RMP DIOXIN STRATEGY

San Francisco Bay was placed on the State of California's 303(d) list of impaired waterways in 1998 as a result of elevated concentrations of dioxins and furans (commonly referred to as only 'dioxin') in fish. RMP studies of contaminants in Bay sport fish conducted every three years since 1994 have found that dioxin concentrations have remained relatively unchanged over this time period and in some species, continue to exceed screening values for human consumption. Our understanding of dioxin in the Bay is extremely limited however and improving this is a necessary first step in the process to reduce concentrations in Bay fish and resultant health risks to fish-eating humans and wildlife. This strategy is being developed to ensure that the RMP is providing information that is of highest value and most urgently needed by managers for development of a dioxin TMDL.

QUESTIONS FOR DIOXIN

The following questions articulate the needs and priorities for obtaining information on dioxin in the Bay:

1. Are the beneficial uses of San Francisco Bay impaired by dioxins?

Dioxin concentrations in white croaker collected by the RMP since 1994 have exceeded the screening value for human consumption of fish (0.14 pg/g wet weight TEQ) by a factor of five or greater. Continued assessment of fish dioxin concentrations is needed to determine whether the screening threshold continues to be exceeded and if management actions are having an impact on accumulation of dioxins in fish.

2. What is the spatial pattern of dioxin impairment?

The distribution of dioxin concentrations in the Bay presently represents a major information gap. Information on spatial variation in sediment and/or wildlife concentrations may allow management actions to focus on regions of the Bay where concentrations are highest and provide information on the influence of different dioxin loading pathways (e.g. runoff from the Central Valley watershed vs. highly-urbanized Central and South Bay).

3. What is the dioxin reservoir in Bay sediments and water?

Contaminated sediment is a major reservoir of organic chemical contaminants that accumulate in aquatic foodwebs, therefore reducing concentrations of dioxin in sediment is likely critical for reducing concentrations of dioxin in fish. Reduction of dioxin impairment in the Bay is accomplished by reducing loads of dioxin to Bay sediments and water. Estimates of the current reservoir in Bay sediments and the water column are needed for predicting the long-term fate of dioxin in the Bay.

4. Have dioxin loadings/concentrations changed over time?

Due to the potentially large historical releases of dioxins, an estimate of the historical loadings is needed to put current dioxin loads in perspective. Changes over time in dioxin loadings and concentrations in wildlife have the potential to influence management actions to reduce dioxin impairment in the Bay. For example, in sediments, higher dioxin concentrations below the active sediment layer can act as an internal source to the water column in a net-erosional environment, and levels in pre-industrial sediments may indicate possible minimum loading rates. Likewise, in wildlife, changing concentrations may indicate whether existing actions are sufficiently effective.

5. What is the relative contribution of each loading pathway as a source of dioxin impairment in the Bay?

Management of dioxin loadings requires an understanding of the relative contribution of each potential loading pathway to the Bay from external sources (inputs from the Central Valley watershed, municipal and industrial wastewater discharges, urban and non-urban stormwater runoff, and direct atmospheric deposition). Estimates of dioxin loading from each pathway are needed for assigning load allocations as part of a strategy for reducing impairment in a dioxin TMDL.

6. What future impairment is predicted for dioxins in the Bay?

The ability to predict how dioxin concentrations are likely to change under various future loading scenarios is essential for determining the loading reductions necessary for reducing impairment in fish. Models used to make these predictions require a comprehensive understanding of dioxin fate in the Bay, including loading from various pathways and the processes that affect its removal or uptake into the food web.

FIVE YEAR PLAN FOR RMP DIOXIN WORK

The CEP Conceptual Model/Impairment Assessment report prepared in 2005 presented a one-box model for dioxin in the Bay using the limited local, regional, and national data available for dioxin inventories, loading estimates, and fate processes. The report concluded that there are many uncertainties associated with the model, primarily due to lack of local, reliable dioxin data, and recommended that future projects obtain additional data and conduct more analysis of the source, fate, transport, and effects of dioxin. RMP studies will be conducted from 2008-2012 to improve our understanding of the status, trends, and loadings of other chemical contaminants to the Bay and present valuable opportunities to gain additional information on dioxin. The studies listed below address the dioxin management questions and are considered priority first steps towards improving our understanding of dioxin in the Bay. A five-year plan for dioxin studies is proposed below, with the intent that it will be re-evaluated each year based on the most recently available information. This work will be designed and performed under the guidance of an RMP dioxin strategy workgroup, which consists of stakeholder representatives from the RMP Steering and Technical Committees and the Regional Board.

