FINAL

Dioxins in San Francisco Bay

Conceptual Model/Impairment Assessment

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Executive Summary

This report has been produced for the Clean Estuary Partnership (CEP). The CEP is a collaboration of the Bay Area Clean Water Agencies, Bay Area Stormwater Management Agencies Association, the San Francisco Bay Regional Water Quality Control Board, and other participants. This cooperative partnership facilitates efforts to improve water quality in San Francisco Bay by providing financial and staff support for technical studies, discussion of management questions and strategies, and stakeholder outreach activities.

Several Conceptual Model/Impairment Assessment (CM/IA) reports have been commissioned by the CEP for pollutants that have been identified in the past as possible causes of impairment to beneficial uses in San Francisco Bay. These CM/IA reports have several objectives:

- Evaluate the current level of impairment of beneficial uses, including descriptions of standards or screening indicators and relevant data.
- Develop a conceptual model that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment, and biota.
- Identify potential studies that might reduce uncertainties associated with the report's conclusions.

This CM/IA report examines dioxins in San Francisco Bay. Dioxins comprise a group of several hundred chemical compounds with similar chemical structures and toxicological properties. While all the compounds are collectively referred to as dioxins, they actually fall into two related groups: polychlorinated dibenzo-p-dioxins (known themselves as dioxins and also known as PCDDs or CDDs) and polychlorinated dibenzofurans (also known as furans, PCDFs, or CDFs).

Impairment Assessment

The impairment assessment first reviews past information, which led the U.S. Environmental Protection Agency to determine that sport fishing in San Francisco Bay was impaired by dioxins. The assessment then uses the most recent, available data on concentrations of dioxins in fish tissues, water, sediments, and wildlife to make an independent assessment of the current level of impairment of sport fishing and other uses of the Bay. The assessment uses the data to determine whether there is a weight of evidence indicating:

- **No impairment:** The available data demonstrate no negative effect on beneficial uses of the Bay, and there is sufficient information to make the finding.
- **Impairment unlikely:** The data indicate that dioxins cause no impairment to the Bay. However, there is some uncertainty, due to lack of sufficient information or disagreement about how to interpret the data.
- **Possible impairment:** There is some suggestion of impairment, but the uncertainties preclude making a definitive judgment.
- **Definite impairment:** The data clearly demonstrate a negative effect on the beneficial uses of the Bay.
- **Unable to determine impairment:** There is insufficient information to make any determination.

Dioxins are present in the environment in very low concentrations, and chemical analyses are difficult and expensive. Consequently, relatively few measurements have been made of dioxins in the water, sediments, and biota of San Francisco Bay. Much of the data that are available are difficult to interpret, because many specific dioxin compounds are present at levels below the analytical detection limits. These constraints make an impairment assessment nearly impossible. Nonetheless, the available fish and water data do indicate **possible impairment** of the Bay for sport fishing. (The degree of impairment from dioxins and furans alone is small compared to impairment by the dioxin-like PCBs, which are being addressed by a separate TMDL.) Because there is so little available information, there is virtually no evidence of impairment of other beneficial uses.

Conceptual Model

The conceptual model provides a framework for prioritizing management decisions and actions for reducing contamination by dioxins in San Francisco Bay. The conceptual model:

- Presents a simple **one-box model** of the Bay.
- Synthesizes information on **sources** of PCDD/Fs to San Francisco Bay, including use of national and regional studies of PCDD/Fs to augment the limited available local data.
- Describes **pathways and estimates loads** from single-point and more diffuse sources.
- Describes the dominant local **processes** that determine the fate of PCDD/Fs in the Bay.
- Presents inputs to and outputs from the one-box **mass balance model** of the current inventory, long-term change, loading estimates, and loss pathways.

The conceptual model also identifies areas of uncertainty, which limit the ability to quantify responses and rates.

Dioxins are mostly produced as byproducts of combustion 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,

emissions from facilities such as incinerators and smelters were thought to be the largest sources of dioxins. These sources have been controlled, reducing the major historic sources of dioxins. More disperse sources, such as yard burning and vehicle emissions, remain uncontrolled and persist at levels similar to those in the past.

Because there is little local information, estimates of loads to the Bay are subject to great uncertainties. However, it is clear that the legacy of dioxins in the watershed and the sediments outweigh the other sources. Model estimates of the degradation and transport rates for dioxins suggest that current inputs of dioxins to the Bay may be sufficient to continue the current level of impairment.

Information Gaps

There are many uncertainties and information gaps in this report's conclusions. Perhaps the greatest uncertainty is in dioxin measurements themselves—because so many compounds occur at extremely low concentrations, the available analyses include estimated as well as measured values. Dioxins are thought to be so toxic that these estimated values can affect data interpretation.

Future projects will obtain additional data and conduct more analysis of the sources, fate, transport, and effects of dioxins. In other documents or forums, the CEP will develop appropriate strategies for addressing dioxins in the Bay and its watersheds. There may be control measures, remediation, and regulatory actions that can and should begin now, even with existing uncertainties. CEP partners are committed to identifying these actions. Future CEP data gathering and technical analysis should focus on determining the potential effectiveness and actual effects of actions to reduce or eliminate impairment and to restore beneficial uses of the Bay.

Table of Contents

Executive Summary i
Impairment Assessment i
Conceptual Model ii
Information Gaps iii

1. Introduction 1
1.1 Regulatory Background 1
1.2 San Francisco Bay 2
1.3 Dioxins 5
2. Impairment Assessment 7
2.1 Basis for the Current Impairment Listing 7
2.2 Current Conditions 10
2.2.1 Fish and Shellfish 10
2.2.2 Water Quality 20
2.2.3 Sediments 22
2.2.4 Wildlife Health Concerns 23
2.3 Impairment Summary 24
3. Conceptual Model 25
3.1 One-Box Model 25
3.2 Sources 26
3.2.1 Local and Regional Sources 27
3.2.2 Regional vs. Global Sources 29
3.2.3 Temporal Patterns 29
3.3 Loading Pathways to the Bay 30
3.3.1 Municipal and Industrial Discharges 31
3.3.2 Watershed Loading 35
3.3.3 Direct Atmospheric Deposition 38
3.3.4 Erosion of Buried Sediment 38
3.4 Environmental Processes 39
3.4.1 Atmospheric Transformations 39
3.4.2 In-Bay Processes 41
3.5 Mass Balance Model 44
3.5.1 Ecosystem Inventories 46
3.5.2 Loading Estimates 48
3.5.3 Loss Pathways 49
3.5.4 Model Results 50
4. Information Gaps 54
References 56

List of Figures

Figure 1-1. San Francisco Bay 3
Figure 2-1. Fish sampling locations 16
Figure 2-2. TEQ concentrations in Bay fish 17
Figure 2-3. TEQ in each sampling location for striped bass and white perch 18
Figure 2-4. Sum of TEQs in 100-liter San Francisco Bay water samples 22
Figure 3-1. One-box model 26
Figure 3-2. Past and projected PCDD/F emissions in the U.S. 27
Figure 3-3. Sources of San Francisco Bay Area PCDD/F emissions. 28
Figure 3-4. Sources of dioxin and furan emissions in the San Francisco Bay Area 28
Figure 3-5. Top: PCDD/Fs in ambient water 100-liter samples; Bottom: PCDD/Fs in ambient water 4-liter samples 36
Figure 3-6. PCDD/F homolog concentrations: sources vs. receptors 40
Figure 3-7. San Francisco Bay food web 44
Figure 3-8. PCDD/F sources, pathways (g TEQ/year), and inventories (g TEQ) in San Francisco Bay 45
Figure 3-9. Modeled long-term PCDD fate 52
Figure 3-10. Modeled long-term PCDF fate. 52

List of Tables

Table 1-1. Beneficial uses of San Francisco Bay 4
Table 1-2. Dioxins included on the 303(d) list for San Francisco Bay 5
Table 2-1. Beneficial uses of San Francisco Bay that could be impaired by dioxins. 7
Table 2-2. Analyses cited by USEPA in decision to list San Francisco Bay as impaired by dioxins 9
Table 2-3. Factors used in USEPA assessment of risk for recreational anglers consuming San Francisco Bay fish 10
Table 2-4. Fish consumption rates calculated by the San Francisco Seafood Consumption Study 12
Table 2-5a. Maximum risk level used to calculate screening values 14
Table 2-5b. Cancer slope factors used to calculate screening values 14
Table 2-5c. Body weight used to calculate screening values 14
Table 2-5d. Sources of fish consumption data 14
Table 2-5e. Screening values for dioxins 14
Table 2-6. Fish monitored by the RMP and percent anglers that consume each species . 15
Table 2-7. Number of striped bass samples exceeding screening values 18
Table 2-8. Water quality standards for dioxin 20
Table 2-9. Sum of TEQs in 100-liter San Francisco Bay water samples 21
Table 2-10. Impairment of San Francisco Bay by dioxins 24
Table 3-1. Average municipal discharge PCDD/F concentrations and loads, 1999-2003 data, 1- to 4-liter samples 32
Table 3-2. Average municipal discharge PCDD/F concentrations and loads, 100-liter SPE samples 33
Table 3-3. Average refinery aqueous effluent PCDD/F concentrations and loads, 1999-2003 34
Table 3-4. Average effluent PCDD/F concentrations and loads from other discharges ... 34
Table 3-5. Average Sacramento River PCDD/F concentrations in 100-liter SPE samples and loads 37
Table 3-6. Concentrations of PCDD/Fs in sediments 47
Table 3-7. Estimated loads of PCDD/Fs to San Francisco Bay 48
Table 3-8. Contribution of PCDD/F homologs to loads (local tributaries and air deposition) 49
Table 3-9. Long-term (25-year) fate of PCDDs under various scenarios 51
Table 3-10. Long-term (25-year) fate of PCDFs under various scenarios 51

1. Introduction

This report has been produced for the Clean Estuary Partnership (CEP). The CEP is a collaboration of the Bay Area Clean Water Agencies, Bay Area Stormwater Management Agencies Association, and the San Francisco Bay Regional Water Quality Control Board. Other important participants include the San Francisco Estuary Institute, Clean Water Fund, San Francisco Bay Keeper, Port of Oakland, and the Western States Petroleum Association. This cooperative partnership facilitates efforts to improve water quality in San Francisco Bay by providing financial and staff support for technical studies, discussion of management questions and strategies, and stakeholder outreach activities.

Several Conceptual Model/Impairment Assessment (CM/IA) reports have been commissioned by the CEP for pollutants that have been identified in the past as possible causes of impairment to beneficial uses in San Francisco Bay. The general objectives of these CM/IA reports are:

- Evaluate the current level of impairment of beneficial uses, including descriptions of standards or screening indicators and relevant data.
- Develop a conceptual model that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment, and biota.
- Identify potential studies that might reduce uncertainties associated with the report's conclusions.

Since the state of knowledge varies among pollutants, initial CM/IA reports may lack the resources to fully achieve all these objectives. This CM/IA report should be viewed as a tool for planning and an important step in resolution of dioxin-related issues and not as a conclusive statement on the conceptual model, beneficial-use impairment, or information needed to resolve dioxin-related issues.

This introduction presents the regulatory background for considering waters as impaired, the San Francisco Bay setting and its designated beneficial uses, and a brief description of dioxins.

1.1 Regulatory Background

The federal Clean Water Act (CWA) provides protection to the surface waters of the United States. Section 101(a)(2) of the act establishes a national goal of "water quality which provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water, wherever attainable." Section 303(d) requires states to compile lists of water bodies that do not meet water quality standards and to develop plans (known as total maximum daily loads or TMDLs) for achieving the standards. U.S. Environmental Protection Agency

(USEPA) regulations require that 303(d) lists be compiled every two years. In California, Section 13001 of the California Water Code identifies the California State Water Resources Control Board (SWRCB) and Regional Water Quality Control Boards (RWQCBs) as the principal agencies responsible for controlling water quality.

1.2 San Francisco Bay

San Francisco Bay is located on the central coast of California. It is the largest estuary on the West Coast of the United States, draining a watershed of 60,000 square miles. Much of the Bay is shallow, and the average depth is only about 14 feet. At its deepest, however, the Bay is more than 300 feet deep.

The federal and state regulatory bodies divide San Francisco Bay into eight segments: Sacramento/San Joaquin River Delta, Suisun Bay, Carquinez Strait, San Pablo Bay (including Castro Cove), Richardson Bay, Central San Francisco Bay (including Oakland Harbor and San Leandro Bay), Lower San Francisco Bay, and South San Francisco Bay (Figure 1-1). The Bay is a popular fishing location, visited by thousands of anglers every year. It is also important habitat for wildlife, including birds and marine mammals. It is a staging and wintering area for approximately 1 million migratory waterfowl and 1 million shorebirds and also provides breeding habitat for many bird species. The Bay also supports a significant resident breeding population of Pacific harbor seals (Grigg, 2003).

The Water Quality Control Plan for the region (SFRWQCB, 1995) lists the beneficial uses for the Bay (Table 1-1).

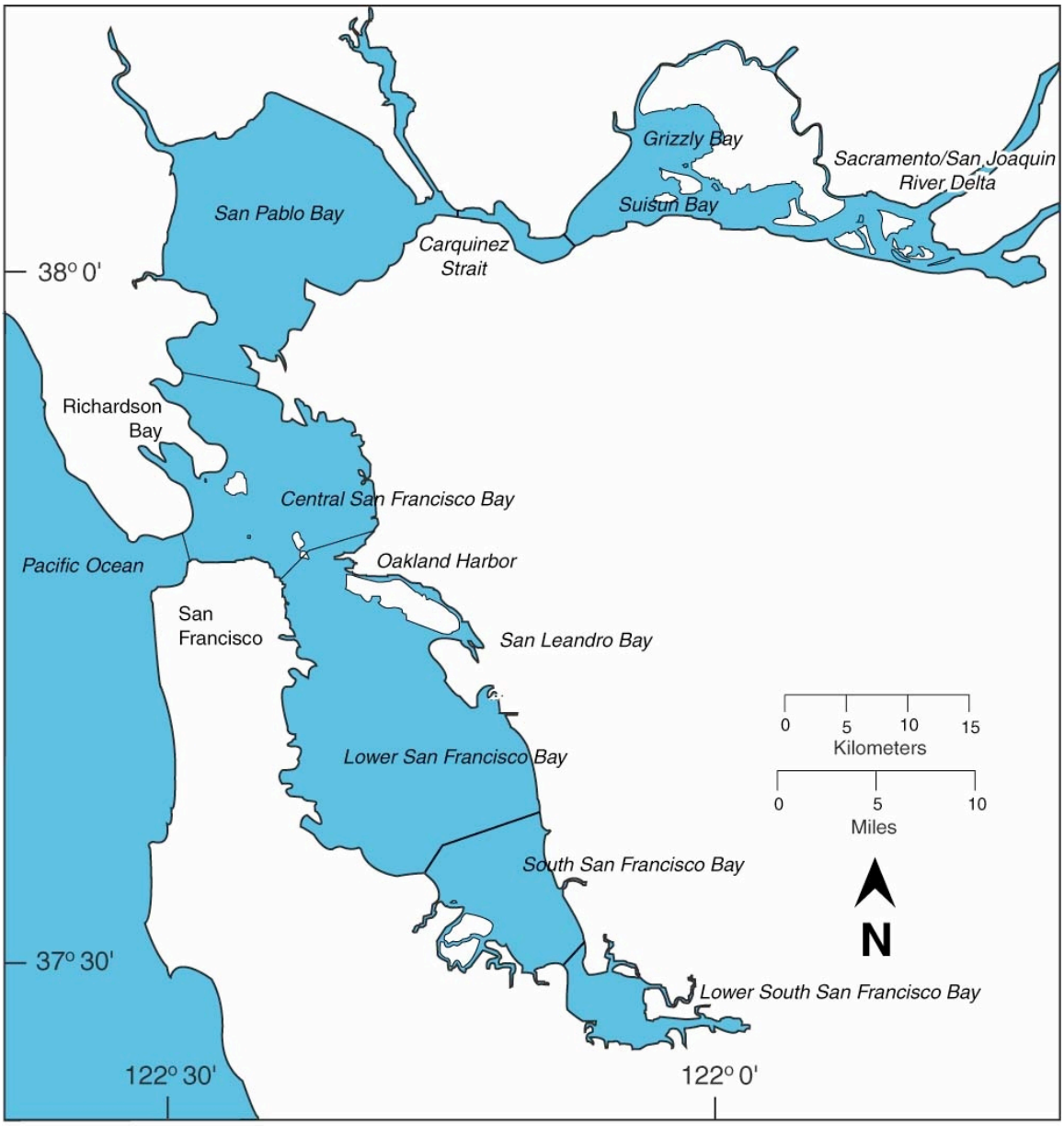


Figure 1-1. San Francisco Bay

*Table 1-1. Beneficial uses of San Francisco Bay**

Use	Abbreviation	Definition
Ocean, commercial, and sport fishing	COMM	Uses of water for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including but not limited to, uses involving organisms intended for human consumption.
Estuarine habitat	EST	Uses of water that support estuarine ecosystems, including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (*e.g.*, estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
Industrial service supply	IND	Uses of water for industrial activities that do not depend primarily on water quality, including, but not limited to, mining, cooling water supply, hydraulic conveyance, gravel washing, fire protection, and oil well repressurization.
Fish migration	MIGR	Uses of water that support habitats necessary for migration, acclimatization between fresh water and salt water, and protection of aquatic organisms that are temporary inhabitants of waters within the region.
Navigation	NAV	Uses of water for shipping, travel, or other transportation by private, military, or commercial vessels.
Industrial process supply	PRO	Uses of water for industrial activities that depend primarily upon water quality.
Preservation of rare and endangered species	RARE	Uses of waters that support habitats necessary for the survival and successful maintenance of plant or animal species established under state and/or federal law as rare, threatened, or endangered.
Water contact recreation	REC1	Uses of water for recreational activities involving body contact with water where ingestion of water is reasonably possible. These uses included, but are not limited to, swimming, wading, water-skiing, skin and scuba diving, surfing, whitewater activities, fishing, and uses of natural hot springs.
Noncontact water recreation	REC-2	Uses of water for recreational activities involving proximity to water, but not normally involving contact with water where ingestion is reasonably possible. These uses include, but are not limited to, picnicking, sunbathing, hiking, beachcombing, camping, boating, tide pool and marine life study, hunting, sightseeing, or aesthetic enjoyment in conjunction with the above activities.
Shellfish harvesting	SHELL	Uses of water that support habitats suitable for the collection of crustaceans and filter-feeding shellfish (*e.g.*, clams, oysters, and mussels) for human consumption, commercial, or sport purposes.
Fish spawning	SPWN	Uses of water that support high quality aquatic habitats suitable for reproduction and early development of fish
Wildlife habitat	WILD	Uses of waters that support wildlife habitats, including, but not limited to, the preservation and enhancement of vegetation and prey species used by wildlife, such as waterfowl.

