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Current Knowledge and Data Needs for Dioxins in San Francisco Bay

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EXECUTIVE SUMMARY

San Francisco Bay was placed on the State of California's 303(d) list of impaired waters in 1998 as a result of elevated concentrations of dioxins in fish. In 2008 the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) Dioxins Workgroup developed a workplan for reducing information gaps that were identified in a 2004 Conceptual Model/Impairment Assessment (CMIA) report on dioxins. Special studies in that workplan were largely completed by 2012, but continued monitoring of biota provided evidence of impairment and an opportunity for evaluating trends. Fish tissue concentrations indicate that the beneficial use of commercial and sport fishing is impaired by dioxins. Although there are dioxin-like PCBs also contributing to impairment, this report only directly addresses polychlorinated dibenzodioxins and furans (here collectively called "dioxins").

Sediment concentrations of dioxins are similar among open water Bay sites, but are sometimes higher at nearshore sites where data are collected by the Dredged Material Management Office (DMMO) and RMP. Loads from the land and limited near-shore transport may cause the strong gradients sometimes seen between near-shore and open water sites, which are much greater than differences among open water Bay segments. Biota concentrations indicate insignificant spatial differences in most wide-ranging species, with only shiner surfperch showing significant inter-site differences, likely reflective of the occasionally high dioxin concentrations in the near-shore sites they often inhabit.

The inventory of dioxins in sediment is much greater than that in water, so recovery by export of dioxins through tidal flushing is likely slow. Although the inventory in near-shore environments is estimated at only 6% of the whole Bay, due to the greater influence of near-shore sediment concentrations on shallow-water biota, there may be opportunities for more focused management actions and risk reduction and recovery at some sites. These actions could be doubly beneficial by reducing exposure to local biota and eventual export to the wider Bay.

Dioxins in sediment cores from wetland and subtidal Bay sites provide evidence of past declines (with the most recent concentrations sometimes 5-fold lower than earlier peaks), but future declines are likely to be slower because surface concentrations are currently about double pre-anthropogenic layers. Continued monitoring of biota, and periodic monitoring of cores or archived surface sediments (particularly from fixed/repeat monitoring sites) will help determine whether declines are occurring.

Special studies in the RMP Dioxin Strategy workplan also helped to improve stormwater runoff and atmospheric deposition load estimates, the expected largest but least well-quantified loads to the Bay. Revised estimates of annual loads from all sources combined are three-fold higher than the estimates in the 2004 CMIA, mostly due to an improved estimate of air deposition using local air concentration data. The air deposition estimate is based on ambient air dioxin data that are fairly old (circa 2002-2006), and dioxins in runoff were last measured in 2010, so updates on these data may be needed in the future to verify expected declines given their importance to total loading.

Sources of dioxins are expected to continue decreasing nationally and locally due to past efforts removing point sources and current management efforts towards reducing atmospheric emissions. Overall, it appears that dioxin will be a pollutant impairing beneficial uses in the Bay for a long time to come, with slow recovery, as evident in statistically significant declines in fish tissue concentrations for South Bay, but not North and Central Bay locations. Subtidal cores from the open Bay also show little difference between surface and deeper layers, suggesting deep mixing, allowing existing contamination to affect biota until those sediments are buried deeply. The long-term fate under different loading scenarios should be modelled to inform

managers on the best approaches to recover beneficial uses. It is important to monitor dioxin in the long term to track status and progress, most particularly in fish tissue, which is most directly tied to the impairment listing.

The inclusion of DMMO data in this review has been valuable, as it reinforces evidence of nearshore gradients (and possible source areas) of dioxin hinted at in a small number of RMP coring sites. Continued monitoring of dioxins in dredging projects, particularly for near-shore sites (e.g., <250 m offshore) at select locations, would help to better define these gradients. Although the dredged material measured will usually be moved offsite, it is unknown whether the original source remains in the landscape, so ongoing measurement and reporting of dioxins concentrations in nearshore samples can help to identify potential upland watershed sources for additional focused management.

For more widespread and lower level contamination across the urban landscape, the correlation to some extent between PCBs and dioxins suggest that even if their sources are not coincident, their persistence and environmental partitioning and transport behaviors are similar enough that some approaches to managing PCBs (such as green infrastructure) could have complementary benefits for dioxins.

SECTION 1: BACKGROUND

The chlorinated dibenzodioxins (CDDs) are a family of 75 different compounds commonly referred to as polychlorinated dioxins. The chlorinated dibenzofurans (CDFs) family contains 135 individual compounds (known as congeners). Of these compounds, those that contain chlorine atoms at the 2,3,7,8-positions of the parent dibenzofuran or dibenzodioxin molecule are the most toxic, with a variety of harmful environmental and human health effects. The combined toxicity from the most toxic tetra-chlorinated form (substituted only at the 2,3,7,8 positions) to the least toxic octa-chlorinated congeners (Van den Berg et al., 2005) is calculated as toxic equivalency (TEQ). In this discussion, we refer to the polychlorinated dioxins and furans by their commonly used name of “dioxins” for the collective group.

San Francisco Bay was placed on the State of California’s 303(d) list of impaired waters in 1998 as a result of elevated concentrations of dioxins in fish. Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) studies of contaminants in Bay sport fish conducted every three to five years since 1994 have found concentrations of dioxins that are relatively unchanged over this time period, and in some species, still exceeding screening values for human consumption. The available information for dioxins in the region was synthesized in a conceptual model/impairment assessment (CMIA) report for the Clean Estuary Partnership (Connor et al., 2004). That report highlighted limited data and significant uncertainties and gaps in our understanding of spatial and temporal distributions of dioxins in Bay waters and sediments, and in estimated loading rates via various pathways.

The final section of the 2004 report summarized the major uncertainties and suggested potential future studies to reduce information gaps. Uncertainties in the impairment assessment arose from the lack of standards for evaluating impairment; sparse data availability for water, sediment, and tissue dioxins; and analytical limitations (particularly frequent non-detects). Other uncertainties in the conceptual model arose from the simplifying assumptions and the gaps in available information, such as the spatial and temporal representativeness of past sampling and analysis, and applicability of national inventories to estimates of regional loading.

The RMP established a Dioxins Strategy Workplan in 2008 to identify and address the highest priority data needs. The RMP conducted special studies to address the priority management questions (MQs) from the RMP Dioxins Strategy Workplan, listed and described briefly below.

MQ1. Are the beneficial uses of San Francisco Bay impaired by dioxins?

This question was highlighted as one of the major continuing information needs in the 2004 CMIA. Dioxins in white croaker and shiner surfperch 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 dioxins tracks whether the screening threshold continues to be exceeded and if there are improvements or other changes. A corollary question listed in the prior CMIA was:

> *How can we reduce the potential for risk posed to humans and wildlife?* Although not directly addressed in any special studies in the RMP Dioxins Strategy, elements focusing on loads and trends provide some information on the potential for risk reduction.

MQ2. What is the spatial pattern of dioxins impairment?

The spatial distribution of dioxins in the Bay was a major information gap in the 2004 CMIA. Information on spatial variation in sediment and biota may allow management actions to focus on regions of the Bay with higher concentrations and/or more influential sources and pathways.

MQ3. What is the dioxins reservoir in Bay sediments and water?

Contaminated sediment is a major reservoir of persistent organic chemical contaminants that accumulate in aquatic food webs, so estimates of the current reservoir in Bay sediments and the water column are useful for predicting the long-term fate of dioxins in the Bay.

MQ4. Have dioxins loadings/concentrations changed over time?

This was also listed as a major information need in the 2004 CMIA. Measuring changes over time is needed to evaluate the effectiveness of and continued need for management actions to reduce impairment in the Bay. For example, lower dioxins concentrations near the sediment surface could suggest benefits of past management, while pre-industrial sediments may indicate possible minimum (non-anthropogenic) concentrations. Likewise, changing concentrations in biota may indicate whether existing actions are sufficiently effective.

MQ5. What is the relative contribution of each loading pathway as a source of dioxins impairment in the Bay?

Management of dioxins loadings requires an understanding of the relative contribution from various inputs (discharge from the Central Valley watershed, municipal and industrial wastewater discharges, urban and non-urban runoff, and direct atmospheric deposition). Estimates of dioxins loading from each pathway can help evaluate the best potential approaches for load reduction. The following particular angles of interest with respect to loads were listed in the prior CMIA.

> *Can dioxins loads be reduced by implementation actions for other TMDLs?* Although studies undertaken have not directly been designed for addressing this question, analysis of correlations between dioxins and PCBs can provide some evidence of potential for co-management.
>
> *How much dioxins load reduction can be achieved by pollution prevention options?* This is also indirectly addressed in the quantification of different loading pathways, assessing the relative importance of pathways with more global (e.g., atmospheric deposition) and historic (e.g., sediment inventory) versus more local and ongoing (e.g., point discharge, urban runoff) influences.

MQ6. What future impairment is predicted for dioxins in the Bay?

The ability to predict how dioxins 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 dioxins fate in the Bay, including loading from various pathways and the processes that affect removal or uptake into the food web.