Sport fish ($22,000 every 3 years)

In 2009 and 2012, dioxin will be analyzed in twenty samples of white croaker and shiner surfperch collected from popular fishing areas in the Bay as part of S&T monitoring. White croaker and shiner surfperch were selected because their PCB and dioxin concentrations were higher than other Bay species in previous years, they are commonly caught in near shore areas by Bay anglers, and they are the main indicator species used in the PCB TMDL to assess trends in PCBs, which have physical-chemical properties similar to dioxins.

Dioxin data from both species will be used to determine whether the screening threshold continues to be exceeded (Question 1). While concentrations in white croaker will be used as an indicator of regional food web accumulation, shiner surfperch have a smaller home range and will thus be used to assess spatial variation in food web uptake from sediments (Question 2). Concentrations in white croaker will be compared to data from previous years to assess concentration trends (Question 4), and shiner surfperch concentrations can be compared to evaluate short term trends and/or variability. Data from both species can be used in foodweb modeling (Question 6). Cost of dioxin analysis in fish tissue is $750/sample.

Bird Eggs ($10,000)

In 2012, dioxin will be analyzed in nine samples of cormorant eggs collected from three sites (3 samples per site) spatially distributed throughout the Bay as part of S&T monitoring. Because of their high position in the foodweb and relatively wide foraging ranges, cormorants are valuable indicators of regional contamination in the Bay and have been analyzed for dioxin every two years since 2002.

Cormorant egg dioxin data will be used to assess spatial variation of contamination in the Bay (Question 2) and will be compared to data from previous years to assess concentration trends (Question 4). Cost of dioxin analysis in bird eggs is $750/sample.

Surface Sediment ($57,000/year when analyzed)

Dioxin will be analyzed in surface sediment samples collected at 47 stations as part of RMP S&T monitoring in 2008, 2009, and 2012. Starting in 2008, RMP sediment sampling will alternate between dry (July/August) and wet (February/March) seasons. This sampling strategy will allow for dioxin analysis in consecutive years to be conducted within only 7-8 months of each other, and aims to avoid confounding seasonal fluctuations in concentrations. Although NOAA-EMAP analyzed Bay sediments for dioxin in 2000, most congeners were below detection in sediments. Use of high resolution mass spectrometry and the extraction of larger samples in this study will likely provide quantitative results for the higher TEQ congeners in more samples. The need for additional surface sediment data will be re-evaluated each year. If dioxin concentrations are found to be uniform among segments and shoals/channels within segments, additional collections and analyses will be conducted only every three years. However, if distributions are highly variable (e.g. within-segment RSD of 50% or greater), more data will be needed to reduce our uncertainty.

Sediment dioxin data will be used to assess spatial variation of contamination in the Bay (Question 2) and to estimate the total reservoir in Bay sediments (Question 3). When compared to sediment core data, surface sediment data will also be used to determine if recent loadings are different from historical loadings (Question 4). Data will be used in foodweb modeling and development of a one-box model (Question 6). Cost of dioxin analysis in sediment is $850/sample.

In-Bay Surface Water ($20,000/year when analyzed)

In 2009 and 2011, dioxin will be analyzed in twenty ambient surface water samples collected as part of S&T monitoring. Dioxin analysis will coincide with the analysis of PCBs since they can be extracted together. Dioxin concentrations in ambient surface water are expected to be very low relative to watershed/stormwater runoff and thus high volume water samples (100 L) are required to obtain detection of the less chlorinated congeners which often dominate the TEQ concentrations in fish.

Surface water dioxin data will be used to assess spatial variation of dioxin contamination in the Bay (Question 2) and to estimate the total dioxin reservoir in the water column (Question 3). Data will be used in foodweb modeling and development of a one-box model (Question 6). Cost of dioxin analysis in water is $700/sample.