** All beneficial uses do not apply to all Bay segments.*

1.3 Dioxins

Dioxins comprise a group of several hundred chemical compounds with similar chemical structures and toxicological properties. While all the compounds are often collectively referred to as dioxins, they actually fall into two related groups: polychlorinated dibenzo-p-dioxins (known themselves as dioxins and also known as PCDDs or CDDs) and polychlorinated dibenzofurans (also known as furans, PCDFs, or CDFs). Together, the two groups are called "dioxins," "dioxins and furans," or PCDD/Fs. A third, related group, not considered by this report, is the dioxin-like polychlorinated biphenyls (dioxin-like or co-planar PCBs).

Toxicity of the individual dioxin and furan compounds varies and is defined by toxic equivalency factors (TEFs), which are based on results of *in vivo* and *in vitro* studies (Van den Berg *et al.*, 1998). The most toxic compounds are given a TEF of 1.0, and TEFs of other compounds reflect their relative toxicity (Table 1-2).

Table 1-2. Dioxins included on the 303(d) list for San Francisco Bay

Compound	TEF Mammals	TEF Fish	TEF Birds
Dioxin compounds			
2,3,7,8-TCDD (tetrachloro-dibenzo-p-dioxin)	1	1	1
1,2,3,7,8-PeCDD (pentachloro-dibenzo-p-dioxin)	1	1	1
1,2,3,4,7,8-HxCDD (hexachloro-dibenzo-p-dioxin)	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDD (heptachloro-dibenzo-p-dioxin)	0.01	0.001	<0.001
OCDD (octachloro-dibenzo-p-dioxin)	0.0001	<0.0001	0.0001
Furan compounds			
2,3,7,8-TCDF (tetrachloro-dibenzofuran)	0.1	0.05	1
1,2,3,7,8-PeCDF (pentachloro-dibenzofuran)	0.05	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	1
1,2,3,4,7,8-HxCDF (hexachloro-dibenzofuran)	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,5,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF (heptachloro-dibenzofuran)	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF (octachloro-dibenzofuran)	0.0001	<0.0001	<0.0001

Dioxin and furan compounds are not purposefully manufactured, but are created inadvertently, as byproducts of chemical production processes and combustion. Dioxins are formed during waste incineration, burning of fuels, forest fires, and chlorine bleaching of pulp and paper. Cigarette smoke includes small amounts of dioxins. Sources of dioxins to San Francisco Bay include cars and trucks, residential wood burning, sewage treatment plants, industrial discharges, and remobilization of historic sediment deposits. A more detailed discussion of sources, including relative magnitudes, is presented in the conceptual model section of this report.

Total concentrations of dioxins are usually presented as toxic equivalents (TEQs). TEQs are calculated as the sums of the concentrations of individual compounds, weighted by their TEFs. That is, the TEQ equals the sum of the concentrations of individual compounds after they have been multiplied by their TEFs.

Dioxins are present in very low concentrations in environmental samples. Units used to report levels in this report are typically in the range of picograms per gram or picograms per liter (pg/g or pg/l). One pg/g is equivalent to one nanogram per kilogram or one part per trillion.

Measurement of dioxins in environmental samples is difficult. Concentrations of dioxins in the environment, particularly in water samples, are often at levels that are below the method detection limit for standard analytical techniques (USEPA Method 1613, with 1-liter samples). Since there is a wide range in TEFs for individual compounds, TEQs are influenced by the difficulties in detecting some of the more toxic but less abundant compounds, such as the tetra-and pentachloro-isomers. Because dioxins are not soluble and adsorb to particles, the presence or lack of just a few particles in water samples can greatly affect the variability in analyses of water samples.

One method of mitigating the challenges of dioxin analyses in water samples is to increase the sample size. Increasing the sample size both increases the overall signal at the analytical instrument, leading to fewer measurements below detection limits, and decreases the influence of randomly captured contaminated particles, leading to less variability between replicate samples. This approach is not perfect—a study of dioxins in refinery effluent found that increasing the sample size lowered the variability between samples but also lowered the mean concentrations measured in the samples (Ultramar, 2002).

Concentrations of dioxins are typically higher in sediment and tissue samples, so the uncertainty introduced by compounds that are below detection limits is less than that of water samples. However, there are almost always compounds present at levels below detection limits. TEQs can be calculated with the assumption that those "nondetected" compounds are not present. "Assumed" concentrations can also be used. Using one-half the detection limit as an assumed concentration is typical. Substituting the full value of the detection limit is also an option. Typically, TEQs are calculated with and without assumed concentrations, and both values are reported.

There can also be problems when comparing results between analytical laboratories. For many environmental matrices, there are no reference materials with certified values, so laboratories cannot compare their results to standard materials.

2. Impairment Assessment

The San Francisco Bay segments have a variety of established beneficial uses, but only a few could be threatened by dioxins (Table 2-1). The current 303(d) listing cites the beneficial use of sport fishing as impaired for all segments. Effects on rare and endangered species, fish spawning, and wildlife are also possible.

Table 2-1. Beneficial uses of San Francisco Bay that could be impaired by dioxins.

Use	Abbreviation	Impairment
Ocean, commercial, and sport fishing	COMM	Sport fishing the most likely impairment. Cited as USEPA reason for the current listing.
Preservation of rare and endangered species	RARE	Possible
Fish spawning	SPWN	Possible
Wildlife habitat	WILD	Possible
Estuarine habitat	EST	Possible

This section of the report, the impairment assessment, first reviews the basis for the current listing. This object of this review is not to determine impairment but to provide background information for why dioxins became a concern.

The assessment then uses the most recent available data to determine whether there is a weight of evidence indicating:

- **No impairment:** The available data demonstrate no negative effect on beneficial uses of the Bay, and there is sufficient information to make the finding.
- **Impairment unlikely:** The data indicate that dioxins cause no impairment to the Bay. However, there is some uncertainty, due to lack of sufficient information or disagreement about how to interpret the data.
- **Possible impairment:** There is some suggestion of impairment, but the uncertainties preclude making a definitive judgment.
- **Definite impairment:** The data clearly demonstrate a negative effect on the beneficial uses of the Bay.
- **Unable to determine impairment:** There is insufficient information to make any determination.

The assessment also attempts to distinguish possible impairment for individual segments as well as for the Bay as a whole.

2.1 Basis for the Current Impairment Listing

Dioxins were not included on California's 303(d) list as a result of actions taken by SWRCB or the RWQCB. The state declined to make the listing, citing several reasons:

- Water-column dioxin levels did not exceed water quality criteria.
- Concentrations of dioxins and furans were within national background levels.
- The fish consumption advisory issued by the State was an interim advisory, which was not based on a quantitative risk assessment for dioxins and which mentions dioxins only because of exceedances of screening values in a study of San Francisco Bay fish tissue.

USEPA added dioxins ("dioxin-like compounds") to the 1998 list, finding that that the State had not adequately analyzed the potential human health risk from consumption of seafood (May 12, 1999, letter from A. Strauss to W. Petit and accompanying November 3, 1998 staff report). Specifically USEPA found that SWRCB had not adequately addressed available fish tissue data:

> *"EPA is identifying dioxin-like compounds for inclusion on the 303(d) list for San Francisco Bay (including all Bay segments) based on (1) the reference to these pollutants in a fish consumption advisory issued in December 1994… and (2) EPA's analysis of available data which indicate potential health risk from eating fish contaminated with these pollutants. EPA has found that the fish consumption beneficial use of San Francisco Bay is being impaired, and the narrative standards which prohibit the discharge of toxic pollutants in amounts which adversely affect beneficial uses are not being met."*

USEPA also found that the issue of national background levels of dioxins and furans was not relevant to the question of whether to list the Bay.

The fish consumption advisory referred to by the State and USEPA is an interim advisory that has been in place since 1994. The Office of Environmental Health Hazard Assessment (OEHHA) interim health advisory is directed at consumption of sport fish from San Francisco Bay:

- **Adults should consume no more than two meals per month of sport fish from the Bay, including sturgeon and striped bass.**
- **Adults should not eat striped bass over 35 inches long.**
- **Pregnant women, nursing mothers, and children under the age of six should limit their consumption of sport fish to one meal per month.**
- **Pregnant women, nursing mothers, and children under six should not eat striped bass over 27 inches long or shark over 24 inches long.**

The interim advisory does not apply to some sport fish, such as salmon, anchovies, herring, and smelt. Neither does it apply to the commercial fisheries (bait shrimp, herring, and Dungeness crabs). It is based on a 1994 study

(SFRWQCB *et al.,* 1995), which indicated that dioxins, as well as PCBs, mercury, and legacy pesticides, were present at levels of potential concern. The study measured contaminants in fish from 13 locations chosen to represent all areas of the Bay, including areas suspected of low or high contamination and locations known to be popular for sport fishing.

The advisory was based on a preliminary review of the data, with OEHHA stating that:

> *"More specific advisories and recommendations will be issued when a thorough evaluation of the study data is completed by OEHHA in conjunction with other public agencies."*

One issue that could not be resolved by a data review was whether the advisory could be issued for specific locations instead of for the entire Bay. Different species were caught at different locations, making comparisons among stations difficult. OEHHA has reviewed data from subsequent rounds of fish sampling in 1997 (Davis *et al.,* 2002) and 2000 (Greenfield *et al.*, 2003) and has left the interim advisory in place.

USEPA used several internal studies to determine that the risk of dioxins in fish was a problem (Table 2-2).

Table 2-2. Analyses cited by USEPA in decision to list San Francisco Bay as impaired by dioxins

Study	USEPA Findings
California Toxics Rule Economic Analysis (USEPA, 1997)	Risk assessment estimated excess cancer risk associated with dioxin for the 90th percentile fish consumption level (107.1 g/day) is 3.8 x 10^{-4}. PCBs, mercury, and dioxin are the contaminants with the greatest potential to cause adverse health effects for Bay anglers.
USEPA internal evaluation of fish tissue data in comparison to national guidance	Average concentration of dioxin TEQs in fish tissue was about 1.6 ppt (1.6 pg/g). USEPA guidance indicates that 3 meals a month (1.5 pounds) of fish with 2 ppt dioxin results in cancer risk of 10^{-4}, which is 10-100 times greater than acceptable. Many regular consumers of Bay fish consume far more than 1.5 pounds of fish per month.
Detailed USEPA internal reevaluation of fish data to examine quality assurance issues and relative importance of dioxins and furans compared to PCB risk	If data below detection limits are excluded from analysis, dioxin-like PCBs constitute a 5-60 fold greater risk than dioxins and furans. However, average dioxin/furan tissue residues significantly exceed a screening value of 0.15 ppt TEQ.

The risk assessment conducted by USEPA as part of the analysis of the implementation of the California Toxics Rule (USEPA, 1997 and presented in USEPA, 1999) relied on the same pilot study that OEHHA used to develop the interim fish consumption advisory (Table 2-3).

Table 2-3. Factors used in USEPA assessment of risk for recreational anglers consuming San Francisco Bay fish (from USEPA, 1999)

Factors	Source
Fish consumption rates	Median fish consumption rate of 21.4 g/day and 90th percentile consumption rate of 107.1 g/day, based on Santa Monica Seafood Study (MBC Applied Environmental Services, 1994)
Fish contaminant concentrations	Bay Protection and Toxic Cleanup Program to measure concentrations of contaminants in fish (SFRWQCB *et al.*, 1995)
Species-weighted contaminant concentrations	National Marine Fisheries Services Marine Recreational Fishing Statistics Survey of the Pacific Coast for 1987, 1988, 1989, and 1993: ▪ White croaker 43% ▪ Surf perch 35% ▪ Striped bass 13.9% ▪ Shark 8%
Baseline risk levels	USEPA, 1989, assuming length of residence of 70 years and body weight of 70 kg

2.2 Current Conditions

Because the 303(d) listing focuses on fish-tissue data, this section of the report begins with a review of fish and shellfish data. The report then evaluates other relevant data: water quality, sediment quality, and wildlife health. For each of these data sets, the assessment presents:

- The relevant **regulatory standards**, if there are any, focusing on the best local standards, but including a discussion of alternatives and national or historic standards when needed for context.
- **Available data**, interpreted relative to the standards.
- A discussion of whether the data are **indicative of impairment**.

2.2.1 Fish and Shellfish

Fish and Shellfish Standards

There are no state or federal standards limiting contaminant levels in fish and shellfish in the sport fishery. Therefore, USEPA has issued guidance for states to use in developing their own screening values for recreational fish and shellfish (USEPA, 2000a, b). These screening values are not meant to be regulatory standards, but rather indicators that more intensive site-specific monitoring and/or evaluation of human health risk should be conducted.

Volume 1 of that guidance (USEPA, 2000a) presents an equation for calculating screening values for carcinogens:

Screening value = [(Risk level/Cancer slope factor) x Body weight] / Consumption rate

where

Screening value = Screening value for a carcinogen (mg/g; ppm or pg/g; ppt)

Risk level = Maximum acceptable risk level (unitless)
Cancer slope factor = Oral cancer slope factor $(mg/kg\text{-}d)^{-1}$
Body weight = Mean body weight of general population of concern (kg)
Consumption rate = Mean daily consumption rate of the species of interest by the general population of concern over a 70-year lifetime (kg/d)

Each factor in the equation is open to some interpretation:

Risk level: USEPA (2000a) uses an acceptable risk level of 10^{-5}, that is, a level of risk not to exceed one excess case of cancer per 100,000 people over a 70-year lifetime. However, states can use other levels—values ranging from 10^{-4} to 10^{-7} are typical (one additional cancer in 10,000 to 10,000,000 people). USEPA regards choice of an acceptable risk level as a management rather than a scientific issue (USEPA, 2000a). This report uses 10^{-5} and also discusses the implications of using 10^{-6}, which is more protective (both 10^{-5} and 10^{-6} were cited in the USEPA decision to list dioxins).

Cancer slope factor: For more than a decade, USEPA has been conducting a reassessment of dioxin toxicity, and that review is ongoing. Consequently, there is no current agreement on cancer slope factors, and 2,3,7,8-TCDD (the dioxin compound against which toxicity of all others is compared) is not included in the USEPA Integrated Risk Information System (IRIS). USEPA (2000a) recommended a cancer slope factor of 156,000 $(mg/kg\text{-}d)^{-1}$. That cancer slope factor has been used to calculate screening values for San Francisco Bay (*e.g.,* Greenfield *et al.,* 2003). The OEHHA database cites a slope factor of 130,000 $(mg/kg\text{-}d)^{-1}$. This report uses the more protective value from USEPA (2000a), but also calculates screening values based on the value in the OEHHA database .

Body weight: USEPA uses 70 kg (154 pounds) as representative of all adults, with adult males weighing 78 kg (172 pounds) and adult females weighing 65 kg (143 pounds).

Consumption rate: USEPA's decision to include dioxins on the 303(d) list was largely based on a risk assessment that assumed consumption of 107.1 grams of fish per day (about 14 meals per month). That 107.1 g/day consumption rate was the 90th percentile consumption rate measured in the Santa Monica Seafood Study (MBC Applied Environmental Services, 1994), a widely cited study of seafood consumption rates. The median

consumption rate calculated by the study was 21.4 grams of fish per day (about three meals per month).

The Santa Monica Seafood Study is not the only source of data on fish consumption rates for recreational fish. In its guidance for assessing data for use in fish advisories (USEPA, 2000a), USEPA recommends using 17.5 g/day, a value taken from a 1994 and 1996 U.S. Department of Agriculture study of food intake. In another application, the development of water quality criteria, USEPA used 6.5 g/day, based on data from a 1973-1974 study of per capita consumption of freshwater and estuarine fish and shellfish.

Fortunately, there is local information for San Francisco Bay. The San Francisco Seafood Consumption Study (SFEI, 2000) surveyed more than 1,000 recreational anglers from party boats, private boats, and popular shore-based sites to determine catch and consumption rates. Of those interviewed, 87% reported that they had eaten Bay fish at some time, and 13% said that they had not. Of those who had consumed fish from the Bay, 47% reported having eaten it within the past four weeks.

Table 2-4 presents San Francisco Seafood Consumption Study consumption rates calculated for several groups:

- **Recent consumers**, that is, anglers who had consumed fish caught in San Francisco Bay during the four weeks prior to being interviewed.
- **Recent consumers, adjusted for "avidity,"** a measure of how frequently anglers go fishing. Statistically, anglers who fish often would be more likely to be over-sampled by the survey, and infrequent anglers would be under-represented. The avidity adjustment corrects for the over- and under-sampling.
- **All anglers, based on a "four-week recall,"** that is, the angler's memory of fish consumption over the previous four weeks (adjusted for avidity).
- **All anglers, based on a twelve-month recall** (these data could not be adjusted for avidity.)

Table 2-4. Fish consumption rates in g/day, calculated by the San Francisco Seafood Consumption Study (SFEI, 2000)

Subset of anglers	Median (50th percentile)	95th percentile
Recent consumers (not adjusted for avidity)	16.0	108
Recent consumers (adjusted)	16.0*	80
All consumers, four-week recall (adjusted)	0.0	32.0*
All consumers, twelve-month recall (not adjusted)	2.5	44.2

* values used in this impact assessment

The Clean Estuary Partnership has suggested centering this impairment assessment on consumption rates of 16 and 32 grams of fish per day as representative of median and 95th percentile consumption rates (CEP Technical Committee Special Meeting, Review of CMIA Reports, April 2, 2004).

Besides the total amount of fish eaten, there is also discussion about the species that make up the diets of recreational anglers and their families and friends. The USEPA decision to list dioxins cited a mix of several species: 43% white croaker, 35% surf perches, 13.9% striped bass, and 8% sharks. These relative values were based on the National Marine Fisheries Services (NMFS) Marine Recreational Fishing Statistics Survey of the Pacific Coast for 1987, 1988, 1990, and 1993. USEPA assumed that the species proportions were the same for fishing catches and consumption.