Studies undertaken as part of the RMP Dioxins Strategy have helped to address many of these information gaps, and will help define future data needs for dioxins monitoring and management. This report is organized into sections mirroring those in the prior CMIA: Section 2 assesses the current state of impairment due to dioxins (MQ1); Section 3 describes the current distribution and inventory of dioxins in the Bay (MQ2 and MQ3); Section 4 estimates loads of dioxins entering the Bay compared to the previous simple mass balance to evaluate the coherence of the available data and anticipate likely future trends (MQ5 and MQ6); Section 5 considers whether the current empirical data show any evidence of a decreasing trend in dioxins (MQ4); finally Section 6 assesses remaining data gaps and suggests strategies for optimizing future dioxins data collection to focus on the highest priority needs.

SECTION 2: IMPAIRMENT ASSESSMENT

A key question for management of dioxins is whether there are risks or impacts.

MQ1. Are the beneficial uses of San Francisco Bay impaired by dioxins?

Dioxins are ubiquitous in the environment at very low concentrations, and chemical analyses are relatively expensive. Consequently, there are limited data available on dioxins concentrations in water and fish, as well as other Bay environmental matrices. Furthermore, data analyses are sometimes limited by individual dioxins compounds present in the environment at concentrations below analytical detection limits. Nonetheless, the available fish and water data do indicate potential impairment of the Bay for the commercial and sport fishing beneficial use. Because there are limited available data, there is uncertainty as to the impairment of other beneficial uses by dioxins.

In the following impairment assessment, we review past information used by the U.S. Environmental Protection Agency (USEPA) to establish the impairment of sport fishing in the Bay by dioxins. We also evaluate currently available data for dioxins in two Bay environmental compartments, fish and water, to evaluate the current level of impairment of commercial and sport fishing and potentially other beneficial uses of the Bay.

Regulatory Background

The federal Clean Water Act (CWA) provides protection to the surface waters of the United States. Section 101(a)(2) of the CWA 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 "impaired" water bodies that do not meet water quality standards and to develop total maximum daily loads (TMDLs) or other strategies for achieving the standards in impaired water bodies.

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.

Dioxins were not previously included on California's 303(d) list by the SWRCB or the RWQCB. The State declined to make the listing for several reasons.

- Water-column dioxins concentrations did not exceed water quality criteria.
- Concentrations of dioxins were within national background concentrations.
- The fish consumption advisory issued by the State and in effect from 1994 to 2011 was an interim advisory, which was not based on a quantitative risk assessment for dioxins and which mentioned dioxins only because of exceedances of screening values in a study of Bay fish tissue.

USEPA added dioxins ("dioxin-like compounds") to the 303(d) list in 1998, finding 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 the SWRCB had not adequately addressed available fish tissue data. USEPA also found that the issue of national background concentrations of dioxins and furans was not relevant to the question of whether to list the Bay.

USEPA used several studies to determine that the risk of dioxins in fish was a problem, including:

- California Toxics Rule Economic Analysis (USEPA, 1997)
- USEPA internal evaluation of fish tissue data in comparison to national guidance – The average concentration of dioxins toxic equivalents (TEQs) in fish tissue was about 1.6 pg/g (wet weight, ww). USEPA guidance indicates that three meals a month (1.5 pounds) of fish with TEQs of 2 pg/g results in cancer risk of 10^{-4}, which is 10-100 times greater than acceptable.
- Detailed USEPA internal reevaluation of fish data to examine quality assurance issues and relative importance of dioxins and furans compared to PCB risk – If values below detection limits are excluded from the analysis, dioxin-like PCBs constitute a 5-60 fold greater risk than dioxins and furans. However, average dioxins tissue residues significantly exceed a TEQ screening value of 0.14 pg/g.

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

Background

In calculating dioxins TEQs, the measured concentration of the chemical is multiplied by a toxic equivalency factor (TEF), the relative toxicity or potency of a dioxin-like compound compared to the most toxic dioxin compound, 2,3,7,8-tetrachlorodiobenzo-*p*-dioxin (2,3,7,8-TCDD). The TEFs used in this report were established by the World Health Organization (WHO, 2005). For dioxins and furans with concentrations less than the analytical detection limit, we used a concentration of zero for calculation of the dioxins TEQs.

Many other contaminants also have dioxin-like potency, most prominently PCBs. Specifically, several coplanar PCBs (especially PCB 126) have significant dioxin-like potency that results in PCB TEQs that usually exceed the dioxins TEQs. However, it was demonstrated that attainment of the TMDL target for PCB concentrations in fish (through a 90% reduction) would likely also result in attainment of the dioxin-like PCBs TEQ in fish. We have therefore excluded dioxin-like PCBs from this assessment.

In this report, we have evaluated the screening level for dioxins in fish tissue as follows:

$$\text{Equation 1:} \quad SVc = [(RL/CSF)*BW]/CR$$

where,

SVc = Screening value for a carcinogen in mg/kg
RL = Maximum acceptable risk level, 10^{-5} or one in 100,000 (USEPA, 2000a)
CSF = Oral cancer slope factor, central estimate is 156,000 mg/kg-day (USEPA, 2000b)
BW = Mean body weight of the population (70 kg)
CR = Fish consumption rate by all consumers based on a four-week recall, 32 g/day (2.14 lbs/mo)

The calculated screening value is 0.14 pg/g ww (parts per trillion) TEQ for the assessment of risk to human health due to dioxins. This screening value applies directly to the attainment of the commercial and sport fishing beneficial use.

We also calculated advisory tissue levels (ATLs, Table 2-1) using similar formulas as those for screening values, with a cooking reduction factor adjustment, and another for exposure duration (30 of 70 years), following the methods used by the California Office of

Environmental Health Hazard Assessment (Klasing and Brodberg, 2017). ATLs provide a number of recommended fish servings per week that correspond to the range of contaminant concentrations found in fish and are designed to prevent consumers from being exposed to more than the average daily reference dose for carcinogens like dioxins, to a risk level greater than $1x10^{-4}$ and $1x10^{-5}$ (not more than one additional cancer case in a population of 10,000 -100,000 people consuming fish at the given consumption rate over a lifetime). ATLs were calculated as follows:

Equation 2: $ATL = RL*BW / (CSF * CR * SPW * CRF * ED)$

where,

ATL = Screening value for a carcinogen in mg/kg
RL = Maximum acceptable risk level, 10^{-5} or 10^{-4}
BW = Mean body weight of the population (70 kg)
CSF = Oral cancer slope factor, central estimate is 156,000 mg/kg-day
CR = Daily consumption rate for one serving per week consumer (32 g/day)
SPW = Servings per week based on a four-week recall
CRF = Cooking Reduction Factor = 0.7
ED = Exposure duration factor, 30 of 70 years (0.43)

Table 2-1. Calculated Advisory Tissue Levels (TEQ pg/g)

Servings per week	ATL 10^{-4} Risk	ATL 10^{-5} Risk
1	4.7	0.47
2	2.3	0.23
3	1.6	0.16
4	1.2	0.12
5	0.9	0.09
6	0.8	0.08
7	0.7	0.07

There are no dioxins water quality criteria for the protection of aquatic life. There are dioxins standards for the protection of human health for water and organism consumption. The applicable standard to the Bay is for organism consumption, which is used to assess impairment to the sport fishery. The USEPA California Toxics Rule includes standards for the protection of human health for one dioxin compound, 2,3,7,8-TCDD. This compound has a TEF of 1.0, so can be used to assess total dioxins TEQs. The water quality criterion for organism consumption is 0.014 pg/L.

In 2004, USEPA published an updated compilation of nationally recommended water quality criteria (USEPA, 2004), including decreases in the criteria for dioxins to protect human health. These criteria have not been adopted by California, and are used here for comparison with water concentrations of dioxins TEQs. The new EPA water quality criterion for organism consumption is 0.0051 pg/L.

In 2010, the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) adopted a Revised Tentative Order (R2-2010-0054) modifying the method for calculating TEQs in abiotic

matrices (SFBRWQCB, 2010) by incorporating bioaccumulation equivalency factor (BEFs) to account for differences in uptake rates of dioxins congeners into tissue relative to 2,3,7,8-TCDD, in addition to the TEFs (relative to TCDD) derived for toxicity for concentrations within tissues. BEFs are applied only to abiotic matrices, so tissue TEQs are unaffected, but for some water or sediment samples where primarily HpCDD/Fs and OCDD/F are detected, calculated TEQs are reduced.

Current Impairment Status

Fish Tissue Dioxins

Overall, 125 of 138 tissue samples collected from 1994-2014 exceeded the screening level and the ATL for consumption of four servings/week at a 10^{-5} risk (0.12 pg/g). Only three tissue samples, all white croaker, exceeded the ATL for consumption of two servings/week at a 10^{-4} risk (2.3 pg/g).

For the rest of the discussion, we focus on the most studied fish species in the Bay, shiner perch and white croaker. These species have had the highest PCB concentrations, and therefore have been sampled most intensively.

In 1994, fish were collected throughout the Bay and analyzed for a suite of contaminants including dioxins (SFBRWQCB, 1995). All shiner perch and eight of nine whiter croaker samples collected had tissue dioxins concentrations exceeding the calculated screening level.