Sediment Cores ($57,000)

The RMP recently collected sediment cores from eleven sites throughout the Bay to support PCB modeling and TMDL development. In 2008, dioxin will be analyzed in sediment from 4-5 sections of these cores at varying depths. The need for additional sediment core data will be re-evaluated each year.

Sediment core data will be used to estimate the total dioxin reservoir in Bay sediments (Question 3), and when compared to surface sediment data, will also be used to determine if loadings have changed over time (Question 4). Data will also be used in development of a one-box model (Question 6). Comparison of congener profiles over time may also provide information on changing dioxin sources. Cost of dioxin analysis in sediment is $850/sample.

Dated material from the sediment cores was used for PCB analysis and is not available for dioxin analysis. The sediment sections closest to the dated core material will therefore be used for this study. The uncertainty associated with using the adjacent, undated core sections is not greater than the difference between the dated core sections (i.e. its age must be between those of the dated sections) so its use will not greatly affect our ability to distinguish changes in loading history over time.

Tributary Loadings ($34,000/year)

The Central Valley watershed and local tributaries are the dominant pathways for loading of other halogenated organic chemical contaminants (e.g. PCBs and PBDEs) to the Bay and the highest loading by a factor of five was associated with local watershed/stormwater runoff in the

CEP Dioxin Conceptual Model/Impairment Assessment report, based on data from a single study in the region. Dioxin loadings from these pathways have not been adequately quantified and are essential for development of a dioxin model and TMDL for the Bay. To estimate loadings from these pathways, dioxin will be analyzed in addition to other pollutants of concern in water samples collected during studies being conducted in Water Years (WY) 2009-2011 as part of the Sources, Pathways and Loadings Workgroup (SPLWG):

- In WYs 2009, 2010, and 2011, samples will be collected from a small tributary to estimate dioxin loads from urban streams to the Bay. In 2009, samples will be collected from Zone 4 Line A in Hayward or a similar urbanized tributary. In 2010 and 2011, another small tributary will be selected to provide information on variation of contaminant loads from this pathway.
- In 2010, samples will be collected from Mallard Island on the Sacramento River to estimate dioxin loading from the Central Valley watershed. This sampling location is the site of an ongoing RMP study to measure loads of pollutants of concern entering the Bay as a result of Delta outflow. Concentrations of Hg, PCBs, PBDEs, OC pesticides, and PAHs were determined for water collected from this site in WYs 2002-2006.
- In 2011, samples will be collected from Guadalupe River to estimate dioxin loads from a tributary which receives runoff from both urban and agricultural sources. Guadalupe River has been studied for loadings by the RMP since WY 2003. Concentrations of Hg and other trace metals, PCBs, PBDEs, and OC pesticides were determined for water collected from this site in WYs 2003-2006.

Whole water samples will be collected for dioxin analysis alongside those for other pollutants of concern during the rising and peak stages of wet season storm events. Although 32 samples per wet season are planned for other pollutants in SPLWG studies, 16 samples (4 samples during 4 storm events per year) will be collected for dioxin analysis in these studies to provide a cost-effective estimate of dioxin loads. Based on method detection limits, it is anticipated that collection of 10 L water samples will allow detection of most dioxin congeners.

Dioxin concentrations in water samples from these studies will be used to refine the loading estimates provided in the CEP Conceptual Model/Impairment Assessment report by providing additional data on loadings from the Central Valley watershed, small tributaries that receive primarily urban runoff, and a small tributary that receives runoff from both urban and agricultural sources (Question 5). Loading estimates from these pathways will be used in development of a one-box model (Question 6) and in the dioxin TMDL to determine the focus of management actions. Cost of dioxin analysis in 10 L of whole water is $1450/sample.

Atmospheric Deposition ($25,000)

Using a previous loading estimate in a SFBRWQCB review of Bay Area dioxin data, atmospheric deposition was identified as the second highest contributor of dioxin to the Bay, though it is not clear what empirical data was used to derive this estimate. Direct atmospheric deposition data for dioxin in the Bay have never been collected, and while ideal for estimating loads, it is difficult to collect because of the logistics associated with collecting enough sample volume to reach detection limits and the high cost of analysis.