The most recent NMFS data for Northern California, from 2002 (www.st.nmfs.gov) indicate a different recreational fishery, with catches made up of 3% white croaker, 3% surf perches, 26% striped bass, and 5% sharks (statistics are by weight for northern California inland marine and estuarine waters). Further, catch rates do not necessarily dictate consumption rates. The San Francisco Seafood Study examined the species composition of the meals consumed by recreational anglers and their family and friends. Among the 87% of survey respondents who said they had consumed Bay fish, about three fourths said they ate striped bass, while fewer people ate other species. Only 16% ate white croaker, and 4% ate shiner surfperch.

One cautionary note—while local data on fish consumption are valuable, it is important to remember that the interim fish advisory could affect consumption rates. Sixty percent of San Francisco Seafood Study respondents who identified themselves as consumers said that they were aware of the advisory, although only 6% understood the recommendation to limit consumption to two meals per month. Consumers who ate more fish than recommended were more likely to demonstrate a poor understanding of the advisory than those who consumed less fish. How consumption rates would change in absence of the advisory is unknown.

The ranges of factors that could be used to calculate screening values are presented in Tables 2-5a through 2-5e. Those data can be used to calculate a range of screening values. It is important to remember that although values are used in this assessment, they are not standards, and the methodology for calculating the values was not prepared as guidance for determining impairment of water bodies.

Table 2-5a. Maximum risk level used to calculate screening values

	Acceptable risk level
Many studies	10^{-4} to 10^{-7}

Table 2-5b. Cancer slope factors used to calculate screening values($(mg/kg\text{-}d)^{-1}$)

	Slope Factor
USEPA, 2000a	156,000
OEHHA	130,000
IRIS	Not available

Table 2-5c. Body weight used to calculate screening values

	Body weight
All studies	70 kg

Table 2-5d. Sources of fish consumption data

Consumption (g/day)	Source
107.1	90th percentile value from Santa Monica Seafood Study. Cited in USEPA listing decision
32	95th percentile of all consumers based on 4-week recall (SFEI, 2000)
21.4	Median value from Santa Monica Seafood Study
17.5	Average value from U.S. Department of Agriculture studies and recommended for calculating screening values (USEPA, 2000b)
16	Median value for recent consumers in San Francisco Bay (SFEI, 2000)
6.5	USEPA data from 1973-1974 for per capita freshwater/estuarine finfish and shellfish
0	Median value for all consumers of San Francisco Bay fish, based on 4-week and 12-month re-call (SFEI, 2000)

Table 2-5e. Screening values for dioxins (risk level of 10^{-5}; values used in subsequent figures in this report are in bold)

Cancer slope factor $(mg/kg\text{-}d)^{-1}$	Consumption rate g/day	Screening value ppt (pg/g)
1.56×10^5 USEPA, 2000a	17.5	0.26*
	16	**0.28**
	32	**0.14**
1.30×10^5 OEHHA	17.5	0.31
	16	0.34
	32	0.17

*This screening value, rounded to 0.3, has been used by Brodberg and Pollack, 1999 and Greenfield et al., 2003

Fish and Shellfish Data

The 1994 study that led to the interim health advisory for people consuming sport fish from San Francisco Bay was a pilot project conducted by the Bay Protection and Toxic Cleanup Program to measure concentrations of contaminants in fish (SFRWQCB *et al.*, 1995). As a follow-up to that program, the San Francisco Estuary Regional Monitoring Program (RMP) began to monitor contaminants in sport fish from the Bay. Sampling occurs every three years, and has been completed for 1997, 2000, and 2003. Data are available for 1997 and 2000 (Davis *et al.*, 1999, 2002; Greenfield *et al.*, 2003). Special studies augment the core sampling effort.

The RMP focuses on seven of the most popular sport fish species taken from the Bay and consumed (SFEI, 2000) (Table 2-6):

Table 2-6. Fish monitored by the RMP and percent anglers that consume each species

Common name	Scientific name	Percent anglers consuming
Jacksmelt	*Atherinopsis californiensis*	17
Shiner surfperch	*Cymatogaster aggregata*	4
White croaker	*Genyonemus lineatus*	16
Striped bass	*Morone saxatilus*	74
California halibut	*Parlichthys californicus*	24
Leopard shark	*Triakis semifasciata*	6
White sturgeon	*Acipenser transmontanus*	17

For 2000, there are data on dioxin concentrations in jacksmelt, shiner surfperch, white croaker, and striped bass (Greenfield *et al.,* 2003). There is also limited information on red rock crab (*Cancer productus).*

Sampling locations for 2000 included:

- San Pablo Bay.
- Berkeley.
- San Francisco Waterfront.
- Oakland Harbor.
- San Leandro Bay.
- Two South Bay Bridges sites: Redwood Creek and Coyote Creek.

The program has not sampled fish from the most northern segments of the Bay: Carquinez Strait, Suisun Bay, or the Sacramento/San Joaquin Delta (Figure 2-1).

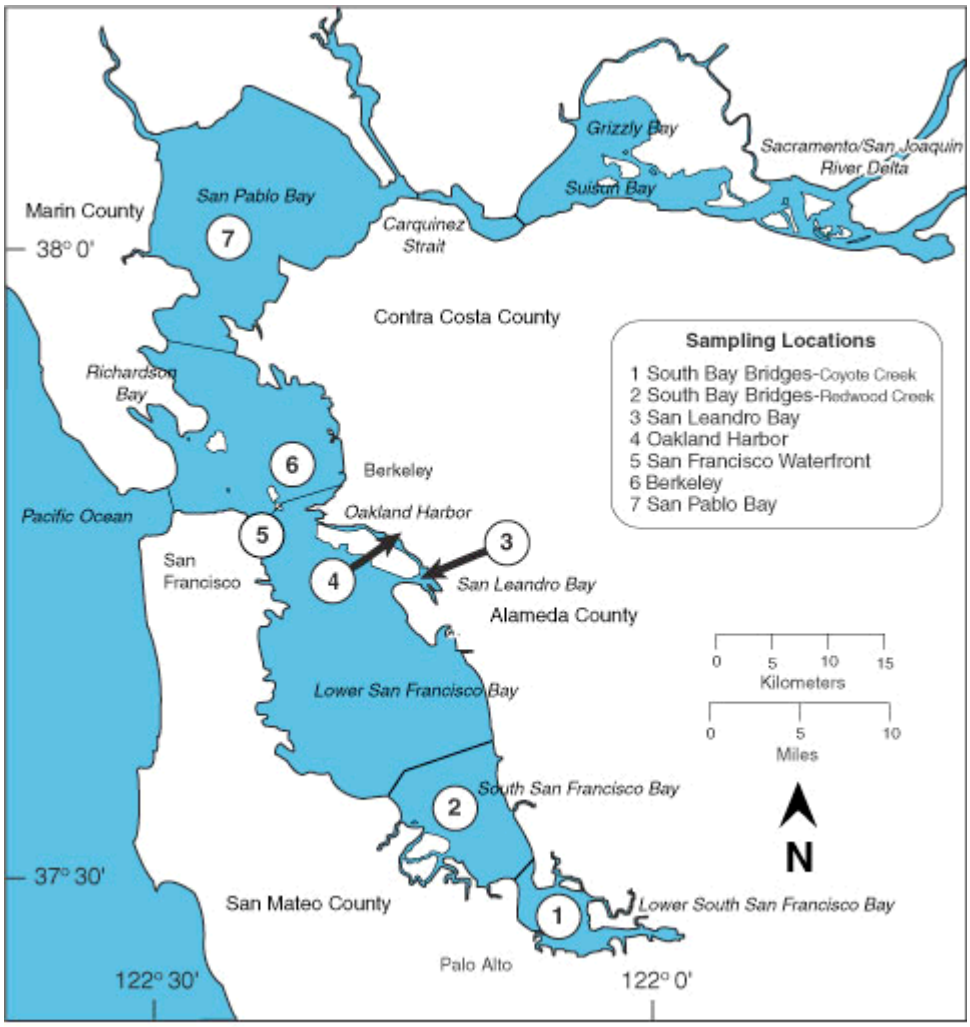


Figure 2-1. Fish sampling locations

Fish fillets were prepared for analysis using methods that mimicked those used by many people who cook and consume each species—that is, jacksmelt and shiner surfperch had their heads, tails, and guts removed, leaving the muscle, skin, and bones. White croaker samples included muscle and skin, but no bones. Striped bass samples included only muscle. (A complete discussion of consumption methods by fish species and angler ethnicity, income, and education can be found in SFEI, 2000.) Samples were composited for analysis.

Concentrations of many dioxin compounds in the fish samples were usually below detection limits, and these results affected the overall precision of the data. However, concentrations of the compounds that contributed most to the TEQs, either because they were especially toxic or especially abundant, tended to be above detection limits. For example, concentrations of 2,3,7,8-TCDF, 2,3,4,7,8-

PCDF, and 1,2,3,7,8-PCDD were generally about ten times higher than the detection limits.

For white croaker and shiner surfperch, the method of handling data below detection limits was insignificant. All samples of these species had TEQs that exceeded screening levels (Figure 2-2).

Concentrations were lower in striped bass and for the single jacksmelt sample, and the method of handling data that were below detection limits affected the results. There are three commonly used substitutions for data that are below detection limits: the detection limit, one half the detection limit (the method used for Figure 3-2), or zero. Figure 2-2 indicates an exceedance of the higher screening value, 0.28 pg/g, in one of nine striped bass samples. The lower screening value, based on consuming 32 grams of fish per day, was exceeded in five of the striped bass samples and in the single jacksmelt sample. Substituting zero for undetected compounds resulted in fewer exceedances for striped bass (Table 2-7) and no exceedance for the jacksmelt sample. (All samples would have exceeded screening values based on a risk level of 10^{-6} rather than 10^{-5}.)

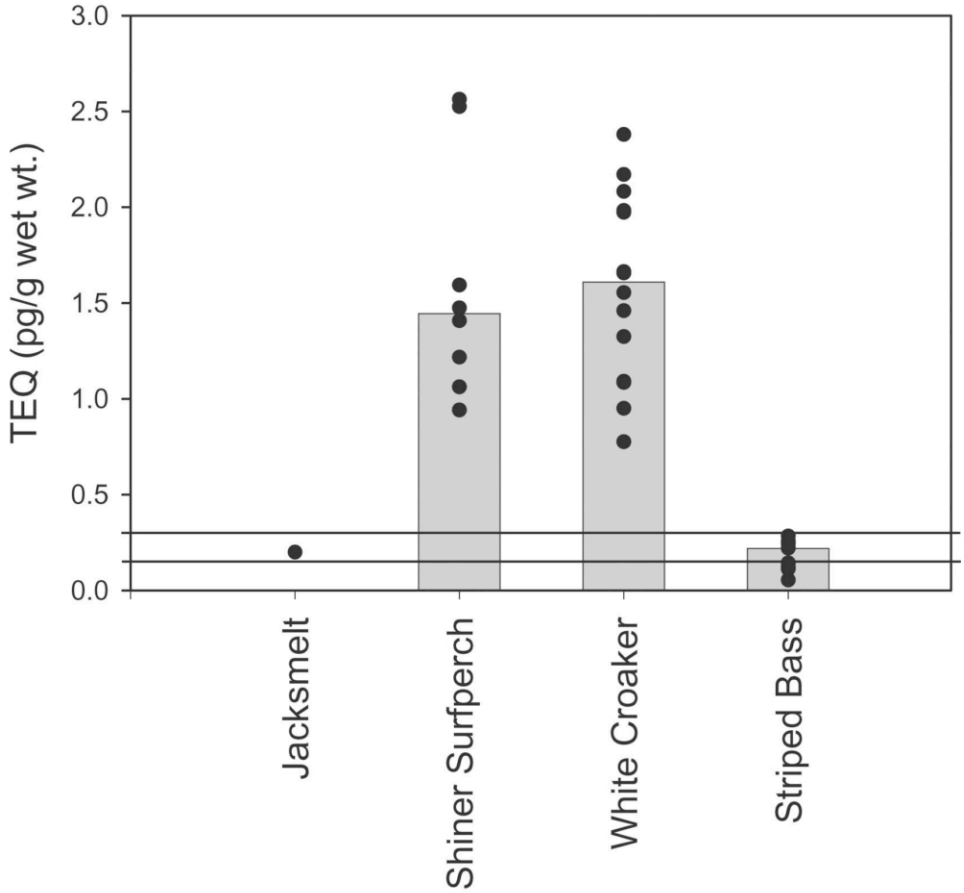


Figure 2-2. TEQ concentrations in Bay fish (pg/g wet, summer 2000). Horizontal lines depict screening values from Table 2-5e.

Table 2-7. Number of striped bass samples (of nine samples) exceeding screening values

Screening value	Substitution for below detection limits		
	Zero	Half detection limit	Detection limit
.28 pg/g	0	1	2
.14 pg/g	4	5	6

The 2000 data indicated that four compounds accounted for most of the TEQs. Furans accounted for most of the TEQs, with 2,3,4,7,8-PCDF contributing 36% and 2,3,7,8-TCDF contributing 22% of the total TEQ. A combination of 2,3,7,8-TCDD and 1,2,3,7,8-PCDD contributed 36% of the TEQ.

Few samples were analyzed from each of the sites, making spatial patterns impossible to discern (Figure 2-3). No clear temporal trends were evident when results from 2000 were compared to data from 1994 or 1997 (data not shown).

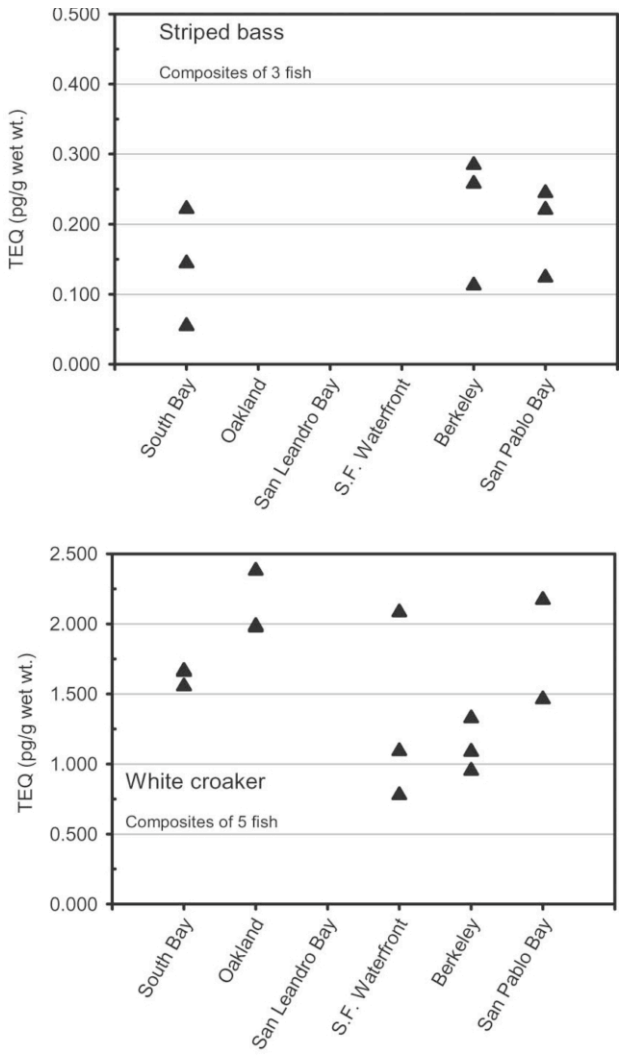


Figure 2-3. TEQ in each sampling location for striped bass and white perch

The limited crab data found 0.1 pg/g TEQ in muscle, and 11 pg/g TEQ in hepatopancreas, in a single composite sample of 20 crabs. While the muscle TEQ was relatively low, the hepatopancreas sample had a TEQ that was higher than those measured in fish.

Additional data on dioxins in fish from San Francisco Bay recently became available from the Biomonitoring Environmental Status and Trends (BEST) and Environmental Monitoring and Assessment Program (EMAP) joint monitoring effort (Nicks and Tillitt, 2003). The BEST/EMAP collaboration is evaluating the environmental health of West Coast estuaries. During June-September 2000, the program sampled bottom-dwelling fish—Pacific staghorn sculpin, English sole, starry flounder, and California halibut—from sites throughout the Bay.

The program did not directly measure PCDD/Fs in fish tissue, but used a semi-quantitative bioassay, the H4IIE bioassay, which measures the overall toxicity of PCDDs, PCDFs, and dioxin-like PCBs. Their results were then evaluated relative to toxicity of 2,3,7,8-tetra-PCDD.

Dioxin-like toxic potency was found in fish from 28 of 31 sites within the Bay, almost all at levels indicative of potential hazard. Differences in species collected, methods of data reporting, and the inclusion of dioxin-like PCBs in the BEST/EMAP data make comparisons between information from the RMP and the BEST/EMAP collaboration difficult. At a first approximation, the PCDD/F TEQs in RMP samples were one to five times the magnitude of those in BEST/EMAP samples (Greenfield, pers. comm.). Dioxin-like toxic potency was greater in fish from San Francisco Bay than in fish from other areas sampled by the program, Puget Sound and the lower Columbia River.

Fish and Shellfish Data as Indicators of Impairment

The fish and shellfish data indicate **possible impairment** of the beneficial use of sport fishing in San Francisco Bay by dioxins. The uncertainties in the data preclude making a definitive judgment. Data from the 2003 RMP should be incorporated into the assessment as soon as they are available. Additionally, there are varied areas of uncertainty and potential issues for additional research:

- **There are no regulatory standards for impairment.** The screening values calculated for this report have no regulatory standing. Completion of the long-awaited USEPA assessment of dioxins and adoption of regulatory standards would allow a more definitive assessment.
- **Fish tissue data come from only six locations, making segment-specific impairment impossible to determine.** Ideally, impairment would be established separately for each segment of San Francisco Bay. The RMP data do not allow for a segment-by-segment review. There are no data at all from the Carquinez Strait, Suisun Bay, or the Sacramento/San Joaquin Delta. Water quality data, presented in Section 2.2.2, are also not available for each segment and cannot provide a surrogate measurement

for geographic patterns in fish concentrations. Additional fish collection, particularly from areas known to be contaminated and known as fishing spots, would be useful.