Dioxins concentrations exceeded the screening level of 0.14 pg/g in all 37 shiner surfperch samples analyzed (Figure 2-1), as well as the ATL for consumption of four servings/wk at a 10^{-5} risk (0.12 pg/g). None exceeded the ATL for consumption of two servings at a 10^{-4} risk (2.3 pg/g), but 23 exceeded the ATL for consumption of seven servings at the same risk level (0.7 pg/g). Furthermore, no trend in the dioxins concentrations were observed in the data when evaluated on a wet weight basis.

Dioxins concentrations exceeded the screening level in 79 of 81 white croaker samples analyzed, as well as the ATL for consumption of four servings at a 10^{-5} risk (Figure 2-1). Three of 81 exceeded the ATL for consumption of two servings at a 10^{-4} risk, but 63 exceeded the ATL for consumption of seven servings at the same risk level. Furthermore, no trend in the dioxins concentrations were observed in the data when evaluated on a wet weight basis.

Conclusion: Due to the overall exceedance of the screening level and various calculated ATLs, as well as the lack of decreasing tissue concentrations in shiner surfperch and white croaker, the above information does not warrant a change to the finding that dioxins impair beneficial uses of the Bay.

Water Dioxins Concentrations

We have limited our review of data for the impairment assessment to observations of total concentrations of dioxins in water samples collected in 2009 and 2011, the only available data. Nineteen of 34 samples exceeded the California Toxics Rule (CTR) water quality criterion (including BEFs in calculating TEQs), and all exceeded the new USEPA nationally-recommended water quality criterion. If method detection limit (MDL) values or half MDL values are substituted for non-detects, respectively 34 or 33 of the 34 samples would exceed the CTR criterion (including BEFs in calculating TEQs).

Conclusion: As with the available fish tissue dioxins data, due to exceedances of the CTR limits for the majority of water samples, the available information does not warrant a change to the finding that dioxins impair beneficial uses of the Bay.

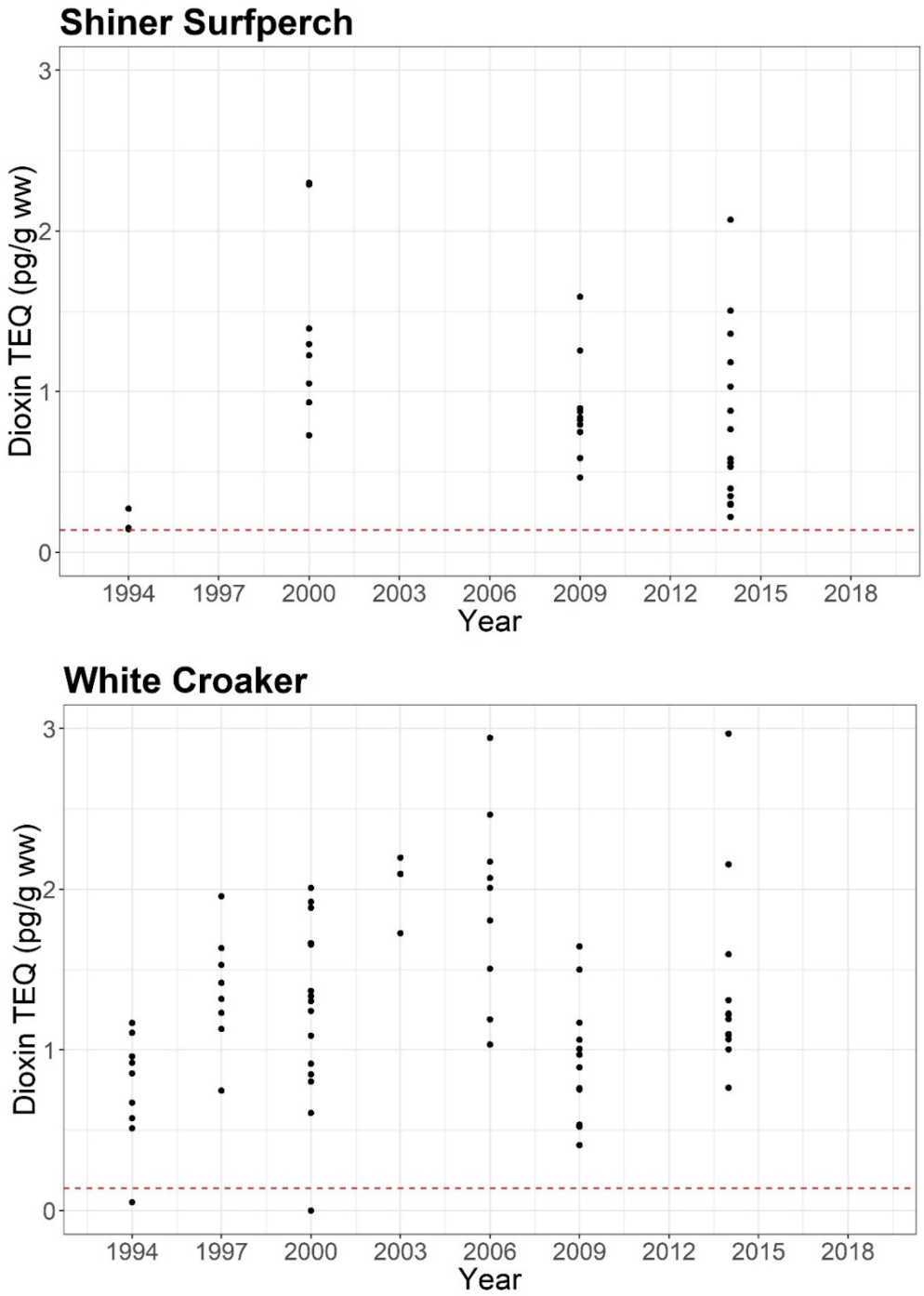

Figure 2-1. Scatterplots of shiner surfperch and white croaker dioxins concentrations (pg/g wet weight) by year. Each point represents a composite sample of 20 fish (shiner surfperch) or five fish (white croaker). Results are highly variable among sites and years, but nearly all are above the 0.14 pg/g ww screening level (red dotted line). Sample counts in 1994 are lower and may not be representative (particularly for shiner surfperch). White croaker samples in 2014 were mistakenly analyzed whole body without guts, and thus are not directly comparable to other years, which are reported for skin-on fillets. Beginning in 2009, white croaker concentrations are planned to be primarily reported by RMP as skin-off fillets, but results are shown here for skin-on fillets from the same fish for comparison to other years (given no prior years reported skin-off).

SECTION 3: CURRENT STATUS AND INVENTORY

Following the CMIA report in 2004, efforts were made to add to the existing data set by continuing to measure dioxins in tissue matrices, and particularly to add ambient measurements of dioxins in Bay sediment and water (downloadable via the CEDEN (California Environmental Data Exchange Network) or the SFEI data page, cd3.sfei.org), which were sparse at the time. This section of the report addresses management questions MQ2 and MQ3 about the degree and extent of dioxins contamination in these matrices.

MQ2. What is the spatial pattern of dioxins impairment?

Tissue monitoring

Since the 2004 CMIA report, fish tissues were collected from shiner surfperch (*Cymatogaster aggregata)* in 2009 and 2014, and in white croaker (*Genyonemus lineatus)* in 2006, 2009, and 2014. Samples were previously also collected from these species in 2000, along with jacksmelt (*Atherinopsis californiensis)* and striped bass (*Morone saxatilis*). The white croaker data prior to 2009 were analyzed as skin-on fillets, with 2009 samples analyzed from skin-on and skin-off fillets to compare these two preparation techniques. Samples after 2009 were intended to be reported primarily as skin-off fillets, but 2014 samples were mistakenly analyzed on whole body fish, without heads or guts.

One common challenge with dioxins analysis is low concentrations with frequent non-detects, especially for the congeners that also tend to have higher TEFs. Estimated total TEQs will therefore be possibly dependent on the frequency of detects versus non-detects for these congeners. However, for higher concentration samples, there is generally a moderately good correlation between TEQs and total dioxins mass, so patterns found in TEQs can generally be approximated by tracking or using the total mass as a proxy, at least within a given matrix. The ratio of TEQ to total dioxins concentrations will differ between matrices due to different partitioning and biological uptake characteristics of individual congeners, but within a matrix the ratios tend to be fairly stable, with more variability at lower total dioxins concentrations. In the RMP fish tissue data there was moderate correlation (R^2 = 0.865) for a linear regression between sum of TEQs and sum of dioxins concentrations (Figure 3-1), with a tendency for values to be underestimated in samples with low total dioxins, as would be expected with substitution of zero for non-detects. Substitution of half the detection limit for non-detects (NDs) minimally improved the correlation (R^2 = 0.867), while substitution of the full MDL reduced the correlation slightly (R^2 = 0.865). Similarly, the slope for half-MDL substitution resulted in a slope and y-intercept midway between the zero and full MDL substitution cases. This relationship is likely if the abundance of various congeners is similar among samples, such that the substitution only affects the lowest concentration samples, with results underestimated for NDs substituted as 0, or overestimated for NDs substituted as half or full MDL.