The California Air Resources Board (CARB) recently completed an ambient air monitoring study in which they analyzed atmospheric dioxin concentrations at five sites in the Bay Area from 2002-2005. In 2009, an estimate of dioxin loading from direct deposition will be modeled using the recently collected CARB ambient air data and known physico-chemical parameters for dioxins. The goal of this modeling effort is to refine the mass loading estimate for atmospheric deposition of dioxin to the Bay using recently collected air data. The relative importance of atmospheric deposition, compared to other dioxin loading pathways, will then be evaluated to determine if further refinement of the loading estimate is needed via collection of direct deposition samples. A refined estimate of dioxin loading via direct atmospheric deposition will be used to predict the fate of dioxin in the Bay using a dioxin one-box model and in the dioxin TMDL (Questions 5,6). The modeling effort will also include extensive data gathering to determine the information needed to conduct a more detailed atmospheric study and develop a broader strategy for quantifying the contribution of dioxin to the Bay from this pathway.

One-box Mass Budget Model ($20,000)

Similar to the model developed for PBDEs, a one-box mass budget model will be developed to enhance understanding of the fate of dioxin in San Francisco Bay. Loading estimates reported in the Dioxin Conceptual Model/Impact Assessment, 2008 S&T monitoring sediment data, and known physico-chemical parameters for dioxin congeners will be used to create the model. Loading estimates used for the model will be refined as additional data is obtained from tributaries, Delta outflow, and atmospheric deposition studies. Model development will begin in 2010 once sediment dioxin data has been received.

The mass budget model will be used to predict the rate of change in Bay dioxin concentrations (Question 6) under various loading scenarios. When linked to a food web bioaccumulation model, this model will be used to determine the external load of dioxin required to attain the sediment concentration goal resulting in attainment of the fish tissue numeric target in the TMDL.

Foodweb Modeling ($20,000)

Similar to the foodweb modeling conducted for the PCB TMDL, sport fish, sediment, and water dioxin data will be incorporated into a foodweb model in 2012 to enhance understanding of dioxin bioaccumulation in the Bay (Question 6). The foodweb model may then be linked with the one-box model in the TMDL to understand the important factors and sources causing dioxin accumulation in fish. Site-specific biota-sediment accumulation factors (BSAFs) will also be calculated from fish and sediment data to determine the relative bioavailability of each dioxin congener to sport fish. BSAFs can then be used to calculate Bay-specific bioaccumulation equivalency factors (BEFs) for each dioxin congener, which provide an indication of bioaccumulation potential relative to the most toxic dioxin congener, 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD).

QA/QC Laboratory Inter-comparison Study ($25,000)

A laboratory inter-comparison exercise will be conducted to determine the influence of analytical variability on the quality of dioxin measurements. A sub-committee consisting of BACWA lab members and the RMP will develop a detailed study plan in the fall of 2008 and the exercise will be conducted in 2009.

FIVE YEAR PLAN FOR RMP DIOXIN WORK

Sample Design Element	Questions Addressed	2008	2009	2010	2011	2012	Total by Element
Sport fish	1,2,4,6		$22,000			$22,000	$44,000
Bird eggs	2,4,					$10,000	$10,000
Surface sediment	2,3 6	$57,000	$57,000			$57,000	$171,000
In-Bay surface water	3,6		$20,000		$20,000		$40,000
Sediment cores	3,4,6	$57,000					$57,000
Trib. loadings, Delta outflow	5,6		$34,000 (Small Trib)	$34,000 (Small Trib) $34,000 (Delta outflow)	$34,000 (Small Trib) $34,000 (Guadalupe)		$170,000
Atmospheric deposition	5,6		$25,000				$25,000
One-box model	6			$20,000			$20,000
Foodweb model	6					$20,000	$20,000
QA/QC lab intercomparison			$20,000				$20,000
	Total by Year	$114,000	$178,000	$88,000	$88,000	$109,000	$577,000

Costs include data management, analysis, and reporting (30% of total)

Questions:

1. Are the beneficial uses of San Francisco Bay impaired by dioxins?
2. What is the spatial pattern of dioxin impairment?
3. What is the dioxin reservoir in Bay sediments and water?
4. Have dioxin loadings/concentrations changed over time?

5. What is the relative contribution of each loading pathway as a source of dioxin impairment in the Bay?
6. What future impairment is predicted for dioxins in the Bay?