- **Indication of impairment comes primarily from white croaker and shiner surfperch, which are eaten by relatively few anglers.** SFEI (2000) found that only 16% of anglers consumed white perch, and 4% ate shiner surfperch. (The USEPA studies that led to the 303(d) listing of the compounds assumed that the recreational fish diet was 43% white croaker and 35% surfperch.) Further investigation of consumption rates by species may be useful.
- **Concentrations of dioxins in some species are affected by analytical constraints.** Concentrations of many PCDD/Fs in the most popular sport fish, striped bass, are below detection limits. This analytical constraint makes data interpretation difficult.

2.2.2 Water Quality

Water Quality Standards

For dioxins, there are no water quality criteria for the protection of aquatic life. There are standards for the protection of human health, and these values can be used to assess impairment to the sport fishery. The USEPA California Toxics Rule (CTR; USEPA, 2000) includes standards for the protection of human health for one dioxin compound, 2,3,7,8-TCDD (Table 2-8). This compound has a TEF of 1.0, so the standards can also be used when assessing total dioxin TEQs.

Recently, USEPA published an updated compilation of nationally recommended water quality criteria (USEPA, 2002). The recommendations included decreases in the criteria to protect human health for dioxin. These criteria have not yet been adopted by California; however, they represent the most up-to-date and scientifically valid numbers.

Table 2-8. Water quality standards for dioxin (2,3,7,8-TCDD)

Compound	Standard (pg/l)	
	Water and organism	Organism only
CTR (USEPA, 2000)	0.013	0.014
USEPA, 2002	0.005	0.0051

Water Quality Data

Dioxins are not regularly analyzed by the RMP, which has monitored water quality and compared results to standards since 1993. However, in 2002 and 2003, SFEI analyzed samples from three sites for PCDDs, PCDFs, and other parameters that are not routinely included in the RMP (SFEI, 2004).

Measurement of dioxins in ambient water samples is difficult, because concentrations of the individual compounds are low. Substantial preconcentration of the water samples is necessary to detect the less abundant but more toxic PCDD/F isomers that often contribute greatly to TEQs. The RMP used 100-liter water samples and solid-phase extraction, a method which has not been approved by USEPA for regulatory compliance monitoring, but which has been used in research efforts. This method increases the sensitivity of detection of less abundant compounds, but it also increases detection of PCDD/F isomers in laboratory blanks. (The method does not introduce contamination; conventional analytical techniques are not sensitive enough to detect the compounds that are probably present even in good laboratory blanks.)

Even with solid-phase extraction preconcentration, some compounds are present in such low concentrations that the method of handling data below detection limits remains an issue. There are no certified reference materials for natural waters at typical ambient concentrations ranges, contributing to the challenge of analyzing the samples.

All of the RMP samples contained measurable PCDD/Fs, with TEQs at or above the CTR water quality standard for dioxin, even when using the optimistic assumption that compounds that were not detected were not present and even when values found in blank samples were subtracted from the measured concentration (Table 2-9; see also Figure 2-4). The compounds contributing the most to TEQs included 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD. Under both the CTR and the 2002 nationally recommended criteria, all of the water samples would have exceeded the water quality criteria for protection of human health.

Table 2-9. Sum of TEQs in 100-liter San Francisco Bay water samples (TEQs calculated using WHO-98 TEFs, assuming ND=0)

Station	Sampling Event	Sum of TEQs (pg TEQ/l)	Sum of TEQs (blank-subtracted)
CTR Standard		0.014	
EPA (2002) Criteria		0.0051	
Sacramento River	January 2002	0.029	0.028
	July 2002	0.048*	0.034
	January 2003	0.025	0.014
	August 2003	0.032	0.028
Yerba Buena Island	January 2002	0.046	0.045
	July 2002	0.071	0.057
	January 2003	0.026	0.015
	August 2003	0.057	0.053
Dumbarton Bridge	January 2002	0.259	0.258
	July 2002	0.073	0.059
	January 2003	0.079	0.068
	August 2003	0.041*	0.037
Blank	January 2002	0.001	
	July 2002	0.014*	
	January 2003	0.011*	
	August 2003	0.004	

* More than 35% of total TEQ from estimated isomers

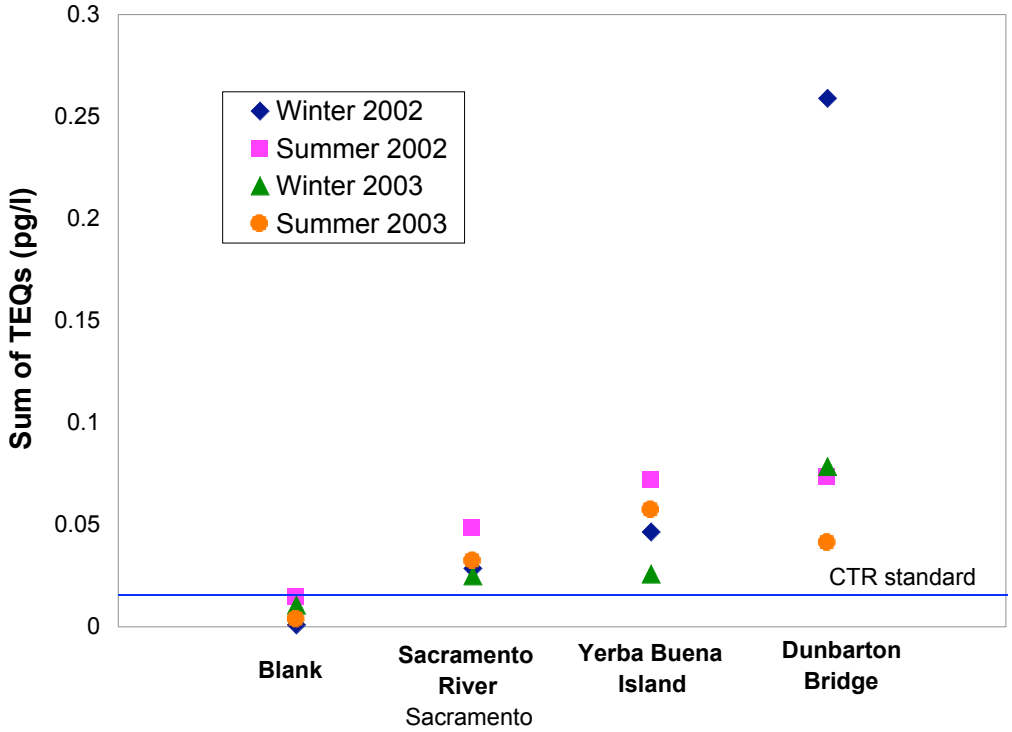


Figure 2-4. Sum of TEQs in 100-liter San Francisco Bay water samples (all field samples exceeded CTR water quality standard)

Water Quality Data as Indicators of Impairment

The 2002 and 2003 water quality data indicate **possible impairment** of the sport fishery of the Bay by dioxins. All the available data exceeded the water quality standards, and those results provide a strong indication of impairment. However, there are few measurements, and the data were acquired using methods that have not yet been adopted for routine monitoring. Further, they provide little information about geographic or temporal trends.

2.2.3 Sediments

Sediment Quality Standards

There are no standards regulating dioxin levels in sediments.

Sediment Data

During 2000, the USEPA Environmental Monitoring and Assessment Program (EMAP) and the NOAA Status and Trends Program evaluated dioxin levels in San Francisco Bay sediments (USEPA Fact Sheet). Ninety-nine stations were sampled throughout the Bay, and 56 samples were analyzed for dioxins, furans, and dioxin-like, co-planar PCBs.

TEQs ranged from 0.02-114 pg/g, with all but 4 samples less than 10 pg/g TEQ.

USEPA and NOAA concluded that dioxin levels (in which they included the dioxin-like PCBs) in San Francisco Bay were low in comparison to other urban bays and estuaries. Concentrations of dioxins in San Francisco Bay sediments were lower than those found in the Hudson-Raritan Estuary, Newark Bay, the northwestern Mediterranean Sea, Lake Ontario, and Lake Michigan.

Sediment Data as Indicators of Impairment

The sediment data are **unable to determine impairment** of the beneficial uses of San Francisco Bay. There are no sediment standards for impairment, so it is not possible to determine whether the sediment data indicate an impairment or lack of impairment of the beneficial uses of the Bay.

2.2.4 Wildlife Health Concerns

Wildlife Health Standards

Marine mammals are susceptible to bioaccumulation of fat-soluble chemicals such as dioxins, because they feed on large amounts of fish. Piscivorous birds are also potentially at risk from dioxins—the most sensitive life stage for dioxin toxicity in birds is early development. However, there are no regulatory standards for dioxins in marine mammals or birds.

Wildlife Health Data

Few studies of dioxin levels in San Francisco Bay mammals have been undertaken. Blubber samples from harbor seals from British Columbia and Washington (Ross *et al.*) found that seals from British Columbia had accumulated compounds (particularly PCDDs) normally associated with the wood pulp industry. (In both populations, PCBs rather than dioxins accounted for the greatest risk to wildlife, 64% of the TEQ for seals from British Columbia and 91% of the TEQ for seals from Washington.)

A study by the US Fish and Wildlife Service is currently underway examining concentrations of dioxins, furans, and dioxin-like PCBs in eggs of Forster's and Caspian terns from Bay colonies. Through collaboration with the RMP, the hatchability of eggs from these colonies was also assessed. Sampling was performed in 2002 and 2003. The results from this study are not yet available, but should provide a picture of the risks to avian reproduction at the top of the food web.

Wildlife Data as Indicators of Impairment

There is insufficient information to determine whether wildlife health is impaired by dioxins in San Francisco Bay—the status is **unable to determine impairment**.

2.3 Impairment Summary

The limited data on PCDD/Fs in the fish, water, sediments, and wildlife of San Francisco Bay make any assessment of impairment nearly impossible. There is some indication of impairment of recreational fishing (COMM) based on fish and water and data. There may be a suspicion that wildlife species could be affected by dioxins, although no data are available to make an assessment (Table 2-10).

Table 2-10. Impairment of San Francisco Bay by dioxins

	Impairment	Uncertainty
Fish & Shellfish	Possible impairment of COMM	Low
Water	Possible impairment of COMM	Moderate
Sediments	Unable to determine impairment	High
Wildlife	Unable to determine impairment	High

3. Conceptual Model

A conceptual model of dioxin and furan (PCDD/F) processes in the San Francisco Estuary ecosystem provides a framework for evaluating and prioritizing additional information needs and potential management actions for reducing impairment of the ecosystem and human health.

The conceptual model:

- Presents a simple **one-box model** of the Bay.
- Synthesizes information on **sources** of PCDD/Fs to San Francisco Bay, including national and regional studies of PCDD/Fs to augment the limited available local data.
- Describes **pathways and loads** from single-point and more diffuse sources.
- Describes the dominant local **processes** that determine the fate of PCDD/Fs in the Bay.
- Presents inputs to and outputs from the one-box **mass balance model** .

The conceptual model also describes areas of uncertainty and assesses the extent to which they limit the ability to quantify responses and rates. Uncertainties arise from the simplifying assumptions and the gaps in available information. For example, there are uncertainties in the representativeness of data used for emissions and loading calculations, the applicability of national inventories to the region, and the analytical limitations (particularly detection limits).

3.1 One-Box Model

A simple way to examine inputs and losses of contaminants to San Francisco Bay has been to use a mass-budget model, called a one-box model, because it considers the Bay to be one box, with inputs and losses to and from the box. The boundaries of the box are a little unusual, as they include both the water column and the sediment "active layer" (Figure 3-1).

Although San Francisco Bay is an ecosystem interconnected with the atmosphere, buried sediments, the ocean, and surrounding watersheds, for the purposes of the model, the system is defined as including only that portion of the water column bounded by the Golden Gate, the mouth of the San Joaquin/Sacramento River Delta, and the mouths of smaller tributaries in surrounding watersheds. The sediments in this system include only those in this area down to a fixed active layer depth of 15 cm.

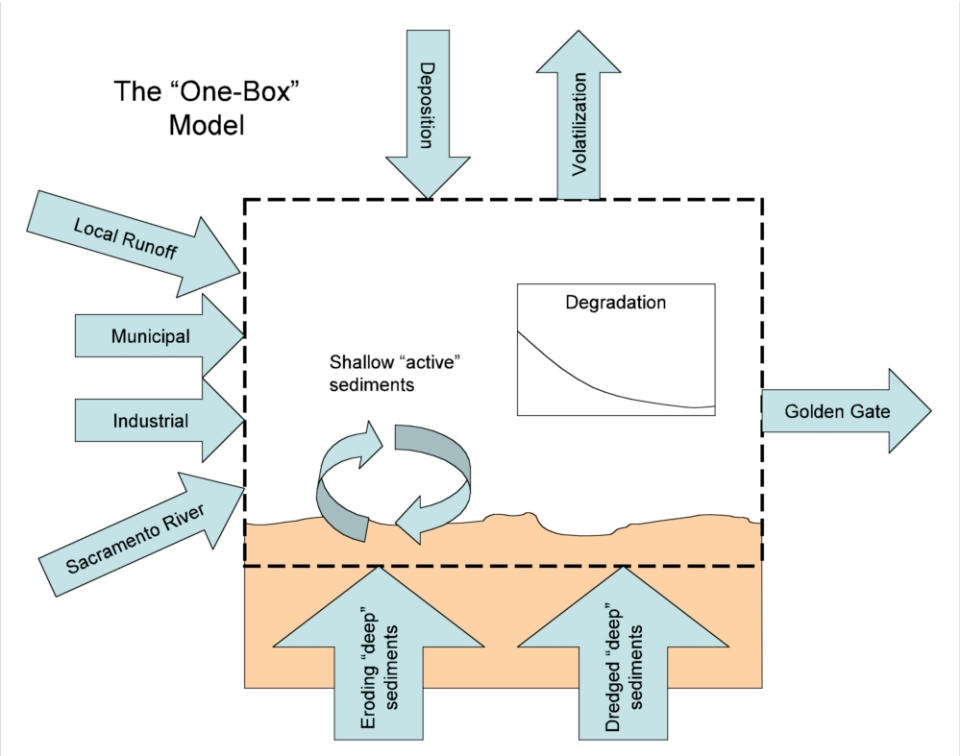


Figure 3-1. One-box model (figure courtesy of Dan Cloak)

The simple mass balance model of a well-mixed Bay has been used as an initial analysis of the current and future status of pollutants (Davis, 2002). Because some of the model assumptions can have large effects on the response of the ecosystem, alternate scenarios for some modeled parameters are used to identify and illustrate critical model uncertainties.

3.2 Sources

Because there are few data on PCDD/Fs in San Francisco Bay, scientists rely considerably on national and regional studies. A variety of information is available:

- **Local and regional source estimates**. Combustion is thought to be the main source of new dioxins to the environment, so data from local air quality agencies are used where available.
- **Global vs. regional source estimates**. Estimates from national emissions data, scaled for local population size, are used when no local or regional information is available.
- **Temporal patterns**. There is some evidence of general declines in loads on a national scale.

3.2.1 Local and Regional Sources

PCDD/Fs 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. As national regulation of dioxins has tightened, it is thought 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 now contribute more dioxins than the point sources (Figure 3-2).

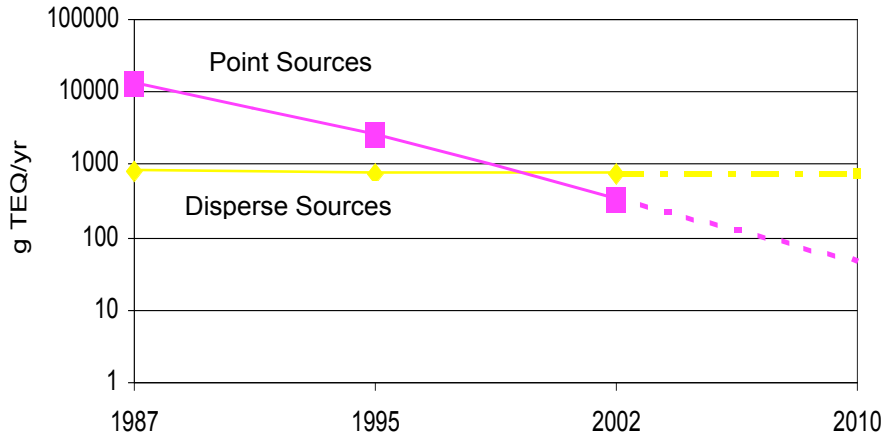


Figure 3-2. Past and projected PCDD/F emissions in the U.S. (Peek et al., 2002)

USEPA is in the process of refining its estimates of wood-burning and diesel emissions. These estimates are subject to a high degree of uncertainty. Ongoing changes in regional air pollution management practices will introduce additional uncertainty about the magnitude of ongoing emissions.

BAAQMD has used methodology similar to the USEPA national dioxins emissions inventory to estimate the magnitudes of local sources. Total regional emissions for combustion and non-combustion sources were estimated by BAAQMD to be about 2.2 g TEQ/yr (BAAQMD, 2002). Estimates from 1999 (Figure 3-3) and 2000 (Figure 3-4) suggest that mobile transportation and residential wood burning were the primary combustion sources. Application of the herbicide 2,4-D was an important non-combustion source.

PCDD/Fs are known trace byproducts of other industrial chlorine processes, such as the manufacture of PVC and PCBs. However, emissions from PVC have been estimated to be small, less than one tenth of those from combustion. PCDD/F contamination in PCB Aroclors was also small (Rappe *et al.* 1985). Even

assuming a loading rate of PCBs to the San Francisco Bay of about 100 kg/yr, the contribution of PCDD/Fs from that source would only be 0.014-0.080 g TEQ/yr.