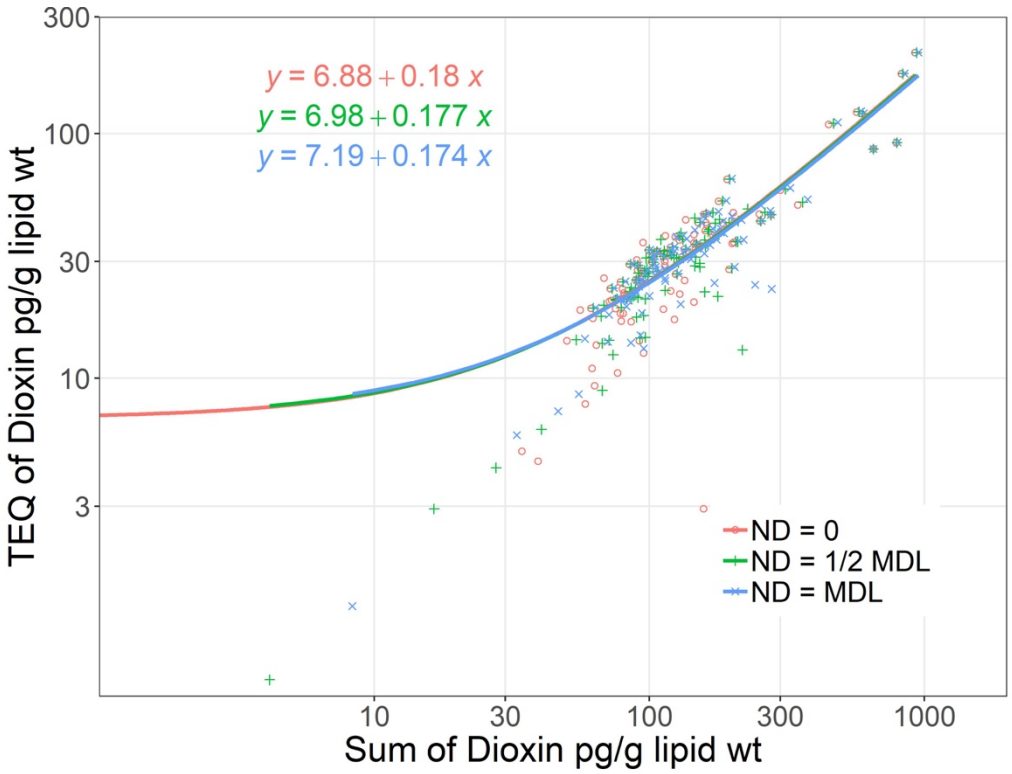

Figure 3-1. Linear regression between total dioxins concentrations and total dioxins TEQs in RMP fish tissue. Non-detect results are substituted with zero for sums of TEQs as well as total concentrations. These parameters are moderately well-correlated (R^2 = 0.66, $p < 0.001$), but TEQs are likely underestimated, particularly at lower concentrations, due to the RMP convention of substitution by zero for low concentration undetected congeners (often with high TEFs).

There appears to be a pattern of higher dioxins in fish tissue in more urbanized and industrialized sections of the Bay for some species (Figure 3-2). For shiner surfperch, higher concentrations were seen in Central Bay, near Oakland and San Francisco (Figure 3-2). There was no apparent temporal trend in Central or North Bay, with lipid-normalized shiner surfperch concentrations very similar in 2000, 2009, and 2014 (always insignificant, with $p > 0.2$, for both linear or geometric (log_{10}-transformed) regression of concentration against year, Table 3-1).

South Bay dioxins in shiner surfperch significantly declined, with an approximate two-fold decrease from 2000 to 2014. They showed significant declines for lipid normalized concentrations, for both linear and geometric regressions (both $p < 0.01$, Table 3-1).

Linear and geometric regressions on the lipid normalized shiner surfperch data combining all regions together showed a weaker, but still significant trend ($p < 0.05$). Given the relatively small sample size each year, a longer time interval, more samples, and a larger decrease would be desirable to increase certainty that this is a real and continuing decline across regions.

The most recent RMP report on sport fish contamination (Sun et al., 2017) also looked at shiner surfperch trends, but with some differences from the analysis here: samples were grouped only by year; statistical analysis used the Tukey Honestly Significant Difference test between year groups (rather than a regression across years). Similar to the analysis in this report, Sun et al. (2017) concluded that the wet weight and lipid weight shiner surfperch data suggested that TEQs of dioxins have declined since 2000 in some regions of the Bay, particularly in South Bay.

Table 3-1. Temporal trends in lipid normalized dioxins TEQs in biota. Geometric (log_{10}) and linear slopes are expressed as percent decline per year for the midpoints of the respective regressions. Decline slopes are only provided for regressions found to be significant ($p < 0.05$). NSD = no significant decline ($p \geq 0.05$)

Species	**Region**	**%/year (geometric)**	**%/year (linear)**
Shiner surfperch (body, no head, tail, gut)			
	Combined	4.8%	5.0%
	North Bay	NSD	NSD
	Central Bay	NSD	NSD
	South Bay	6.1%	5.6%
White croaker (skin-on fillet)			
	Combined	NSD	NSD
	North Bay	NSD	NSD
	Central Bay	NSD	NSD
	South Bay	4.5%	4.6%
Double-crested cormorant (eggs)			
	Combined	5.9%	6.2%
	North Bay	7.2%	6.8%
	North Central Bay	NSD	NSD
	South Bay	6.2%	6.5%

The white croaker samples analyzed as both skin-on and skin-off fillets in 2009 provided an opportunity to examine the influence of fish preparation on exposure to consumers. A pairwise comparison of skin-off and skin-on samples from the same fish, even after lipid normalization, indicates that they are significantly different sample populations (paired Wilcoxon test, $p < 0.0005$), with the lipid normalized skin-on concentrations always lower than skin-off. In contrast, the wet weight dioxins concentrations are higher in skin-on fillets. Thus skin-on and skin off results, even after lipid normalization, cannot be combined in any trend analyses.

For white croaker, concentrations were more similar among sampling locations than shiner surfperch, consistent with the more nomadic feeding and wider home range for this species that underlies the sampling strategy (white croaker are collected wherever they are encountered in the Bay and are considered to be one general Bay population). This outcome is also in line with tracking studies conducted in Southern California, where many individuals did not return to a 20 km^2 area detector array over the course of the study (Wolfe and Lowe, 2015).

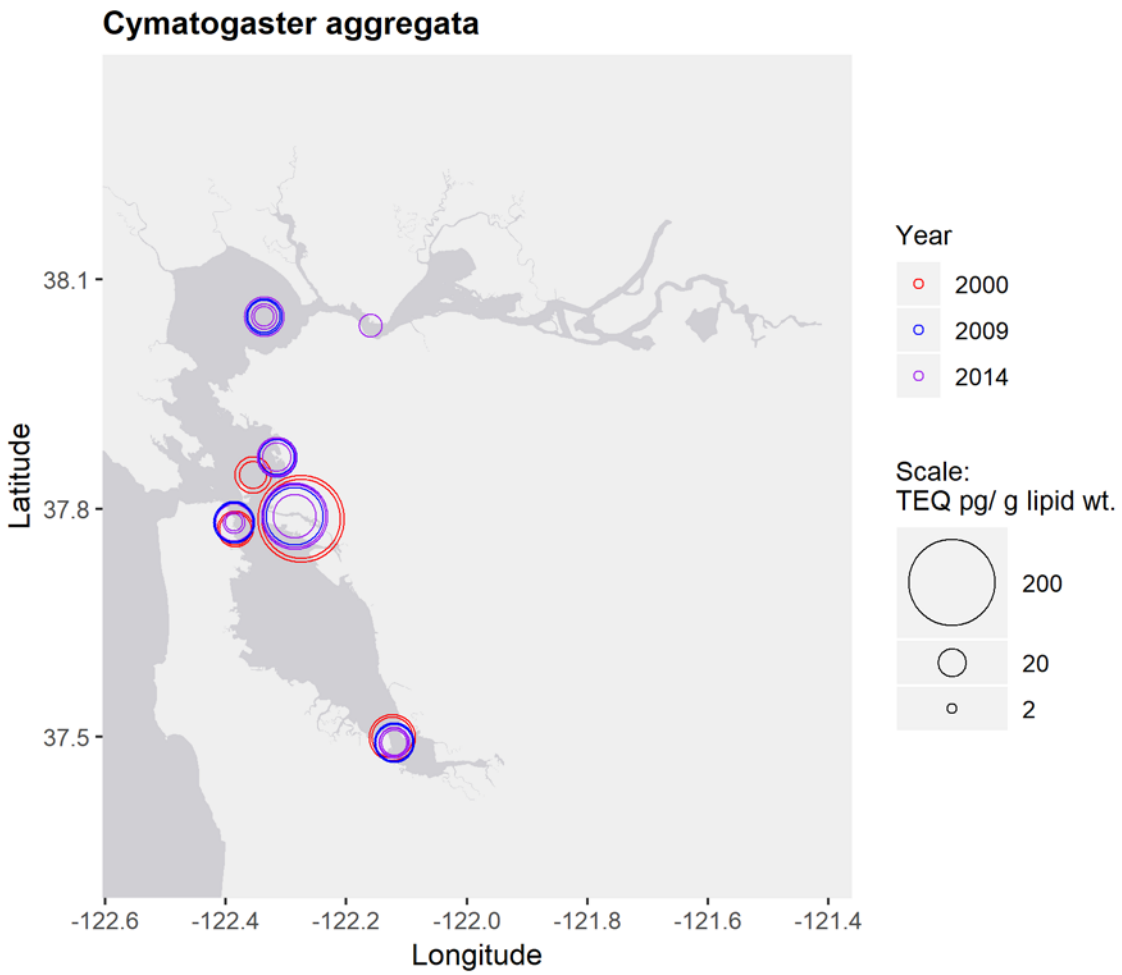

Figure 3-2. Shiner surfperch (*Cymatogaster aggregata*) lipid normalized dioxins TEQs (pg/g lipid weight) at locations around the Bay. Color indicates the year samples were collected at each site. Bubble area is proportional to concentration (legend indicates scale, e.g. the highest concentration is approximately 200 pg/g lipid weight).

