the highest concentration in our samples of storm water, sewage effluent and refinery effluents.

For a given sample the concentration of each congener is multiplied by the TEF for that congener, with the TEF for 2,3,7,8-TCDD being one. These TEF values are then summed to equal the TEQ for that sample. The concept is that the TEQ represents the toxicity of the mixture as if only 2,3,7,8-TCDD had been detected. A calculation example is shown in the table below. This is the calculation of TEQ for a storm water sample from the Bay Area. For this calculation, congeners that are not detected (ND) are assigned a value of zero.

Several points about this example are of note:

- This is typical of samples of storm water from the Bay Area.
- 2,3,7,8-TCDD is not detected.
- The dominant congeners detected are OCDD and HpCDD the least toxic congeners.
- Assuming that the TEQ limit of 0.014 pg/L was applicable, this sample would represent an instance of non-compliance.
- If the limit for this sample had been based solely on 2,3,7,8-TCDD, not TEQ for dioxins, it would have been in compliance.

CONGENER	Toxicity Equivalence Factor	Concentration (pg/l)	Detection Limit	TEQ
2,3,7,8-TCDD	1	ND	0.9	0
Total TCDD		ND	0.9	
1,2,3,7,8-PeCDD	0.5	ND	2.5	0
Total PeCDD		ND	2.5	
1,2,3,4,7,8-HxCDD	0.1	4.5		0.45
1,2,3,6,7,8-HxCDD	0.1	14		1.4
1,2,3,7,8,9-HxCDD	0.1	9.4		0.94
Total HxCDD		75		
1,2,3,4,6,7,8-HpCDD	0.01	230		2.3
Total HpCDD		420		
OCDD	0.001	1700		1.7
2,3,7,8-TCDF	0.1	1.2		0.12
Total TCDF		17		
1,2,3,7,8-PeCDF	0.05	1.8		0.09
2,3,4,7,8-PeCDF	0.5	3.2		1.6
Total PeCDF		60		
1,2,3,4,7,8-HxCDF	0.1	3.8		0.38
1,2,3,6,7,8-HxCDF	0.1	5.3		0.53
2,3,4,6,7,8-HxCDF	0.1	6.4		0.64
1,2,3,7,8,9-HxCDF	0.1	ND	0.98	0
Total HxCDF		75		
1,2,3,4,6,7,8-HpCDF	0.01	46		0.46
1,2,3,4,7,8,9-HpCDF	0.01	2.4		0.02
Total HpCDF		110		
OCDF	0.001	88		0.09
SUM OF 2,3,7,8-TCDD Toxicity Equivalents			11	

Toxicity equivalence factors and TEQ were developed for the evaluation and comparison of mixtures of congeners. Most samples from the storm water study (RWQCB 1997) are dominated by two congeners of dioxin. In this case, where a mixture is limited, the use of TEQ may not be an appropriate measure of compliance.