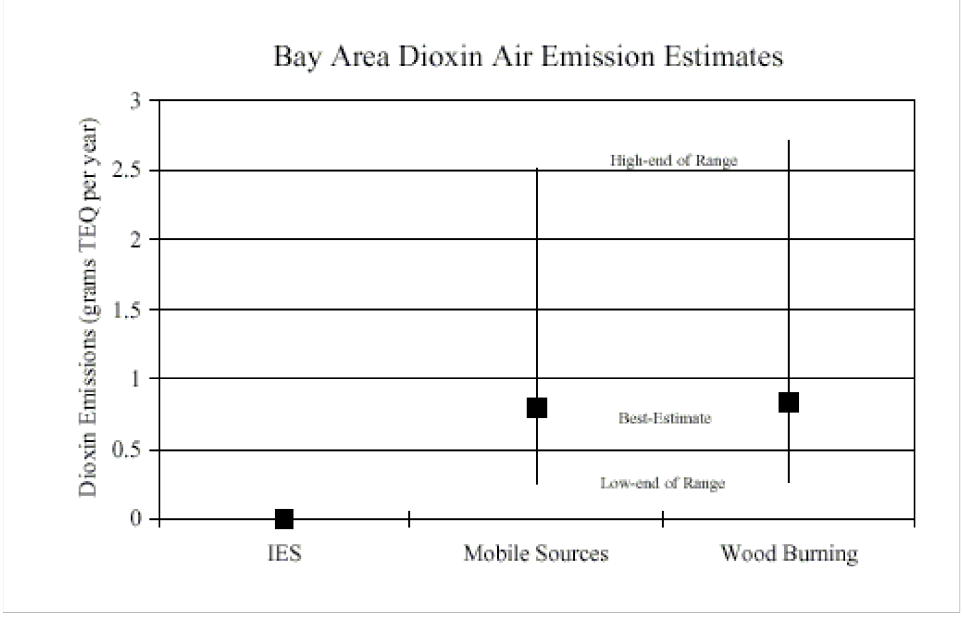


Figure 3-3. Sources of San Francisco Bay Area PCDD/F emissions (BAAQMD, 1999). (IES = an incinerator that is no longer operating.)

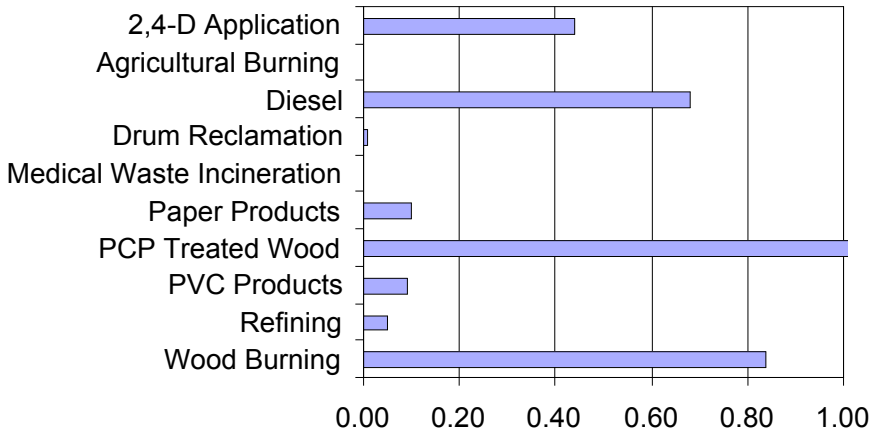


Figure 3-4. Sources of dioxin and furan emissions (g TEQ/year) in the San Francisco Bay Area (BAAQMD, 2002)

All of the largest sources of dioxins can emit or volatilize these compounds into the atmosphere. Once in the atmosphere, dioxins can deposit either directly onto the surface of the Bay (direct deposition) or onto the watershed (including the California Central Valley and Sierra Nevada), where they may be transported to the Bay in stormwater runoff. Dioxin concentrations in ambient air and precipitation can therefore provide an important indication of sources. There are

few readily available data on PCDD/Fs in ambient air in California, with only two National Dioxin Air Monitoring Network (NDAMN) sites in operation during 2000. (Only one site operated during 1999.) Nationally, atmospheric PCDD/F concentrations at 18 rural NDAMN sites averaged 0.0146 pg TEQ/m^3 in 2000, with TEQs ranging from 0.0025 to 0.06 pg/m^3. Suburban sites had similar TEQs, averaging 0.0155 pg/m^3 at two sites. The average TEQ in air measured at eight national parks was lower, 0.0020 pg/m^3.

A project to monitor ambient air concentrations of PCDD/Fs at six urban sites in the San Francisco region is underway, conducted by BAAQMD and USEPA Region 9. These data are not yet available. There are also no data on concentrations of PCDD/Fs in precipitation for the San Francisco Bay area. Once local air data become available, wet deposition load estimates may be scaled to deposition in other areas with similar ambient air concentrations and rainfall patterns.

3.2.2 Regional vs. Global Sources

It is important to understand the relative importance of local and regional *vs.* global sources of dioxins in the atmosphere. Local emissions could conceivably respond to management actions, while the global emissions are beyond local control. There are not yet models for the San Francisco Bay area, but researchers have modeled emissions and contributions to deposition of dioxins on the Great Lakes (Cohen, 2001). Deposition patterns varied considerably among the lakes:

- Lake Michigan: more than 40% of PCDD/Fs came from local sources (less than 100 km away).
- Lake Superior: less than 5% of PCDD/Fs came from local sources.
- Other lakes: about 20% of deposition came from local sources.

Results from NDAMN indicate that air concentrations are typically higher at urban sites and areas surrounding urban centers, while concentrations at remote national parks in the west have been among the lowest measured. These data suggest that for areas with local sources, dioxins transported from great distance make up only a small portion of the total. In the urbanized San Francisco Bay area, where winds typically come from the west across a large expanse of ocean, local sources may be expected to be of greater importance than global ones.

3.2.3 Temporal Patterns

There is some evidence in other regions that there have been decreases in environmental concentrations of PCDD/Fs in recent decades. This evidence is based on sediment cores taken from lakes (Baker and Hites, 2000b) and concentrations in food items (Winters *et al*., 2000). Similar trends could be difficult to verify in San Francisco Bay, since much of the Bay sediment is well mixed. Cores taken from quiescent, depositional waters (*e.g.*, vernal pools or

wetlands) might reveal a similar trend to that seen in other areas. Local concentrations would likely follow the same trend as the rest of the country, because there are fewer incineration facilities and other large single sources in the region than in the past, and emissions have been reduced at those few facilities that remain. Recent decreases may be slowed or reversed if further improvements in treatment technologies and source reduction efforts cannot keep pace with increased diffuse combustion sources, such as transportation and home heating activities, which will increase with continued urbanization of the region.

3.3 Loading Pathways to the Bay

Regardless of their original sources, PCDD/Fs enter San Francisco Bay through the same pathways:

- **Municipal and industrial discharges**.
- Water flows from the Central Valley and other local **watersheds**.
- **Direct atmospheric deposition**.
- **Erosion of buried sediment**.

Municipal and industrial discharges are among the better characterized loading pathways. As a condition of National Pollutant Discharge Elimination System (NPDES) permits, dischargers have been required to periodically monitor concentrations of pollutants in their discharges, including PCDD/Fs, and discharge flow rates are well monitored. Measured concentrations vary greatly among individual dischargers and between sampling events at individual dischargers, so there is moderate uncertainty in the size of the contribution to PCDD/F loadings to the Bay. However, using mid-range (geographic mean) estimates of discharged concentrations, it appears that municipal and industrial discharges are minor contributors of PCDD/Fs.

Loads from surrounding watersheds have the largest uncertainties in loading estimates for the Bay, as discharges from various watersheds and storm drains are episodic and spatially heterogeneous, making calculations of "average" loads highly dependent on the locations and periods sampled. Similarly, atmospheric deposition is difficult to measure directly, and estimates generally must be based on total concentrations in air, combined with particle-size distributions and modeled settling and diffusion rates.

Although this report attempts to project the long-term behavior of PCDD/Fs in the system as realistically as possible, quantitative accuracy of the loads is not critical in the evaluation at this stage. A range of the possibilities for loading will be considered to highlight areas in which acquiring additional information is most critical.

3.3.1 Municipal and Industrial Discharges

Wastewater discharges contribute a small amount to the total load of PCDD/Fs TEQs to the Bay. Although there are temporal and inter-facility differences in measured PCDD/F concentrations, flows are known with a high degree of certainty, and effluent concentrations are relatively easily measured.

One uncertainty in load estimates results from inter-laboratory variability in analytical results (there are no analytical reference materials that could be used to compare results from different laboratories). Another source of uncertainty is the large proportion of results that are below detection limits when USEPA standard compliance monitoring methods and analyses are used. A number of regional wastewater treatment plants have measured PCDD/Fs in the recent past. The methods used have generally followed the standard USEPA Method 1613, using one-liter samples. This method is only moderately sensitive at detecting PCDD/Fs: most compounds are present at levels below detection limits, with occasional quantitative measurements of hepta- and octachloro- dioxins and furans. Recently, a number of local wastewater treatment plants have measured PCDD/Fs in effluent using a solid-phase extraction (SPE) method similar to that used by the RMP for measuring concentrations of various organic contaminants in ambient water samples.

Using 1999-2003 concentration data reported to SFRWQCB and assuming non-detected results indicated zero concentrations of PCDD/Fs, loads from municipal treatment plants would average 0.095 mg TEQ/day. For the same data, but assuming that non-detected sample concentrations were half the detection limit, wastewater loads would total 35 mg TEQ/day. Refinery loads would total 0.009 to 0.3 mg TEQ/day, and loads from other dischargers would account for an additional 0.02 to 0.14 mg TEQ/day. Thus total PCDD/F loads from municipal and industrial discharges could range from 0.13 mg TEQ/day to 35 mg TEQ/day. The geometric mean of these estimates (2.1 mg TEQ/day or 0.77 g TEQ/year) represents our current best estimate. The estimate is higher than that previously used by the SFRWQCB, which assumed that non-detect concentrations were zero.

Average measurements of PCDD/Fs in effluent from some preliminary data provided to SFRWQCB in recent years also includes data derived by handling of results not detected or quantified with non-detected concentrations assumed to be zero or one half the detection limit (Table 3-1). (SFRWQCB uses the first method.) Total masses of PCDD/Fs (18 and 120 pg/l respectively) and TEQs (0.04 and 15 pg TEQ/l) calculated by these averaging methods are also presented in the table.

Table 3-1. Average municipal discharge PCDD/F concentrations and loads, 1999-2003 data, 1- to 4-liter samples (from SFRWQCB; nd = non-detected, MDL/2 = one half the detection limit)

	Concentration (pg/l)		Load (g/day)	
	nd=0	nd=MDL/2	nd=0	nd=MDL/2
2,3,7,8-TCDD	0	1.8	0.0E+00	4.1E-03
1,2,3,7,8-PeCDD	0	5.6	0.0E+00	1.3E-02
1,2,3,4,7,8-HxCDD	0	5.6	0.0E+00	1.3E-02
1,2,3,6,7,8-HxCDD	0	5.6	0.0E+00	1.3E-02
1,2,3,7,8,9-HxCDD	0	5.5	0.0E+00	1.3E-02
1,2,3,4,6,7,8-HpCDD	1.7	7.4	4.0E-03	1.7E-02
OCDD	12	25	2.8E-02	5.8E-02
2,3,7,8-TCDF	0.021	1.7	4.7E-05	3.9E-03
1,2,3,7,8-PeCDF	0.0099	6.9	2.3E-05	1.6E-02
2,3,4,7,8-PeCDF	0.0049	6.9	1.1E-05	1.6E-02
1,2,3,4,7,8-HxCDF	0.032	5	7.4E-05	1.2E-02
1,2,3,6,7,8-HxCDF	0.13	5.1	3.0E-04	1.2E-02
2,3,4,6,7,8-HxCDF	0.0036	5	8.3E-06	1.1E-02
1,2,3,7,8,9-HxCDF	0	5.1	0.0E+00	1.2E-02
1,2,3,4,6,7,8-HpCDF	0.094	5.4	2.1E-04	1.2E-02
1,2,3,4,7,8,9-HpCDF	0	5.3	0.0E+00	1.2E-02
OCDF	3.4	17	7.9E-03	4.0E-02
Sum PCDD/F	**18**	**120**	**4.1E-02**	**2.8E-01**
Total TEQ	**0.042**	**15**	**9.5E-05**	**3.5E-02**
Total TEQ (g/year)			**0.035**	**13**

Another study that included PCDD/F measurements in municipal wastewater effluent (Yee *et al*., 2001) employed a solid-phase extraction (SPE) method not currently approved by USEPA for compliance monitoring. Average concentrations, total mass, and TEQs of PCDD/Fs collected from this study are presented in Table 3-2. SPE extractions may underestimate concentrations (Jarman *et al.*, 1998; Litten *et al.*, 2002). However, SPE pre-concentration allows detection of compounds at concentrations that would otherwise be too low to measure. Because the total toxicity of PCDD/Fs is largely driven by some of the less abundant but more toxic tetra- and pentachloro- isomers, SPE samples provide more protective determinations of the potential for toxicity, particularly in ambient or other water samples with low total PCDD/F concentrations. Although the total average PCDD/Fs measured in the 100-liter SPE samples (Table 3-2) were lower than the other municipal discharge data (Table 3-1), the average TEQ calculated for the 100-liter sample (0.06 pg/l TEQ using the ND=0 concentration assumption) was higher, primarily due to the contribution of the more toxic isomers that were measurable only by the SPE method.

Assuming average discharges of 600 million gallons per day (~2300 million liters per day) for regional municipal wastewater dischargers, total loads of PCDD/Fs and TEQs to the Bay are small but fall within a wide range, between 9.5×10^{-5} and 3.5×10^{-2} g TEQ/day, for the region, depending on the collection method for the data used and assumptions for estimating concentrations of undetected compounds.

Table 3-2. Average municipal discharge PCDD/F concentrations and loads, 100-liter SPE samples (Yee et al., 2001)

	Concentration (pg/l)		**Load (g/day)**	
	nd=0	nd=MDL/2	nd=0	nd=MDL/2
2,3,7,8-TCDD	0.021	0.022	4.8E-05	5.0E-05
1,2,3,7,8-PeCDD	0.0098	0.0099	2.2E-05	2.3E-05
1,2,3,4,7,8-HxCDD	0.0028	0.0037	6.4E-06	8.5E-06
1,2,3,6,7,8-HxCDD	0.024	0.024	5.5E-05	5.5E-05
1,2,3,7,8,9-HxCDD	0.0079	0.0086	1.8E-05	2.0E-05
1,2,3,4,6,7,8-HpCDD	0.089	0.089	2.0E-04	2.0E-04
OCDD	0.41	0.41	9.4E-04	9.4E-04
2,3,7,8-TCDF	0.11	0.11	2.5E-04	2.5E-04
1,2,3,7,8-PeCDF	0.016	0.016	3.7E-05	3.7E-05
2,3,4,7,8-PeCDF	0.017	0.018	3.9E-05	4.1E-05
1,2,3,4,7,8-HxCDF	0.015	0.015	3.4E-05	3.4E-05
1,2,3,6,7,8-HxCDF	0.0089	0.0093	2.0E-05	2.1E-05
2,3,4,6,7,8-HxCDF	0.0017	0.0029	3.9E-06	6.6E-06
1,2,3,7,8,9-HxCDF	0.0074	0.0077	1.7E-05	1.8E-05
1,2,3,4,6,7,8-HpCDF	0.1	0.1	2.3E-04	2.3E-04
1,2,3,4,7,8,9-HpCDF	0.0031	0.0049	7.1E-06	1.1E-05
OCDF	0.045	0.045	1.0E-04	1.0E-04
sum PCDD/F	**0.89**	**0.9**	**2.0E-03**	**2.1E-03**
total TEQ	**0.06**	**0.062**	**1.4E-04**	**1.4E-04**
Total TEQ (g/year)			**0.051**	**0.051**

Refineries are the next largest category of dischargers by volume, contributing approximately 75 million liters per day (2001 average). Data from refineries for the period 1999-2003 (using conventional USEPA analysis methods) were also obtained from SFRWQCB. Average concentrations, total mass, and TEQs are presented in Table 3-3. The more abundant PCDD/F isomers were found at somewhat higher concentrations in refinery effluent compared to municipal discharges, but the total volume of discharge was much smaller. As a result, the maximum estimated loads were about one order of magnitude lower (8.9×10^{-6} to 3.2×10^{-4} g TEQ/day) than for municipal discharges.

Table 3-3. Average refinery aqueous effluent PCDD/F concentrations and loads, 1999-2003

	Concentration (pg/l)		Load (g/day)	
	nd=0	**nd=MDL/2**	**nd=0**	**nd=MDL/2**
2,3,7,8-TCDD	0	1.1	0	8.2E-05
1,2,3,7,8-PeCDD	0	1.4	0	1.0E-04
1,2,3,4,7,8-HxCDD	0	1.7	0	1.3E-04
1,2,3,6,7,8-HxCDD	0.053	1.8	4.0E-06	1.3E-04
1,2,3,7,8,9-HxCDD	0.12	1.7	9.2E-06	1.3E-04
1,2,3,4,6,7,8-HpCDD	7.1	8.1	5.4E-04	6.1E-04
OCDD	77	79	5.8E-03	5.9E-03
2,3,7,8-TCDF	0	0.74	0	5.5E-05
1,2,3,7,8-PeCDF	0	1.4	0	1.0E-04
2,3,4,7,8-PeCDF	0	1.3	0	9.7E-05
1,2,3,4,7,8-HxCDF	0.053	0.89	4.0E-06	6.7E-05
1,2,3,6,7,8-HxCDF	0.049	0.93	3.7E-06	7.0E-05
2,3,4,6,7,8-HxCDF	0.031	0.91	2.4E-06	6.8E-05
1,2,3,7,8,9-HxCDF	0	1.1	0	8.6E-05
1,2,3,4,6,7,8-HpCDF	0.89	1.8	6.6E-05	1.4E-04
1,2,3,4,7,8,9-HpCDF	0	1.6	0	1.2E-04
OCDF	2.4	5.2	1.8E-04	3.9E-04
sum PCDD/F	**88**	**110**	**6.6E-03**	**8.3E-03**
total TEQ	**0.12**	**4.3**	**8.9E-06**	**3.2E-04**
Total TEQ (g/year)			**0.0033**	**0.12**

There are several other, primarily industrial, discharges. Average concentrations in effluent from these dischargers (conventional USEPA analysis methods) are presented in Table 3-4. Although total masses of PCDD/Fs measured in these discharges were generally lower than for the other categories, average TEQ concentrations were slightly higher, due to measured concentrations of TCDF and PeCDF in some samples. However, this category typically discharges less than 10 million gallons per day, resulting in loads of 0.0073--.051 g/year.