Linear regressions by year for lipid normalized TEQs in Central and North Bay white croaker (excluding 1994 for insufficient counts, and 2014 because analyses were done on whole body as noted in the RMP Sport Fish Report (Sun et al., 2017)) showed no significant temporal trends, with $p > 0.7$ for both linear and geometric regressions against year. For South Bay, lipid normalized white croaker concentrations showed significant decline ($p < 0.015$), but unlike the case for shiner surfperch, the variations in Central and North Bay swamped out any signal and no significant decline was detected ($p > 0.3$) when all regions were considered together.

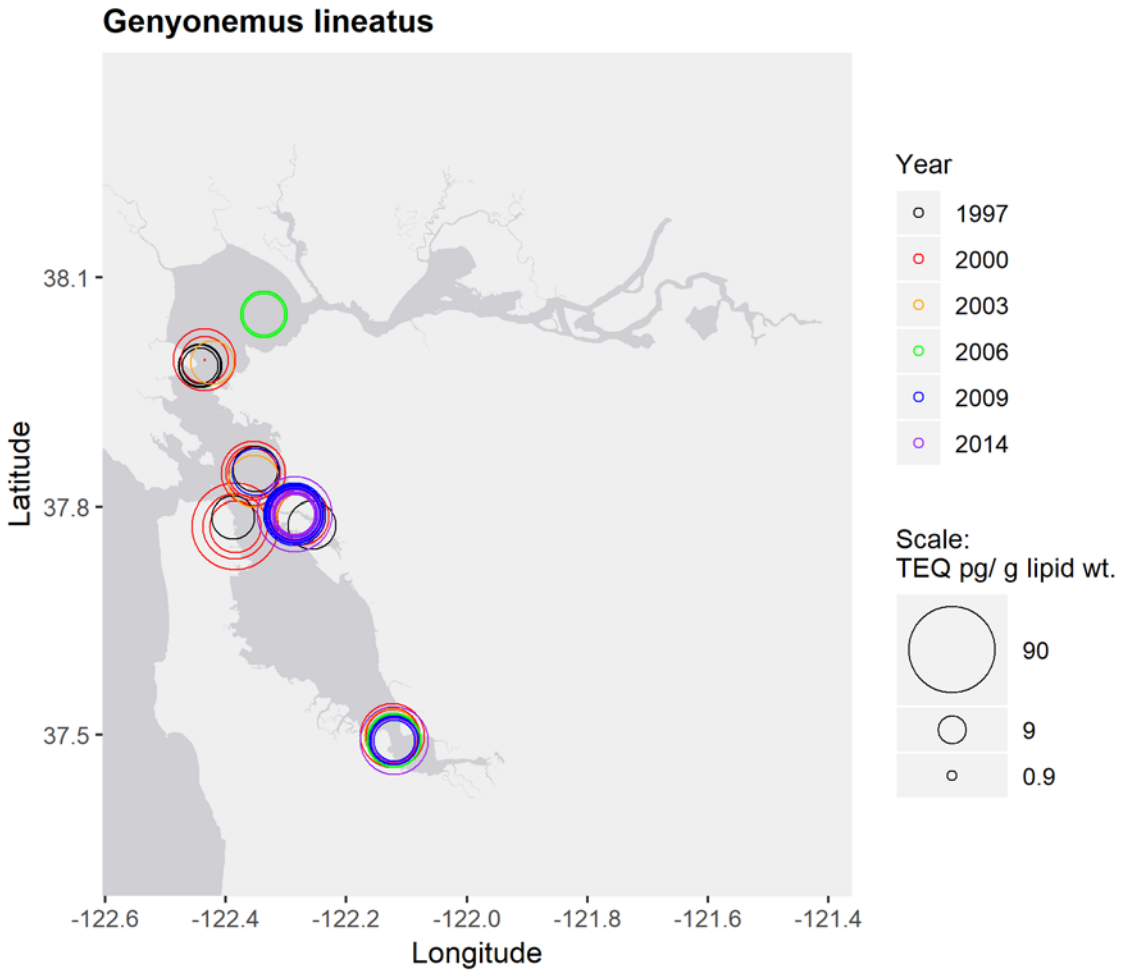

Figure 3-3. White croaker (Genyonemus lineatus) lipid normalized dioxins TEQs around the Bay. Color indicates the year samples were collected at each site. Data for 2009 and prior are shown for skin-on fillets. Data for future RMP sampling rounds will be skin-off fillets. 2014 samples were mistakenly analyzed whole-body. Bubble area is proportional to concentration (legend indicates scale, e.g., the highest concentration is approximately 90 pg/g lipid weight).

Jacksmelt *(Atherinopsis californiensis*) were only analyzed at one location and striped bass *(Morone saxatilis*) were not analyzed in enough events and locations to statistically test for any temporal trends. Similar to white croaker, striped bass showed no apparent spatial differences (Figure 3-4), as would be expected for a wide-ranging species accumulating dioxins from multiple areas.

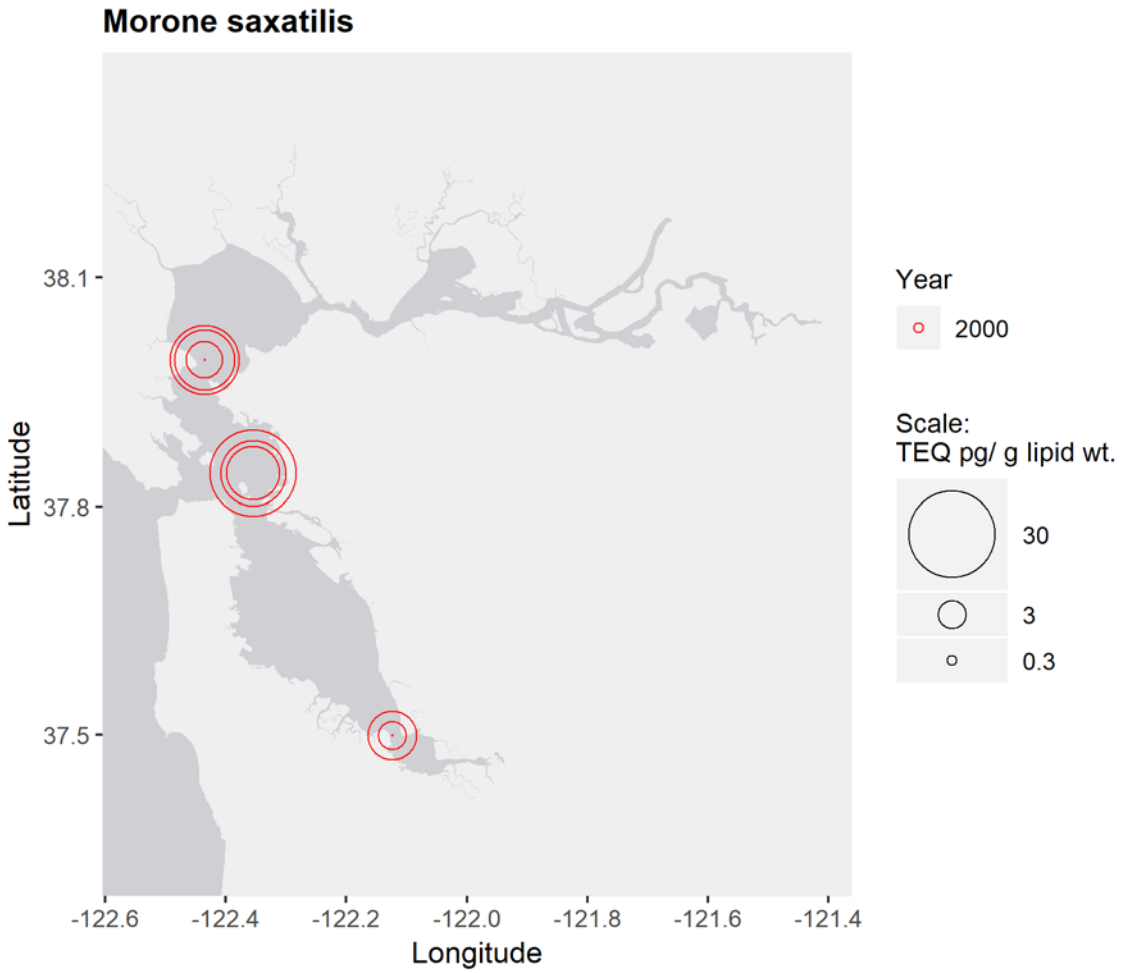

Figure 3-4. Striped bass (*Morone saxatilis*) dioxins TEQs around the Bay for samples collected in 2000. Bubble area is proportional to concentration (legend indicates scale, e.g., the highest concentration is approximately 30 pg/g lipid weight).

Double-crested cormorant *(Phalacrocorax auritus)* eggs were analyzed for dioxins by the RMP from three locations around the Bay in 2002, 2006, and 2012, with two of those locations also sampled in 2004 (Figure 3-5). Similar to the wider foraging fish species, there were no significant spatial differences in concentrations, whether considered on wet weight basis (this report) or lipid weight normalized, as in the RMP report on contaminants in cormorant and tern eggs (Ross et al., 2016). In some cases, there were analytical issues with dioxins congener results reported, so some samples only reported sums for furans.

For temporal trends, considering all sites together, lipid normalized dioxins TEQs showed significant decline ($p < 0.05$) for both linear and $\log_{10}$ (geometric) regression. The sampling areas in North Bay and South Bay each showed significant for both linear and $\log_{10}$ regressions, averaging around 6% to 7% per year. However, for the North Central Bay (Richmond Bridge) site considered alone, the trend in lipid normalized concentrations showed signs of decrease, but the results were not was not statistically significant for linear ($p = 0.05$) nor $\log_{10}$ ($p = 0.09$) regressions.

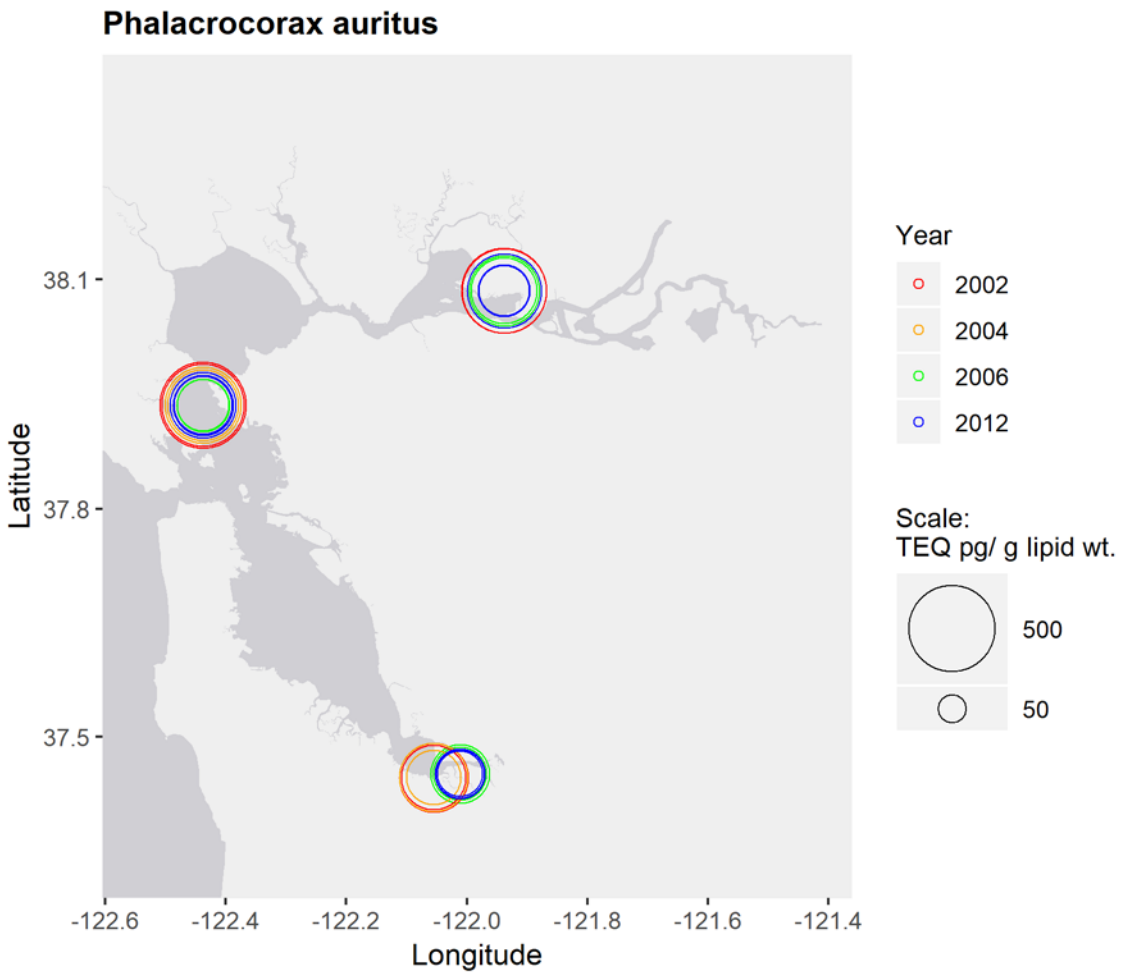

Figure 3-5. Double-crested cormorant *(Phalacrocorax auritus*) dioxins TEQs at locations around the Bay. Color indicates the year samples were collected at each site. Bubble area is proportional to concentration (legend indicates scale, e.g. the highest concentration is approximately 500 pg/g lipid weight).

The additional RMP tissue monitoring since the 2004 CMIA report has provided evidence of statistically significant decreasing trends in dioxins concentrations over time, at least for some locations. These results are in line with those in prior reports, which found significant trends using different groupings and metrics: in fish when all regions were considered together (Sun et al., 2017), or at all sites in cormorant eggs after lipid normalization (Ross et al., 2016). In contrast, there are no species or locations suggesting any upward trend in dioxins. The general qualitative consistency among these analyses suggests that there have been widespread modest to significant declines in dioxins bioaccumulation. The continuation of management efforts to date (mostly indirect, e.g., Bay Area Air Quality Management District (BAAQMD) bans on wood-burning devices in new homes and incentive rebates for conversion to natural gas fireplaces, primarily for reducing particulates, but likely lowering dioxins emissions too), and efforts by local municipalities to reduce PCB runoff (e.g., green stormwater infrastructure), which may also help reduce dioxins loads, combined with continued monitoring, should provide further progress and evidence of continued declines.

Sediment monitoring

RMP monitoring since 2005 has greatly increased the available data on ambient surface (0-5 cm) sediment dioxins concentrations in the Bay, with samples taken at RMP Status and Trend

sites in 2008, 2009, and 2010. The surface sediment samples were collected over too short of a period and integrate older sediment (5 cm represents approximately 20 years of accumulation, keeping up with 2-3 mm/year sea level rise) to be able to show any temporal trend. However, dioxins were also measured in sediment cores collected in 2005 and 2006 from select wetland and subtidal Bay locations, and deeper sections from those cores provide some data to characterize the inventory of dioxins mixed into or buried in sediments, as well as some evidence of past changes in dioxins loadings and concentrations.

Similar to the case for tissue samples, the sum of dioxins concentrations and the sum of dioxins TEQs is generally highly correlated (R^2=0.97) in RMP ambient sediment samples (Figure 3-6). Thus any patterns seen in sediment dioxins mass parallel those for sediment TEQs.

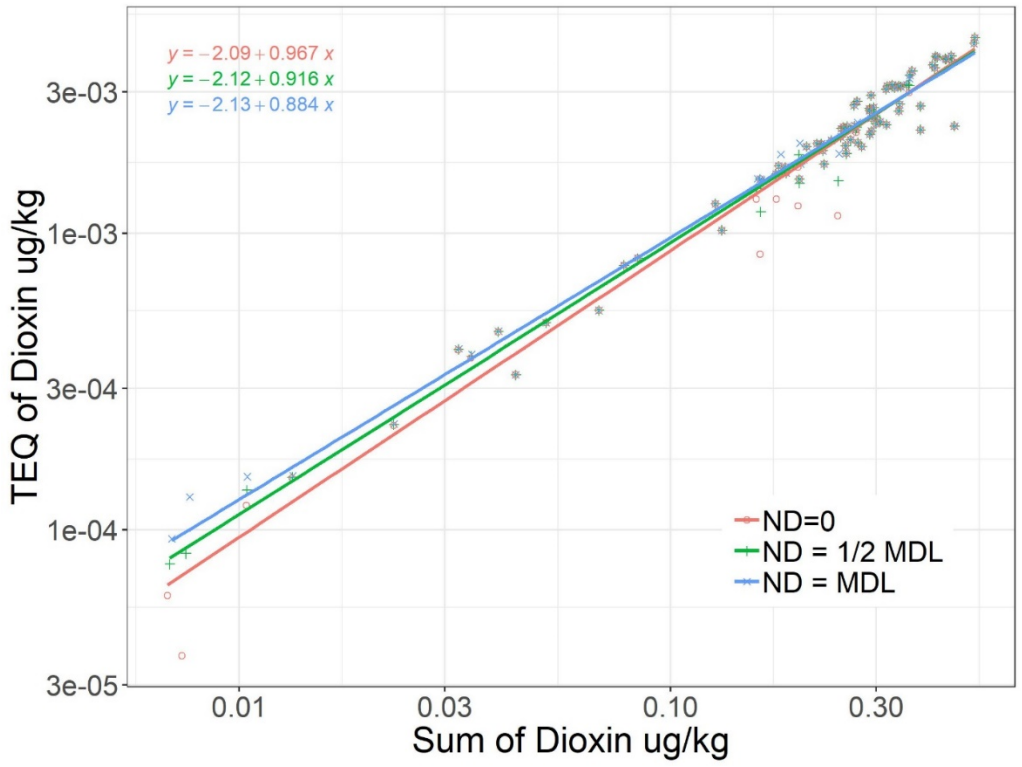

Figure 3-6. Correlation between RMP sediment sample sum of dioxins and furans TEQs with non-detects substituted as zero (TEQ of Dioxin, in ug/kg dw, ND=0) and sum of dioxins and furans concentrations (Sum of Dioxin, ug/kg dw, ND=0). Although shown on a log scale, the equations are for linear regressions between sums of TEQs and concentrations. These parameters are highly correlated (R^2 = 0.97, $p < 0.001$), but TEQs are likely underestimated, particularly at lower concentrations where congeners with high TEFs are frequently not detected.