Table 3-4. Average effluent PCDD/F concentrations (pg/l) and loads (g/day) from other discharges, 1999-2003 data, 10 MGD discharge assumed

	Concentration (pg/l)		Load (g/day)	
	nd =0	**nd= MDL/2**	**nd=0**	**nd=MDL/2**
2,3,7,8-TCDD	0	0.84	0	3.20E-05
1,2,3,7,8-PeCDD	0	0.92	0	3.50E-05
1,2,3,4,7,8-HxCDD	0	1.3	0	5.10E-05
1,2,3,6,7,8-HxCDD	0	1.3	0	5.00E-05
1,2,3,7,8,9-HxCDD	0	1.7	0	6.30E-05
1,2,3,4,6,7,8-HpCDD	1.1	2.4	4.00E-05	9.20E-05
OCDD	12	13	4.60E-04	5.00E-04
2,3,7,8-TCDF	0.56	1	2.10E-05	3.90E-05
1,2,3,7,8-PeCDF	1.8	2.1	6.90E-05	8.20E-05
2,3,4,7,8-PeCDF	0	0.91	0	3.40E-05
1,2,3,4,7,8-HxCDF	3.6	3.9	1.40E-04	1.50E-04
1,2,3,6,7,8-HxCDF	0	0.89	0	3.40E-05
2,3,4,6,7,8-HxCDF	0	0.72	0	2.70E-05
1,2,3,7,8,9-HxCDF	0	1.2	0	4.70E-05
1,2,3,4,6,7,8-HpCDF	0	1.3	0	4.90E-05
1,2,3,4,7,8,9-HpCDF	0	1.4	0	5.40E-05
OCDF	3.2	4.7	1.20E-04	1.80E-04
sum PCDD/F	**22**	**40**	**8.40E-04**	**1.50E-03**
total TEQ	**0.52**	**3.6**	**2.00E-05**	**1.40E-04**
Total TEQ (g/year)			**0.0073**	**0.051**

3.3.2 Watershed Loading

Transport of PCDD/Fs from watersheds probably represents the largest category of loads to the Bay. Watersheds discharging to San Francisco Bay include the drainage areas of the Central Valley, via the Sacramento and San Joaquin rivers, and smaller creeks and storm drains in local watersheds surrounding the Bay. Although there may be specific contaminated sites within each watershed, most contamination is widespread, resulting from atmospheric emissions and legacy uses distributed throughout the surrounding region. Both ongoing and legacy deposits of PCDD/Fs in watersheds are transported to the Bay, and there is currently little information to quantify the relative contributions of these sources.

Central Valley

Concentrations of PCDD/Fs in water from the Sacramento River near its confluence with the San Joaquin River and San Francisco Bay have been measured in recent sampling by the RMP (SFEI, 2004).

PCDD/F concentrations in samples from Sacramento River and other sites in the estuary collected by SPE are presented in Figure 3-5 (top). Concentrations in whole water samples are presented in Figure 3-5 (bottom). Average concentrations at the Sacramento River site were similar to those found at other sites in the Bay. Samples were only taken on two occasions in the wet season and two in the dry season (in 2002 and 2003). No high-flow events were captured on those sampling dates, so they are not fully representative of the possible range of discharge from the Sacramento River.

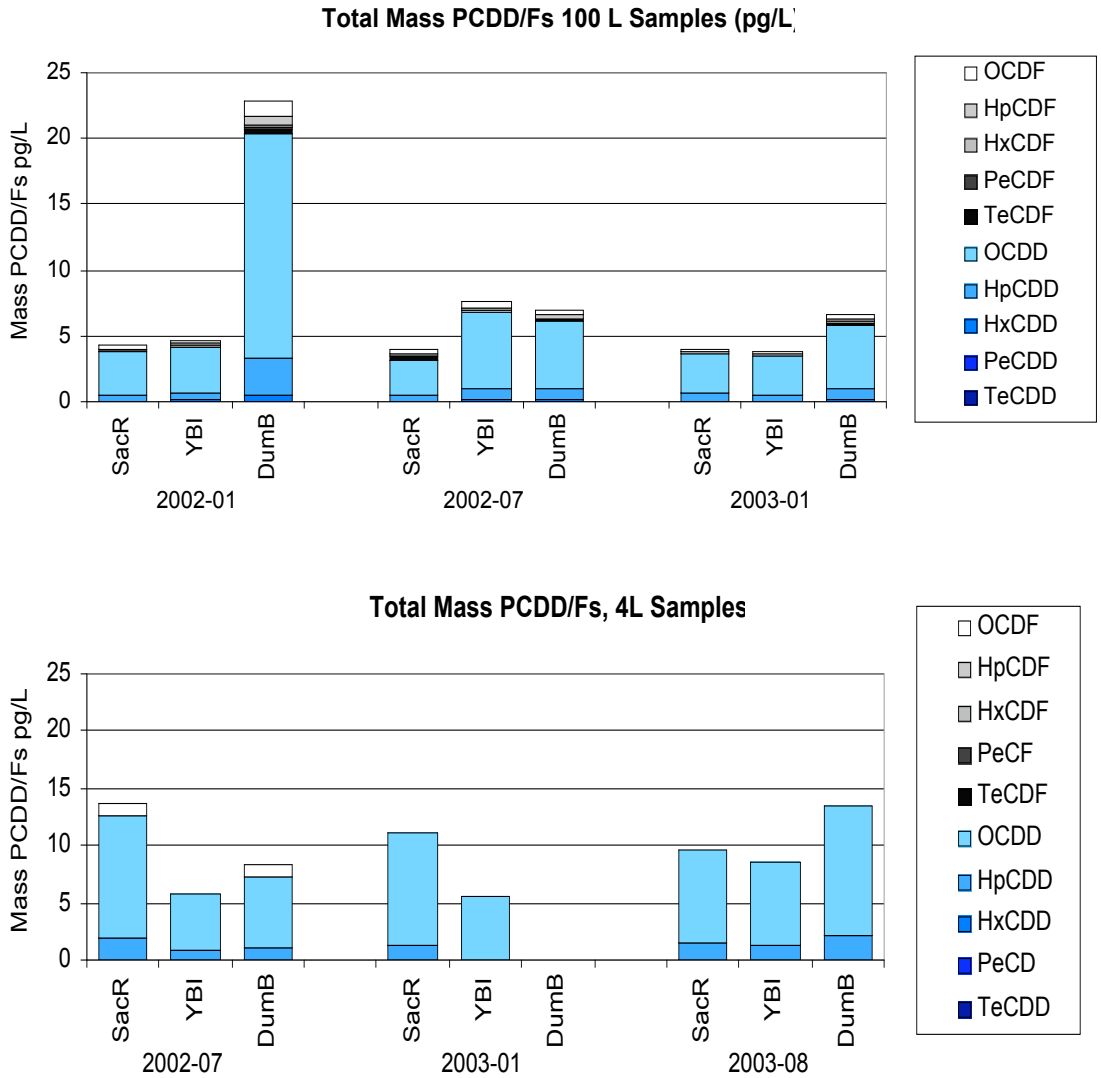


Figure 3-5. Top: PCDD/Fs (pg/l) in ambient water 100-liter samples; Bottom: PCDD/Fs (pg/l) in ambient water 4-liter samples (=Sacramento River, YBI=Yerba Buena Island, DumB=Dumbarton Bridge)

Daily loads, mass, and TEQs of PCDD/Fs from the Sacramento River are presented in Table 3-5. Because nearly all isomers were detected in all samples, differences between the various methods of handling data below detection limits were small. Total PCDD/F loads from the Delta average 0.0024 g TEQ/day (0.88 g TEQ/year), similar to the geometric mean but more than ten times higher than the lowest estimate of discharge from municipal discharges.

Table 3-5. Average Sacramento River PCDD/F concentrations (pg/l) in 100-liter SPE samples and loads (g/day)

Compound	Concentration nd=0	Load (g/day) nd=0	Concentration nd=MDL/2
2,3,7,8-TCDD	0.0022	1.5E-04	0.0026
1,2,3,7,8-PeCDD	0.0037	2.6E-04	0.0039
1,2,3,4,7,8-HxCDD	0.0064	4.5E-04	0.0067
1,2,3,6,7,8-HxCDD	0.023	1.6E-03	0.023
1,2,3,7,8,9-HxCDD	0.030	2.1E-03	0.030
1,2,3,4,6,7,8-HpCDD	0.46	3.2E-02	0.46
OCDD	3.1	2.1E-01	3.1
2,3,7,8-TCDF	0.012	3.5E-04	0.12
1,2,3,7,8-PeCDF	0	0	0.0008
2,3,4,7,8-PeCDF	0.005	3.5E-04	0.006
1,2,3,4,7,8-HxCDF	0.011	7.5E-04	0.011
1,2,3,6,7,8-HxCDF	0.0065	4.5E-04	0.0068
2,3,4,6,7,8-HxCDF	0	0	0.0009
1,2,3,7,8,9-HxCDF	0.003	2.1E-04	0.004
1,2,3,4,6,7,8-HpCDF	0.11	7.8E-03	0.11
1,2,3,4,7,8,9-HpCDF	0.0035	2.5E-04	0.0039
OCDF	0.22	1.5E-02	0.22
Sum PCDD/F	**4.1**	**2.8E-01**	**4.1**
Total TEQ	**0.034***	**2.4E-03**	**0.035***

* Exceeds CTR water quality criterion

Local Watersheds

Concentrations of PCDD/Fs and flow rates from local watersheds transported through small tributaries, including creeks and storm drains, are less well characterized than loads from the Central Valley. In 1995-1996, samples of stormwater runoff from two storm events were taken at storm drain outfall sites around the Bay (SFRWQCB, 1997), representing a mix of areas dominated by urban land use and some open space. sites draining areas in or near petroleum refineries were also sampled at that time. TEQs calculated for those samples ranged from 4 to 30 pg/l for the mixed-use locations, and 5 to 73 pg/l for the samples near refineries.

Hourly sampling of storm drains from sites in Oakland and Benicia was also conducted for the first storm of the 1995-1996 wet season (Wenning *et al.*,1999). TEQs ranged from 0.1 to 65 pg/l over the course of a single storm for the Oakland site, and from 0 (not detected) to 14 pg/l for the Benicia location. The high variability of concentrations measured at these sites illustrates the high uncertainty arising from using single or sparse numbers of grab samples to characterize stormwater discharges of pollutants, particularly in small watersheds and those with high percentages of impervious surfaces, which have highly episodic surface runoff and transport of particulate material.

Using data from these two studies, SFRWQCB (1998) estimated contributions of PCDD/Fs from various sources and pathways, including loads from local watersheds (Figure 3-5). Average annual loads from stormwater runoff in local watersheds totaled 5.1 g TEQ/yr, based on average concentrations of PCDD/Fs measured in stormwater of 8.7 pg TEQ/l.

Stormwater PCDD/F concentrations can vary nearly two orders of magnitude. The higher of these measurements is about 50 g TEQ/year, near the low end of the range of local emissions, including PCP-treated wood (for the mid-range inventory estimate). Lower and upper bounds for watershed loads range from 0.5 to 50 g TEQ/year.

Work is currently underway in the Guadalupe River watershed to evaluate a more refined methodology for calculating pollutant loads using continuous monitoring of a proxy for suspended sediment concentrations and averaged pollutant concentrations normalized to suspended sediment concentrations in grab samples (McKee, SFEI, pers. comm.). Dioxins are not being measured in that study, but results for PCBs and other hydrophobic organic compounds will shed light on the transport of particle-associated contaminants from local watersheds.

3.3.3 Direct Atmospheric Deposition

Although the surface of the Bay is small relative to those of the watersheds draining into it, during the dry season, reduced flows from surrounding rivers and streams increase the relative importance of direct atmospheric input. In previous efforts to quantify regional PCDD/F sources (SFRWQCB, 1998), direct deposition of dioxins to the Bay surface was estimated to be 1.2 g TEQ/year (1.1 mg TEQ/km^2/year).

This estimate of deposition flux is somewhat high in comparison to estimates for other large water bodies. In a modeling study of five Great Lakes, annual deposition PCDD/Fs ranged from 0.16 to 0.32 mg TEQ/km^2/yr (Cohen, 2001). For the San Francisco Bay area, this rate would result in deposition of approximately 0.3 g TEQ/year.

3.3.4 Erosion of Buried Sediment

The contribution of erosion of buried sediments to the water column and active sediment layer cannot currently be assessed. There are few reported concentrations of PCDD/Fs even in surface sediments for the San Francisco Bay area. EMAP has recently measured surface PCDD/F at various sites around the Bay, but that program did not characterize sediment profile concentrations, which would be needed to determine whether erosion would increase or decrease the pool of PCDD/Fs available for exposure to biota. The mass balance model assumes that there is neither net burial nor erosion of sediments throughout the Bay. This assumption is a probably inaccurate, as work by the USGS (Jaffe, 1998) has documented net erosion in San Pablo Bay, Suisun Bay, and the South Bay in the past (at least through the 1980s). However, without data on deeper sediment profile concentrations of PCDD/Fs, estimated loads from erosion of buried sediments to loading would be highly uncertain.

3.4 Environmental Processes

Two major groups of processes affect the levels of dioxins in the Bay: atmospheric transformations and in-bay processes. Dioxins undergo significant transformations between the time they are emitted into the atmosphere and when they are deposited onto the Bay. Within the Bay, dioxin compounds are subject to partitioning between the air, water, and particles and to flow, degradation, bioaccumulation, and other interactions.

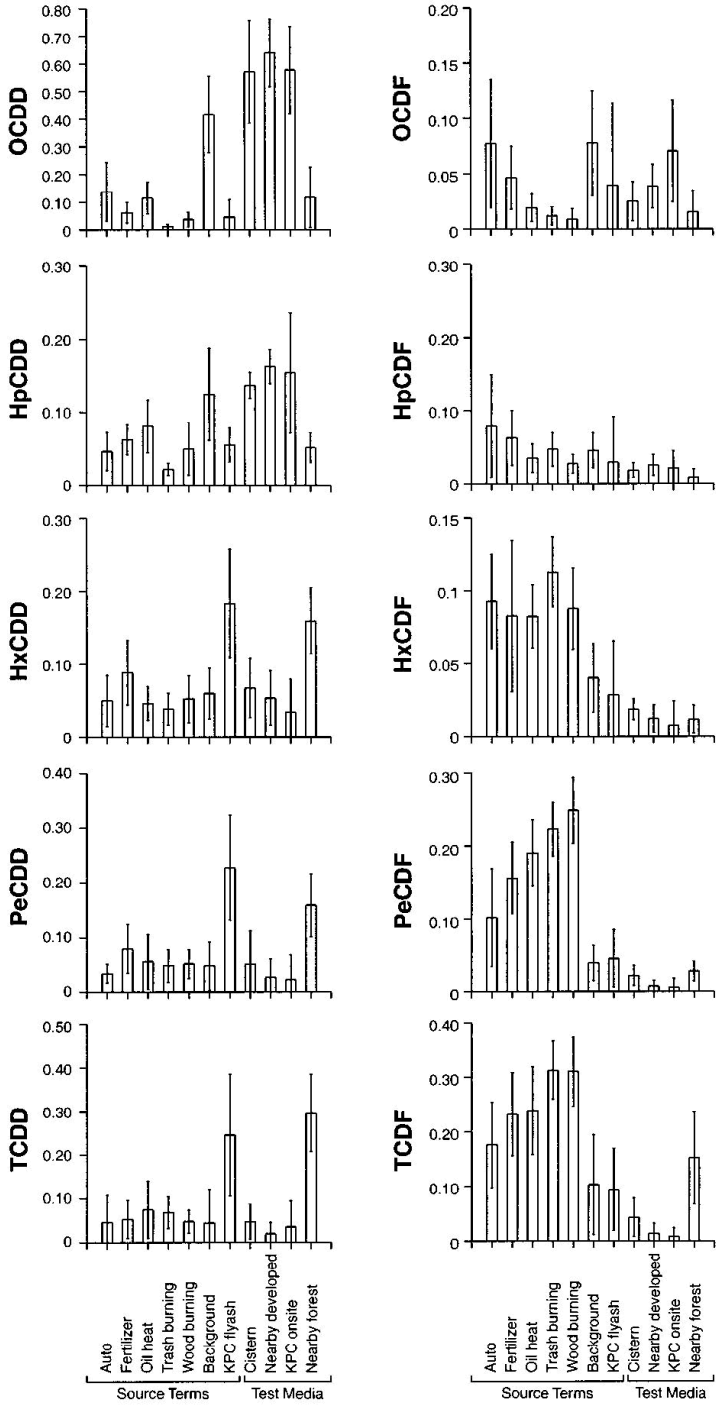
3.4.1 Atmospheric Transformations

Dioxins appear to undergo significant transformation after they are emitted to the atmosphere. Even for PCDD/Fs deposited on roadway tunnels where transportation sources would be presumed to dominate, the isomer profile of deposited material does not closely match the emissions measured directly from heavy-duty diesel vehicle sources (Gullett and Ryan, 2002; Ryan and Gullett, 2000). Typically, diesel vehicle emission profiles averaged 30% (of total PCDD/F mass) 2,3,7,8 TCDD, with OCDD contributing only an average of 10% of the total. In contrast, the on-road composition was less than 2% TCDD and more than 40% OCDD. In general, the relative contributions of PCDDs other than TCDD doubled, and the relative masses of PCDFs declined slightly from the average emitted from vehicles. These findings suggest differential partitioning of PCDD/Fs and degradation (although some of the differences may be caused by other sources of dioxins on the roadway tunnels).

Other studies have contrasted the distribution of PCDD/F homologs from various sources to their contribution in environmental receptors and generally show lower relative contributions of TCDD and lower chlorinated homologs than in source emissions (Figure 3-6, Peek *et al.,* 2002). Some studies have shown differential degradation rates of individual dioxin compounds in the atmosphere (Brubaker and Hites, 1997), which tend to decrease the quantities of lower-chlorinated tetra- and penta-PCDD/Fs relative to the hepta- and octa-isomers.

A recent attempt at global mass balance for PCDD/F emissions and deposition suggested that either overall combustion emission rates are being underestimated, or there are additional sources generally not considered (Baker and Hites, 2000a). There appears to be a worldwide emission deficit of 2,000-10,000 kg PCDD/Fs relative to estimated deposition. The deficit is primarily in two homolog, HpCDD and OCDD, which are not toxic.

Wagrowski and Hites (2000) estimated 2000-3000 kg/yr of global PCDD/F emissions deposition, which fell within the range of estimated global deposition of 2000-15000 kg/yr. However, the average emission estimate was low relative to the mid-range deposition estimate, and the composition of deposition was lower in HpCDD and OCDD than in samples typically seen in soils.



Proportional contributions of PCDD/F homologues for each PCDD/F source. The height of the bar represents the mean proportion by source, and the error bar represents (1 standard deviation.

Figure 3-6. PCDD/F homolog concentrations: sources vs. receptors (from Peak et al., 2002)

Baker and Hites illustrated a mechanism by which a fraction of dissolved pentachlorophenol (PCP) could be transformed in reactions with ultraviolet irradiation to HpCDD and OCDD within a relatively short period, 45 minutes to 4 hours. (PCP is a restricted-use pesticide that is used as a wood preservative.) Yields ranged from 2 x 10^{-6} to 0.001 µg OCDD produced per µg of PCP in water, depending on the reaction conditions and duration. HpCDDs were also formed under some conditions, generally at concentrations about an order of magnitude lower than for OCDD. Such reaction rates would be more than sufficient to account for the annual worldwide emission deficit (relative to estimated deposition) of 2000-10000 kg PCDDs.

A more likely source of the "missing" PCDDs dominating the signal of many environmental samples is the HpCDD and OCDD already present in manufactured PCP. Although current formulations of PCP have lower PCDD/F concentrations than those in the past, dioxins from in-service and discarded PCP-treated wood could constitute a major component of the current environmental inventory.

PCP has been measured in groundwater and soil at some sites in the San Francisco Bay region (*e.g.,* Mountain View, San Mateo, and Concord). It is present due to past handling or disposal of material; runoff from handling or disposal may contribute to PCDD loads to the Bay. Atmospheric transport may distribute these loads throughout the region.

3.4.2 In-Bay Processes

There are several environmental processes that affect the levels of PCDD/Fs found in San Francisco Bay:

- **Dissolved-solid partitioning**.
- **Air-water and air-solid partitioning**.
- **Hydrologic flow**.
- **Degradation.**
- **Bioaccumulation.**
- **Microbial and other biological interactions**.

Dissolved-Solid Partitioning

Because PCDD/Fs are highly hydrophobic (log K_{ow} typically 8 or higher), most of the dioxins in the Bay are expected to be adsorbed to organic material and small particles. The mass budget model used in this report assumes that any contaminant within the system is essentially at equilibrium between the solid and dissolved phases.

Air-Water and Air-Solid Partitioning

The partitioning of PCDD/Fs between the vapor phase and liquid or solid phases will affect their transport and fate in the environment. Henry's Law constants for PCDD/Fs are in a similar range (10^{-5} to 10^{-9} atm m^3/mol) to those of PCBs. A recent study of atmospheric PCBs indicated that there is likely a net efflux of PCBs from the waters of San Francisco Bay, due to high PCB concentrations in the water column (Tsai *et al.*, 2002). Depending on concentrations of PCDD/Fs in water and air, net gaseous flux of these compounds may also be coming out of the Bay. Recent measurements of PCDD/Fs in ambient water (SFEI, 2003) and air (CADAMP, results pending) have been taken. Estimates of the direction and magnitude could be calculated once air PCDD/F and particulate matter concentration data become available.

Hydrologic Flow

Because of the slow degradation rates of PCDD/Fs and the assumption of no net accumulation or erosion of sediment, advective transport is likely to be a major mechanism of PCDD/F import to and export from the Bay. The mass budget model can illustrate the importance of hydrological transport to the long-term fate of PCDD/Fs in the system. Because of the hydrophobicity of PCDD/Fs, the majority of the advective transport is coincident with transport of sediment, particularly fine-grain suspended particulate material. The baseline assumption for advective transport from the Bay is that outflow at the Golden Gate is equivalent to average Sacramento/San Joaquin River discharge of 7x 10^{10} l/day, from averaged DAYFLOW data for the period 1981-2000 (McKee *et al.*, 2002). Advective loss is calculated as the product of average concentration and outflow. An additional contribution to advective loss through tidal exchange can be considered. This tidal exchange, calculated to match the seasonal average salinity seen in RMP measurements, results in additional inflow and outflow at the Golden Gate of approximately 10 x 10^{10} l/day, with a consequent proportional increase in the estimated advective transport loss of PCDD/Fs.

Degradation

Degradation processes provide one pathway for PCDD/F loss from the ecosystem. Photolysis is likely to be an important degradation mechanism for PCDD/Fs. Studies of degradation processes have mostly been conducted under laboratory conditions in simplified matrices (*e.g.,* laboratory water with PCDD/Fs and few other compounds). However, studies of photolysis of selected isomers (primarily TCDD/Fs and OCDD/Fs) have been conducted in some natural waters from lakes and rivers (Dung and O'Keefe, 1992; Friesen *et al*., 1993; Kim and O'Keefe, 1998). Estimated degradation half-lives in the dissolved-phase experiments ranged from less than a day to several days, but only a fraction of PCDD/Fs in water were typically present in the dissolved phase. Experiments with atmospheric-particulate-adsorbed PCDD/Fs showed greatly reduced photolysis, possibly due to light absorption, light shielding, or quenching of reactive species (Koester and Hites, 1992). Particulate-adsorbed PCDD/Fs in the aqueous phase

would also be expected to be influenced by these processes, at the least by light shielding.

Research on the photodegradation of PCDD/Fs has shown that under some conditions, photolytic products of the higher-chlorinated compounds (*e.g.,* OCDD/F and HpCDD/F) include some of the less-chlorinated PCDD/Fs (Choudhry and Webster, 1989; Tysklind *et al.,* 1992). However, the yield of less-chlorinated PCDD/Fs through photodechlorination is generally only a small fraction (less than 10%) of total photodegradation losses (Kieatiwong *et al.*, 1990). Relative yields of the various less-chlorinated isomers are not well characterized and vary greatly among studies due to differences in experimental conditions, so predicting yields of less chlorinated and more toxic isomers from current PCDD/Fs under ambient conditions is not yet possible. However, given the expected slow overall degradation rates of the more chlorinated isomers (*e.g.*, less than 10% per year for OCDD in the water column; Sinkkonen and Paasivirta, 2000), this quantity is small. Even assuming that all water column degradation is from photolysis, with approximately 10% resulting in photodechlorination, only a small yield of PCDD/Fs (approximately 1% of the water column concentration, or 0.3 g OCDD/year throughout the Estuary) would be converted to more toxic isomers.

Bioaccumulation

The primary concern for PCDD/Fs occurrence in San Francisco Bay arises from their persistence, bioaccumulation, and toxicity. The main concern arises from partitioning into low trophic levels, such as bacteria, phytoplankton, and plants, and subsequent biomagnification to higher levels, including fish and wildlife (Figure 3-7). Recent efforts to model accumulation of PCBs through the food web using a fugacity model can be adapted to PCDD/Fs. More simplistic models such as bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) generally cannot account for nuances of food web structure at different locations and are ill-suited for projecting effects, which are complicated by other factors, such as habitat changes and introduction of invasive species. However, for the purposes of this conceptual model, the linear correspondence between concentrations in environmental media and biota assumed by BAFs and BSAFs is sufficiently accurate in the context of the other simplifications used in the model (*e.g.*, well mixed water column and sediment compartments) and other uncertainties (*e.g.*, stormwater loads).

Microbial and Other Biological Interactions

A review of studies on microbial degradation of PCDD/Fs in literature from the 1970s and 1980s (Arthur and Frea, 1989) concluded that 2,3,7,8-TCDD is recalcitrant to microbial degradation. However, some more recent studies indicate that both freshly spiked and aged PCDDs may undergo anaerobic microbial degradation (Barkovskii and Adriaens, 1996) in sediment. This process in sediments is generally slow, with half-lives estimated to be many decades for most PCDD/Fs (Sinkkonen and Paasivirta, 2000). Biological degradation

products of PCDD/Fs result primarily from ring cleavage rather than dechlorination, so degradation of the less toxic isomers does not generally result in significant production of the more toxic compounds.

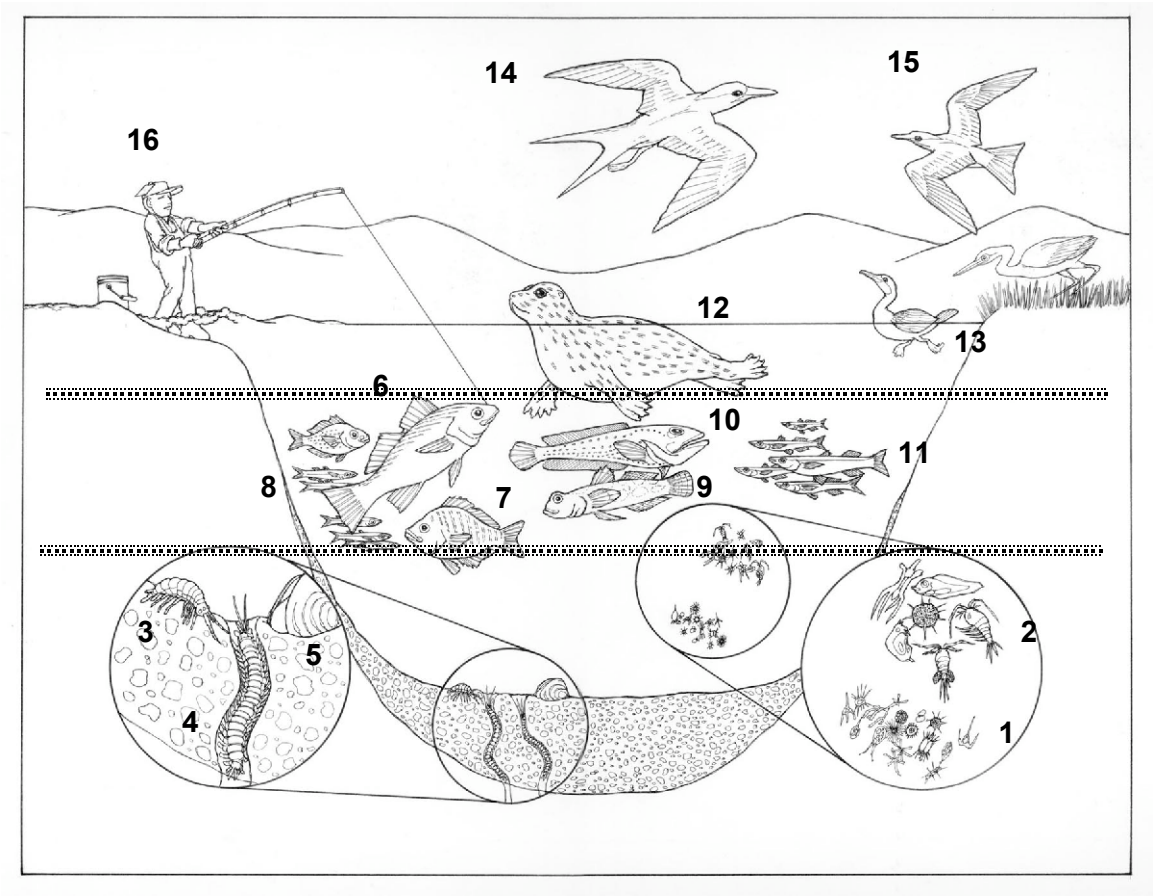


Figure 3-7. San Francisco Bay food web: (1) phytoplankton are consumed by (2) zooplankton and small invertebrates such as (3) amphipods, (4) worms, and (5) clams; (6-11) fish consume zooplankton and invertebrates; (12-16) fish are consumed by humans and wildlife species.

3.5 Mass Balance Model

The mass balance model uses best estimates of ecosystem inventories in the watershed, surface water, and atmosphere; and loss pathways, including transport, degradation, and burial to predict fate of PCDD/Fs in San Francisco Bay over time.

Although total TEQs can be calculated for various environmental compartments and pathways, PCDD/F isomers must be addressed separately in the mass balance model. The individual compounds differ in partitioning and degradation rates, key parameters influencing long-term fate.

Not all isomers occur at measurable levels in each of the environmental matrices included in the model. Therefore, representative PCDD/Fs were used, selected for their measurable concentrations in both water and sediment, their overall abundance, and their contribution to TEQs in both media. PCDDs used for modeling included 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD. PCDFs selected for modeling included 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF, and OCDF.

Figure 3-8 provides a quick sketch of the largest inventories and loading pathways for which quantitative estimates have been made. Some processes, such as sediment erosion, are not quantified, because there are no data on dioxin concentrations in the deeper sediments. (The effect of erosion on concentrations of PCDD/Fs in the active layer may depend more on concentrations in the deeper sediments than on rates of erosion.)

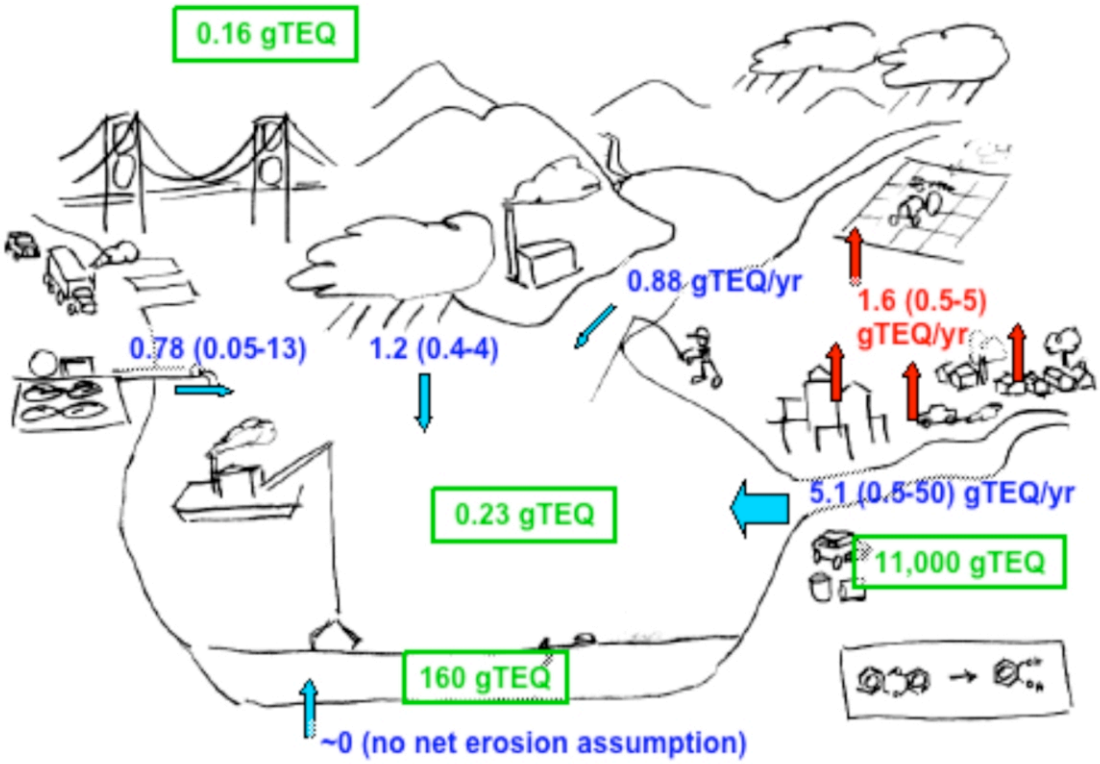


Figure 3-8. PCDD/F sources, pathways (g TEQ/year), and inventories (g TEQ) in San Francisco Bay (green=reservoirs in water, sediments, and watershed; red=emissions rates to atmosphere; blue=annual loads to Bay)

Trends in pollutant concentrations over the long term could be used to constrain the possible values for parameters in the mass budget model. However, there are few reliable and accurate historical measurements of PCDD/Fs in the San

Francisco Bay, and attempting to use the few data that are available would likely result in bias from using an insufficiently representative sample. Thus, rather than attempting to calibrate the model behavior to match historical trends in PCDD/Fs for the Bay, the mass budget model simply projects the outcome of various scenarios for future PCDD/F loading and illustrates the outcomes for various assumptions.

3.5.1 Ecosystem Inventories

Watersheds

There is great uncertainty in estimating the magnitude of the inventory within the watersheds. However, this value is not directly used by the mass balance model. Rather, the model uses information on inputs via river and tributary pathways and assumes that these values remain constant.

Because PCDD/Fs preferentially partition to organic materials, the vast majority of dioxins in the San Francisco Bay region are likely contained in sediments of the Bay and in soils and other solids (*e.g.*, wood products) of the surrounding watersheds. Considering just the dioxins in PCP-treated wood and extrapolating from national data, the inventory of PCDD/Fs in the region totals approximately 11,000 g TEQ.

Sediments

The bulk of the PCDD/F inventory in the system is driven by average sediment concentrations found in the Bay (Table 3-6) and the average depth of the well-mixed, active layer. Although the data on sediment PCDD/F concentrations are from surface grabs, it is assumed that the active sediment layer is well-mixed vertically and uniform throughout the Bay. This assumption is a great simplification and not reflected in the data on sediment concentrations, which may differ by nearly two orders of magnitude (EMAP, preliminary data).

The active sediment layer has a large effect on the modeled system response, as it determines both the initial quantity of PCDD/Fs in the system and the volume of sediment to which additional PCDD/Fs loads are dispersed. The current best estimate of the active layer depth is 15 cm, used in mass budget models for other contaminants in the estuary (Davis, 2002). Effects of assuming shallower and deeper active layers were explored in the modeling.

Assuming a uniform PCDD/F concentration in the top 15 cm, the EMAP data suggest that there are 160 g TEQ dioxins in the active layer of Bay sediments.

Table 3-6. Concentrations of PCDD/Fs in sediments (EMAP)

	Median concentration (pg/g)
2,3,7,8-TCDD	ND
1,2,3,7,8-PeCDD	ND
1,2,3,4,7,8-HxCDD	ND
1,2,3,6,7,8-HxCDD	3
1,2,3,7,8,9-HxCDD	2
1,2,3,4,6,7,8-HpCDD	37
OCDD	240
2,3,7,8-TCDF	3
1,2,3,7,8-PeCDF	0
2,3,4,7,8-PeCDF	1
1,2,3,4,7,8-HxCDF	1
1,2,3,6,7,8-HxCDF	1
1,2,3,7,8,9-HxCDF	ND
2,3,4,6,7,8-HxCDF	0
1,2,3,4,6,7,8-HpCDF	9
1,2,3,4,7,8,9-HpCDF	0
OCDF	14

Surface Water

Due to the hydrophobicity of PCDD/Fs, the bulk of compounds found in the water column are in the suspended particulate phase. Thus the inventory of PCDD/Fs in the water column is highly dependent on the assumptions used in characterizing the average condition of Bay waters. As in Davis (2002), this report assumes an average suspended sediment concentration in San Francisco Bay of 0.085 g/l, as estimated by Schoellhamer for 1994-1995. Although total suspended solids were measured by the RMP over a longer period (1993-2001) stations were biased toward the deeper channel locations in the Bay.