Sediment dioxins TEQs for samples collected by the RMP show a general pattern similar to those for PCBs and other sediment-associated contaminants (Figure 3-7), with similar concentrations for most open water areas of the Bay, somewhat higher concentrations in Lower South Bay (LSB), and the highest concentrations in samples collected from sloughs, wetlands, and nearshore areas. Areas where higher concentrations were observed are closer to likely terrestrial sources and are in areas where contaminated fine sediments are more readily

retained. The median concentration of dioxins in LSB was nearly double those in other Bay segments, as shown in the empirical cumulative distribution function (ECDF) plot of RMP surface sediment concentrations (Figure 3-8). .

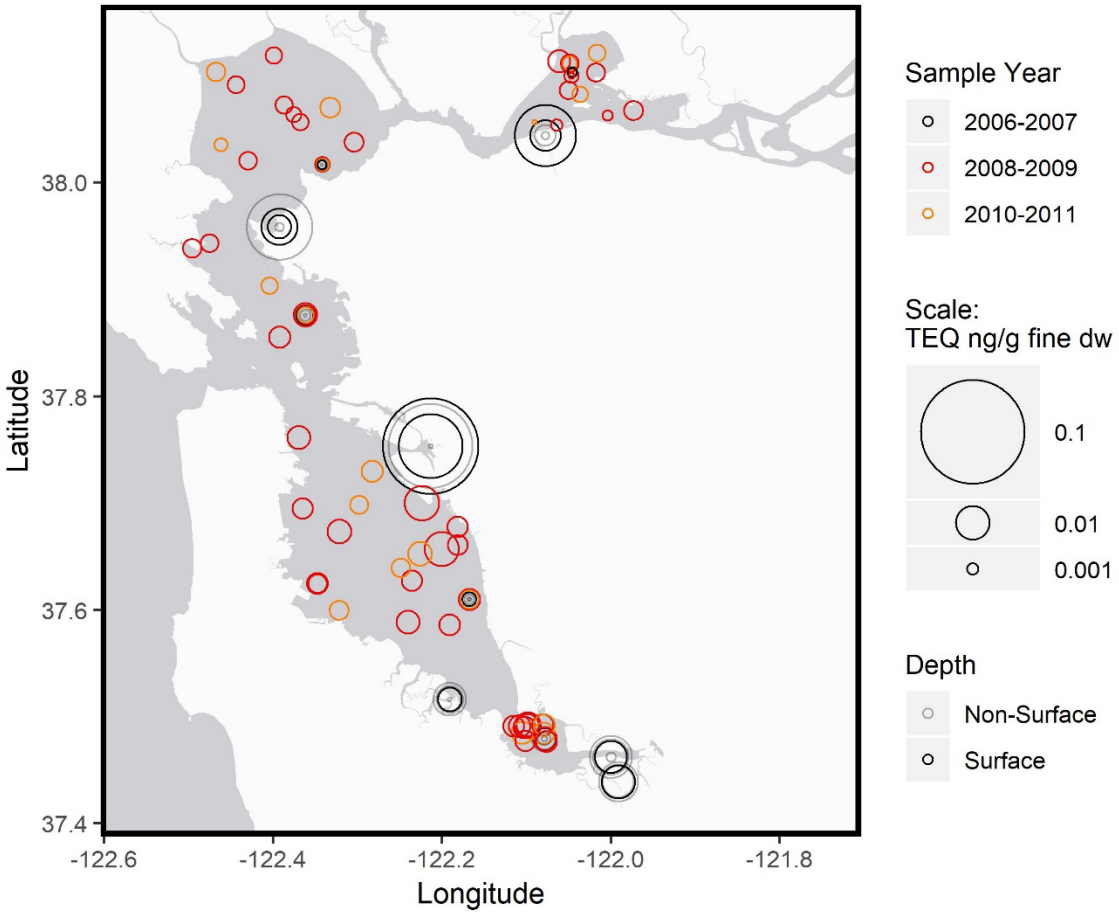

Figure 3-7. Dioxins TEQs normalized to fraction of fine sediments in surface and core samples collected by the RMP. Colors indicate the years samples were collected. Most results are surface samples (10 cm or less sediment depth), with deeper core sections shown in lighter shades at a given location. Bubble area is proportional to concentration (legend indicates scale; the highest TEQ is approximately 0.08 ng/g fine dw).

Coring sites in Figure 3-7 show concentric circles at a single point, with darker and lighter rings representing surface (up to 10 cm depth) and deeper core sections, respectively. At most wetland coring sites, the most contaminated sections are in the top 10 cm, representing about 40-50 years of sediment accumulation in most areas of the Bay (other than LSB, where sediment accumulation has kept up with subsidence of 1-2 m in the past century), consistent with an expectation that the largest dioxins loads occurred with industrial development in the period around World War II and later.

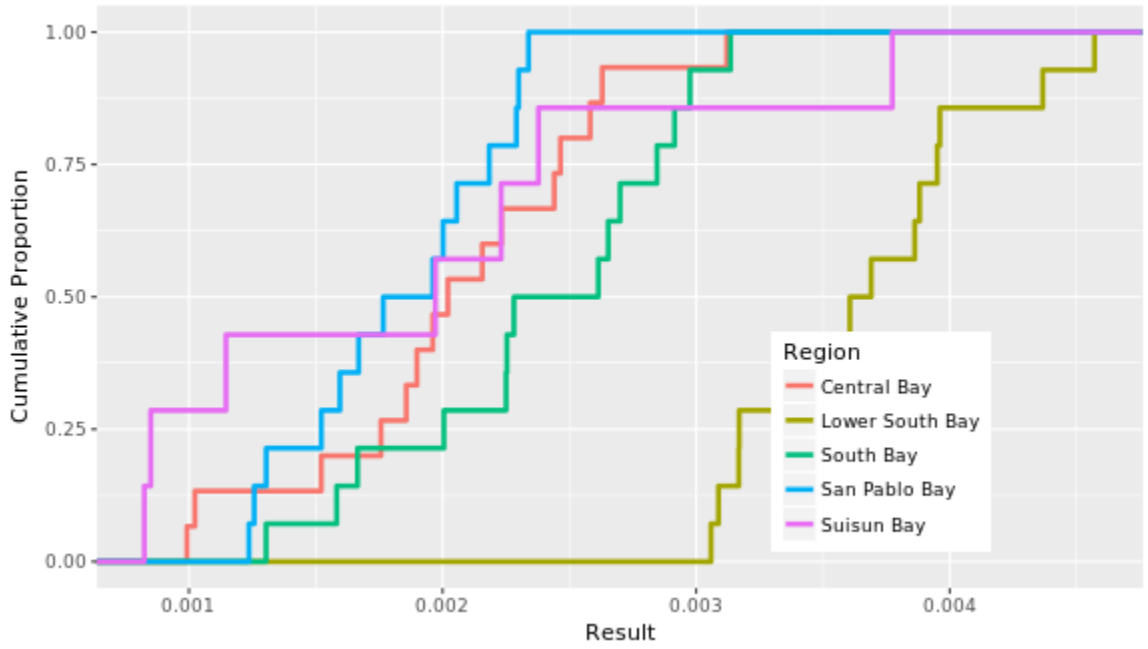

Figure 3-8. Empirical cumulative distribution function (ECDF) plot of RMP surface sediment dioxins TEQs (ug/kg dry weight, assuming ND=0). Concentrations were highest in Lower South Bay, where there is a high proportion of fine sediments and relatively poor flushing of sediment from likely terrestrial loading pathways.

An effort was also undertaken by the Dredged Material Management Office (DMMO) to assemble monitoring data on dioxins and other contaminants from recent dredging projects, downloadable via the DMMO website. This dataset includes locations within ports and marinas, areas not normally sampled for RMP Status and Trends. It should be noted that the DMMO database is not exhaustive, including only data from select recent projects, so attempts to discern the causes of high concentrations observed at specific sites (e.g., whether it is from ongoing loads or from older historic discharges in sites seldom dredged) are beyond the scope of information available from the DMMO database alone; data from older reports not in the database are likely needed for more comprehensive understanding.