Assuming that the concentrations of PCDD/Fs were equal to the median concentrations found in recent samples from the Sacramento River, Yerba Buena Island, and Dunbarton Bridge, the initial mass in the water column would total only 0.23 g TEQ. This estimate is probably low, because other areas of the Bay have greater concentrations of total suspended solids than were found at the stations sample for dioxin.

The initial concentrations of PCDD/Fs in the water column affect the model only in their contribution to the initial inventory (total mass) of PCDD/Fs in the system. Water column PCDD/F concentrations in subsequent time steps as the model progresses are driven largely by the assumed steady-state suspended sediment concentration and the remaining quantity of PCDD/Fs in the system after all inputs and loss pathways are accounted for.

Atmosphere

The atmosphere is primarily considered a pathway for transport or dioxins, but it also has a small inventory. The volume of air above the Bay and extending to 10 km altitude would contain approximately 0.16 g TEQ, assuming a uniform concentration and using the average found by NDAMN, 0.015 pg TEQ/m^3. This measurement suggests that the atmosphere constitutes only a small pool of the total PCDD/Fs in the environment. Local measurements of concentrations of dioxins in the atmosphere would refine this measurement, but the significance of the atmosphere to the system would be unlikely to change greatly.

3.5.2 Loading Estimates

The model used information from Section 3.3, Loading Pathways, as a first approximation of loads, updating estimates from Tang (1998) (Table 3-7). The distribution of PCDD/Fs in the watershed and atmospheric loads was based on their relative composition in water samples (Table 3-8). An assumption that the distribution of isomers would be the same for loading by runoff and by direct atmospheric deposition is probably inaccurate but was necessary in the absence of data.

Since the loading estimates are based on so few high quality data, the modeling effort tests sensitivity of the model by varying the loading estimates by a factor of twelve.

Table 3-7. Estimated loads of PCDD/Fs to San Francisco Bay (g TEQ/year)

	Past Estimate Tang, 1998	Current Best Estimate	Low Estimate	High Estimate
Watershed/Stormwater	5.1	5.1	0.51	51
Air Deposition	1.2	1.2	0.36	3.6
Municipal Effluent	0.13	0.77	0.047	13
Refinery Effluent	0.004	1.1	0.0033	0.11
Sacramento River	-	0.88	0.88	0.88
Total	**6.4**	**9.1**	**1.8**	**69**

Table 3-8. Contribution of PCDD/F homologs to loads (local tributaries and air deposition)

	Average % of TEQ in water	Load g/day (=6.3 g TEQ/yr)
2,3,7,8-TCDD	4.8%	8.3E-04
1,2,3,7,8-PeCDD	21.0%	3.6E-03
1,2,3,4,7,8-HxCDD	2.2%	3.7E-03
1,2,3,6,7,8-HxCDD	8.4%	1.5E-02
1,2,3,7,8,9-HxCDD	7.3%	1.3E-02
1,2,3,4,6,7,8-HpCDD	12.4%	2.1E-01
OCDD	0.8%	1.3E+00
2,3,7,8-TCDF	9.0%	1.5E-02
1,2,3,7,8-PeCDF	1.1%	3.9E-03
2,3,4,7,8-PeCDF	21.7%	7.5E-03
1,2,3,4,7,8-HxCDF	3.3%	5.7E-03
1,2,3,6,7,8-HxCDF	2.4%	4.1E-03
1,2,3,7,8,9-HxCDF	0.3%	4.5E-04
2,3,4,6,7,8-HxCDF	2.3%	4.0E-03
1,2,3,4,6,7,8-HpCDF	3.0%	5.1E-02
1,2,3,4,7,8,9-HpCDF	0.1%	1.4E-03
OCDF	0.1%	9.2E-02

3.5.3 Loss Pathways

The modeling exercise assumed no net deposition or erosion of sediments in the Bay. Because the system is assumed not to be accumulating (or losing) sediment, the primary loss pathways of PCDD/Fs are transport (including sediment and water advection and volatilization) and degradation. However, because estimates of pollutant loss through burial does not require a knowledge of sediment concentration profiles (buried sediment will have the current PCDD/F concentration for each model time step) a range of burial rates can also be considered.

Transport

Losses of water through evaporation are negligible for the Bay as a whole, so all water entering was presumed to exit at the Golden Gate. The long-term average daily outflow from the Delta was 7 x 10^{10} l/day for the period 1981-2000. Local tributaries supplied an estimated additional 4 x 10^{9} l/day to the Bay (Davis *et al.*, 2000) in stormwater runoff. Water column suspended sediments have been modeled to remain at an average concentration of 0.085 g/l throughout the year. Because PCDD/Fs in the water column are partitioned primarily to suspended particles, they are primarily exported from the Estuary through outflow of fine particles.

PCDD/Fs may also be lost through volatilization to the air and transported from the Bay, but similar to the case for PCBs, even if there is net efflux, the mass of PCDD/Fs lost through this pathway is expected to be small relative to export of

suspended sediments. Similarly, dredging and dredged material disposal in the Bay is a negligible (<1%) pathway for the loss of other sediment-associated contaminants in the Bay and would therefore be expected to be a minor loss pathway for PCDD/Fs as well.

Degradation

Degradation rates were obtained from a literature review of degradation half-lives for a variety of compounds (Sinkkonen and Paasivirta, 2000). Half-lives in water for the various isomers ranged from a minimum of 0.5 year (for TCDD) to 22 years (for OCDF). Sediment half-lives of PCDD/Fs were longer, ranging from 29 years for OCDF to 270 years for 1,2,3,7,8,9-HxCDD. To evaluate the response of the model to this input parameter, ranges of degradation of one order of magnitude were considered, with the geometric mean as the "best" estimate of degradation rate.

Burial

The net sediment accumulation rate was modeled as zero, indicating neither accretion nor erosion. For the sensitivity analysis, an average rate of 1 cm/year (Jaffe, 1998) was used to represents an upper limit for sediment accretion. In addition to this extremely high sedimentation rate, a lower rate of 0.1 cm/year was also considered.

3.5.4 Model Results

Model runs used varying parameters to project the long-term mass of PCDD/Fs in the Bay. For example, the first lines of Tables 3-9 and 3-10 show model results for the following parameters:

- Best-estimate PCDD/F loads.
- Outflow (including Delta and local tributary flows and tidal exchange).
- Sediment mixed layer depth of 15 cm.
- No net burial or erosion.
- Midrange estimates of degradation rates.

Other model runs used different parameters, such as low and high degradation rates and loading rates, to illustrate the important processes controlling the long-term fates of PCDD/Fs in the Bay Tables 3-9 and 3-10 show the percent of current inventories of PCDDs and PCDFs that would remain after 25 years.

Table 3-9. Long-term (25-year) fate of PCDDs under various scenarios (percent of current inventory)

	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD
Tidal exchange	91%	121%	110%	110%
No tidal exchange	145%	190%	177%	178%
Degradation low (0.3x)	102%	132%	118%	115%
Degradation high (3.2x)	66%	94%	91%	97%
No loading	9%	11%	14%	17%
Low loading	34%	45%	45%	46%
High loading ~10x	618%	832%	680%	667%
Mixed layer 7.5 cm	97%	134%	119%	117%
Mixed layer 30 cm	85%	107%	101%	103%
Slow burial (0.1cm/year)	84%	112%	102%	102%
Fast burial (1 cm/year)	47%	64%	57%	56%

Table 3-10. Long-term (25-year) fate of PCDFs under various scenarios (percent of current inventory)

	2,3,7,8-TCDF	2,3,4,7,8-PeCDF	1,2,3,4,6,7,8-HpCDF	OCDF
Tidal exchange	6%	17%	16%	14%
No tidal exchange	17%	37%	35%	29%
Degradation low (0.3x)	8%	21%	22%	21%
Degradation high (3.2x)	3%	8%	6%	4%
No loading	6%	17%	16%	14%
Low loading	6%	17%	16%	14%
High loading ~10x	7%	18%	17%	14%
Mixed layer 7.5 cm	1%	4%	4%	4%
Mixed layer 30 cm	22%	36%	32%	27%
Slow burial (0.1cm/year)	5%	14%	14%	12%
Fast burial (1 cm/year)	1%	3%	3%	3%

Some isomers important to determining TEQs have not been detected in sediment samples from the Bay, and mass balances of those compounds are not possible. Therefore, the model results cannot be used to quantify an overall recovery rate (*i.e.*, change in total TEQs) from PCDD/F pollution. However, for isomers for which sediment and water concentrations are available, recovery curves (illustrated as the percent of the initial mass of the isomer) can be used to estimate the change in individual isomers.

Model results for current loading rates, including tidal exchange as a loss pathway, are presented in Figures 3-9 and 3-10. They show a greater decline of PCDFs than of PCDDs (and some increases in PCDDs) over time.

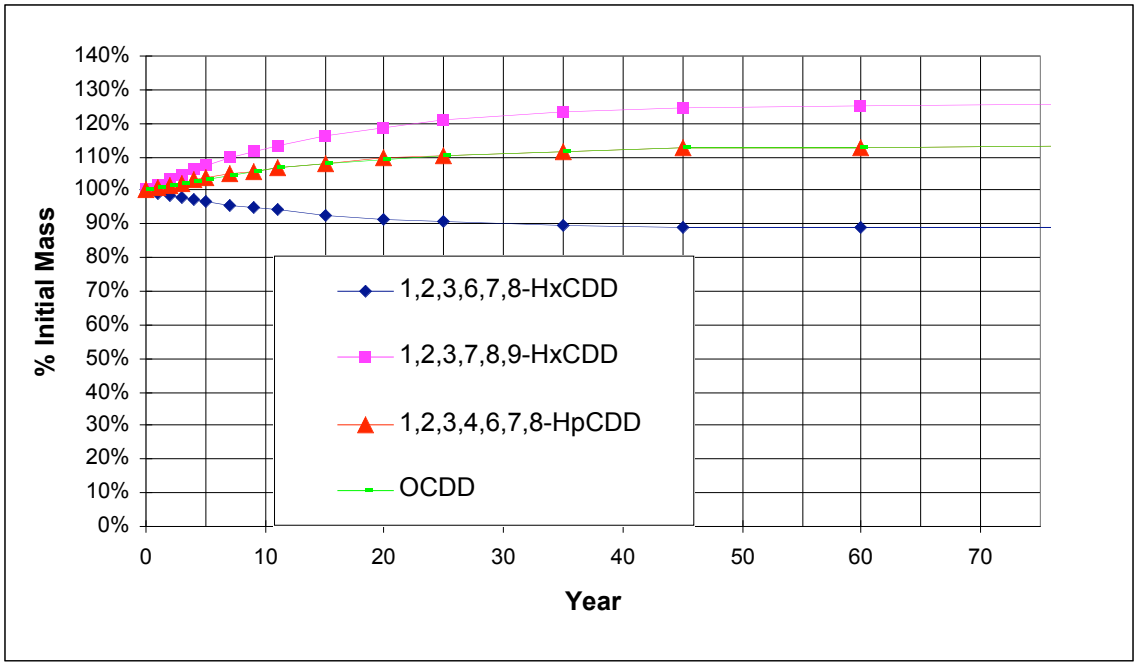


Figure 3-9. Modeled long-term PCDD fate

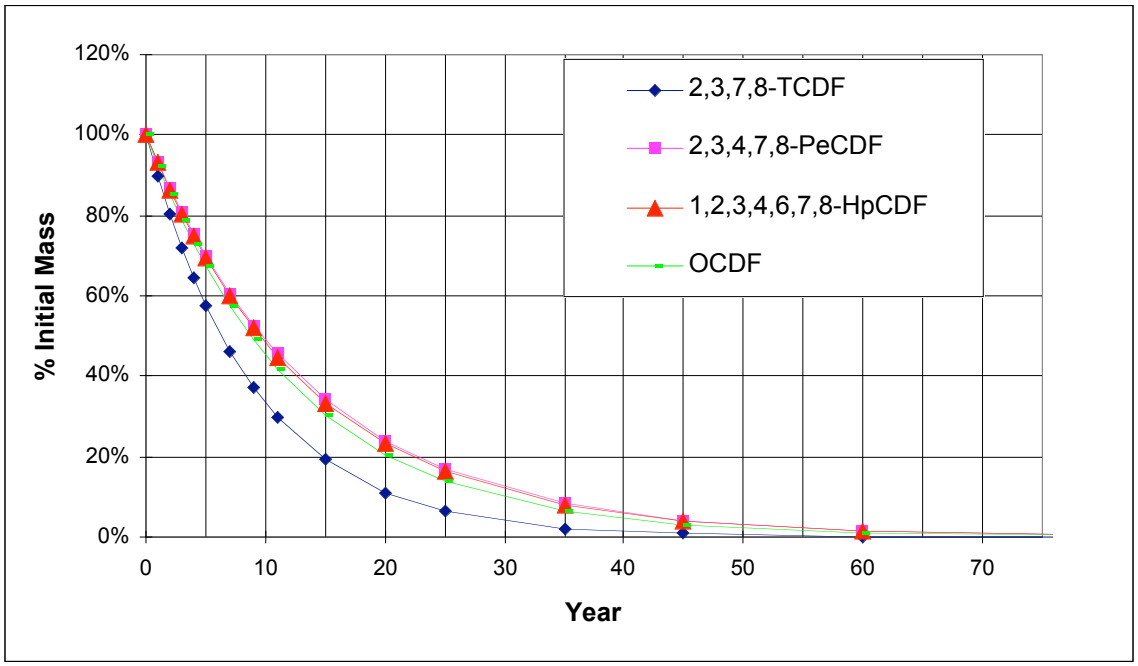


Figure 3-10. Modeled long-term PCDF fate.

The model results are many uncertainties. Complex environmental processes have been simplified, and data from a variety of studies undertaken throughout the country have been extrapolated to illustrate the possible behavior of the local system.

The model runs indicate that current estimates of loading and degradation rates are not sufficient to model PCDDs and PCDFs in the Bay. The increase in the inventory of PCDDs over time, assuming current loading rates, suggests that the loading estimates are too high, the degradation rates are too low, or the estimated size of the sediment inventory is too low. The results are more sensitive to loading rates than to degradation rates. Changing water and sediment degradation rates over an order of magnitude had a moderate effect (about a two-fold difference) on the 25-year change in PCDD concentrations. Varying the loading rate by an order of magnitude resulted in a nearly five-fold difference for some PCDDs.

The mass balance model assumed that new inputs of TEQs from atmospheric deposition and tributaries would be distributed similarly to those already in the Bay. This simplifying assumption probably overestimates the contribution of PCDDs, particularly those that are resistant to degradation. Although dioxins from legacy sources in the watershed may have a similar mix of compounds as those present in the Bay, new sources are likely to have more PCDFs and less PCDDs contributing to the total TEQs.

In contrast, changing loading rates from tributaries by an order of magnitude had little effect on long-term PCDF concentrations, but an order of magnitude change in degradation rates resulted in five-fold differences in future concentrations of some PCDF compounds. These differences in model results highlight the differences in the processes that most affect the long-term fate of PCDDs and PCDFs.

4. Information Gaps

This section summarizes the uncertainties in this report's conclusions and suggests some potential future projects to obtain additional data and conduct more analysis of the sources, fate, transports, and effects of dioxins. In other documents or forums, the CEP will develop appropriate strategies for addressing dioxins in the Bay and its watersheds. These strategies may include:

- Data collection or analysis.
- Implementation of corrective actions.
- Formulating and refining management questions and setting priorities for the above two activities.
- Determining an ongoing process for integrating all of the above.

There may be control measures, remediation, and regulatory actions that can and should begin now, even with existing uncertainties. CEP partners are committed to identifying these actions. Future CEP data gathering and technical analysis should focus on determining the potential effectiveness and actual effects of actions to reduce or eliminate impairment and to restore beneficial uses of the Bay.

The uncertainties of the report's conclusions are great. Uncertainties in the impairment assessment arise from the lack of standards for evaluating impairment, the few available water, sediment, and biota, and analytical limitations (particularly detection limits). Uncertainties in the conceptual model arise from the simplifying assumptions and the gaps in available information. For example, there are uncertainties in the representativeness of data used for emissions and loading calculations, the applicability of national inventories to the region, and the analytical limitations (particularly detection limits).

Steps for future information gathering and other actions should be guided by preliminary management questions:

- **Are the beneficial uses of San Francisco Bay impaired by dioxins and furans?** Although the existing data suggest impairment of sport fishing, a more definitive and ongoing assessment requires establishment of criteria to define impairment and additional measurements, particularly in resident biota. Although measurements of other matrices, such as water and sediments, and modeling can be used to evaluate impairment, they cannot substitute for monitoring dioxin levels in fish and wildlife.
- **Are concentrations of PCDD/Fs in San Francisco Bay increasing, decreasing, or remaining unchanged?** Emissions of dioxins have probably declined in recent years, but the inventory in the surrounding watersheds and the Bay remains high. The decline in emissions may not be evident in the Bay for decades. Evaluating change throughout the Bay

would be difficult and expensive. However, smaller-scale efforts could illustrate trends. For example, measurements in depositional areas, such as wetlands or vernal pools, could capture long-term trends in watershed or atmospheric loading. Differences between these sites could help determine the relative roles of legacy and new dioxin inputs.

- **How can we reduce the potential for risk posed to humans and wildlife? Can dioxin loads be reduced by implementation actions for other TMDLs?** Considerable efforts are being expending in developing and implementing TMDLs for other pollutants that impair the beneficial uses of San Francisco Bay. Some of the steps taken to mitigate other organic pollutants, such as PCBs and organochlorine pesticides, may also reduce the risks of impairment by dioxins. The potential for these benefits is not well understood—modeling efforts are limited by a lack of data. Modeling efforts should continue as additional data are collected. Some steps directed towards mitigating dioxin impairment may be simple and should be taken regardless of uncertainty. These actions could include reduced use or elimination of some PCDD/F-producing activities. Other actions will require careful thought. The mass budget model, although simplistic, has helped to identify areas in which additional information is needed.
- **How much dioxin removal can be achieved by pollution prevention options?** Given the large cost of gathering sufficient data to significantly reduce uncertainties in the sources and loads of dioxins to the Bay, further modeling should be used to evaluate pollution prevention options that will result in loads of dioxins. The February 2004 Bay Area Dioxins Project report describes several demonstration projects that should be evaluated.

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