The data from dredging projects generally represents samples collected and composited to greater sediment depths (often a meter or more) to inform disposal or reuse options, so results are not strictly comparable to those obtained for the top 5 cm sampled by the RMP. Despite these differences in the depths included, the DMMO results (Figure 3-9) are qualitatively similar to those from the RMP, with overall higher concentrations at nearshore sites, nearer likely terrestrial loading pathways, and experiencing less dilution and dispersion with cleaner sediments from the ocean and open Bay areas.

Appendix A contains the same DMMO data as shown in Figure 3-9, with an emphasis on identifying study sites that have had previously measured dioxins concentrations above 10 pg/g dw, without fines normalization. The DMMO bioaccumulation testing trigger threshold is 10 pg/g dw TEQ, so Figure A-1 (Appendix A) shows studies that have required such testing in one or more samples in the past. Table A-1 presents the same information (dioxins TEQs, not fines normalized) in tabular form to allow simple identification of specific samples that exceeded the trigger threshold.

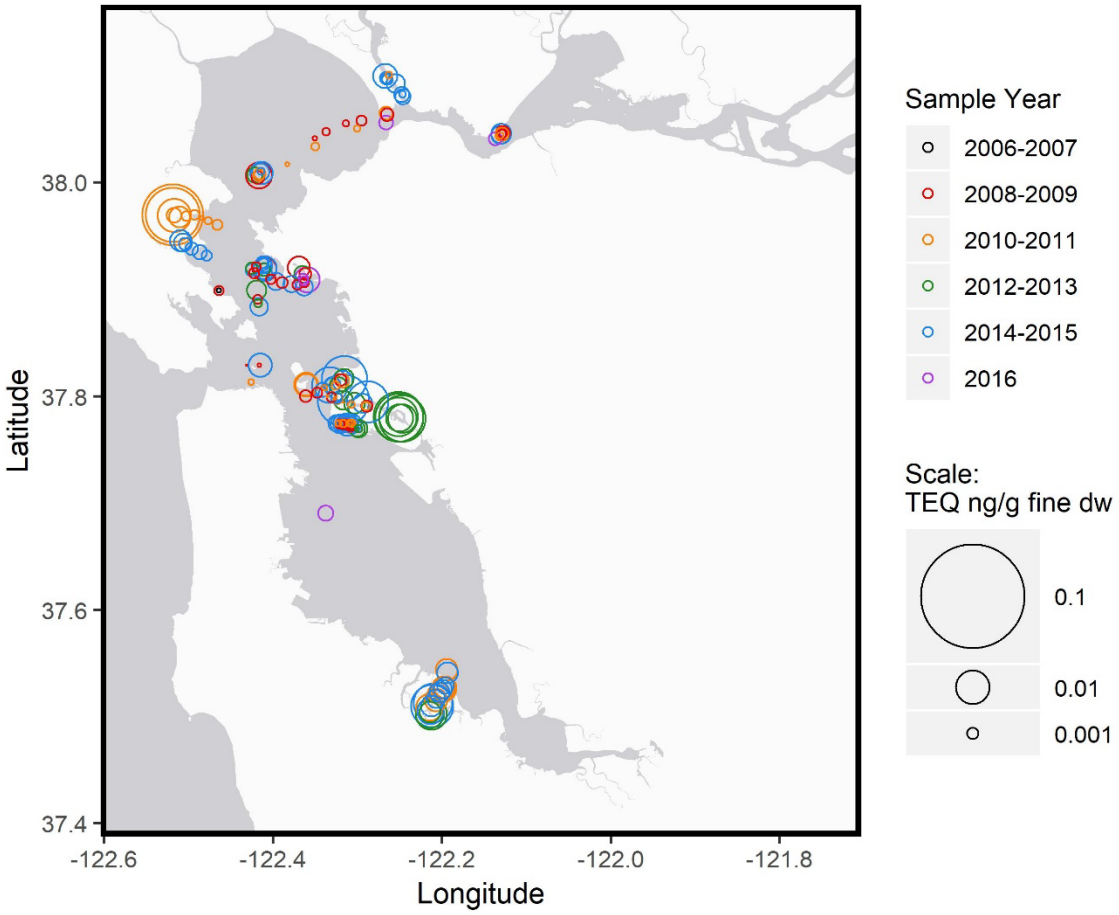

Figure 3-9. Dioxins TEQs normalized to fraction of fine sediments in samples collected by the DMMO. Colors indicate the year each sample was collected. Bubble area is proportional to concentration (legend indicates scale, e.g., the highest TEQ is approximately 0.03 ng/g fine dw).

The greater proportion of DMMO sites in nearshore areas and near highly developed industrialized sections of the Bay provide further evidence of localized sources or loading pathways that have been suggested by the few wetland cores collected under the RMP, so these data are useful in refinement of our conceptual model of dioxins sources and processes in the Bay. A plot of dioxins concentrations against distance to the nearest shoreline illustrates this spatial pattern (Figure 3-10). Concentrations in RMP ambient samples collected from open water areas of the Bay (distances up to approximately 7 km from shore) have similar concentrations, with dioxins TEQs normalized to the fine sediment fraction about 0.05 ng/g fine dw or less. Similarly, concentrations in the DMMO database for sites away from shore are also 0.05 ng/g dw or lower. However, samples collected less than 250 m from shore, are the only samples with fines-normalized TEQs well above 0.05 ng/g dw, even though there are still numerous sites with lower concentrations. The distribution of dioxins concentrations in the data from these studies collectively suggest dredging sites away from shore generally present a fairly uniform and lower risk, similar to the RMP ambient data. Some optimization of efforts in dioxins monitoring could be developed given these patterns. For example, sites away from the shoreline could be assumed to be near ambient conditions and monitored less frequently than sites near the shore where higher concentrations are more likely to be found.

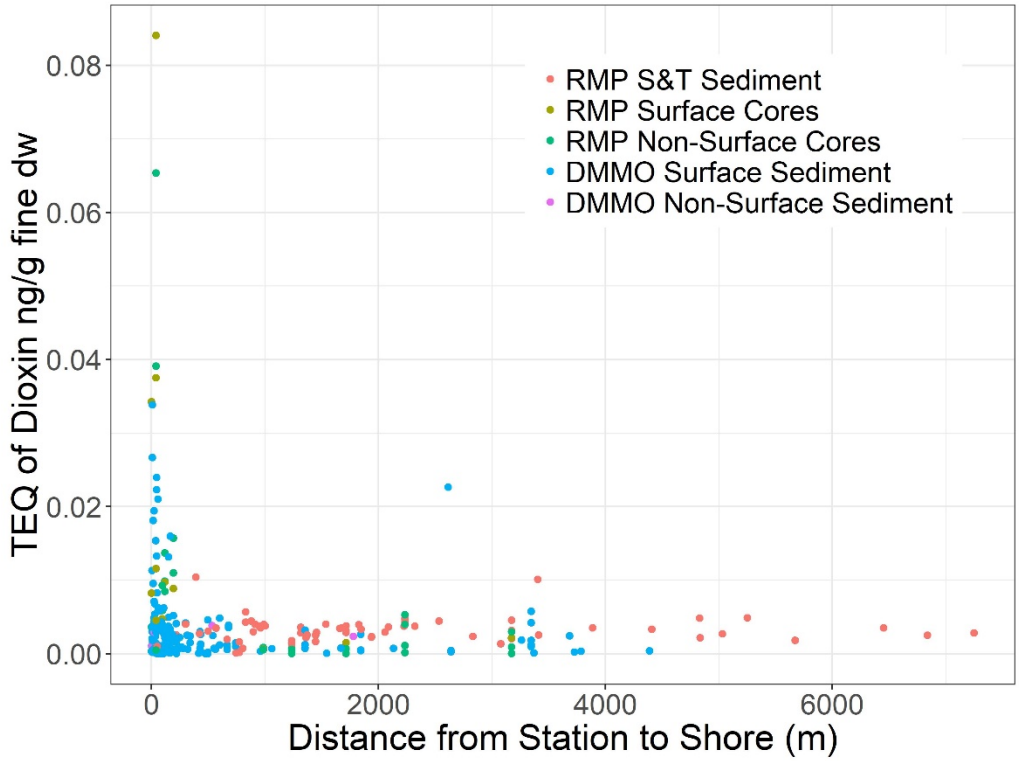

Figure 3-10. Sum of dioxins TEQs (ug/kg dw) normalized to fine sediment fraction versus distance to nearest shore (m). The distribution of concentrations, with the highest concentrations occurring only in sites near shore (<250 m) suggest a large influence from nearby terrestrial loading pathways and reduced transport and dispersion.

Water monitoring

Monitoring of dioxins in water was conducted at RMP Status and Trends sites in 2009 and 2011 (Figure 3-11), greatly increasing the dataset of Bay water column concentrations, which had previously consisted of a few samples at three fixed sites monitored in 2002-2003 to characterize the less-monitored California Toxics Rule pollutants (Yee 2003). The majority of all samples were analyzed only for whole water (total fraction) concentrations, but the few sites analyzed in 2009 and 2011 for separate dissolved and particulate fractions showed dioxins primarily (80% or more) contained in the particulate fraction. The handling of non-detects for water samples affects reported concentrations to a greater extent than for other matrices due to the higher proportion of non-detects. If undetected congeners in water are assumed to be at half MDL or MDL, even factoring in BEFs, summed TEQs would exceed water quality criteria in 33 or 34 of 34 samples.

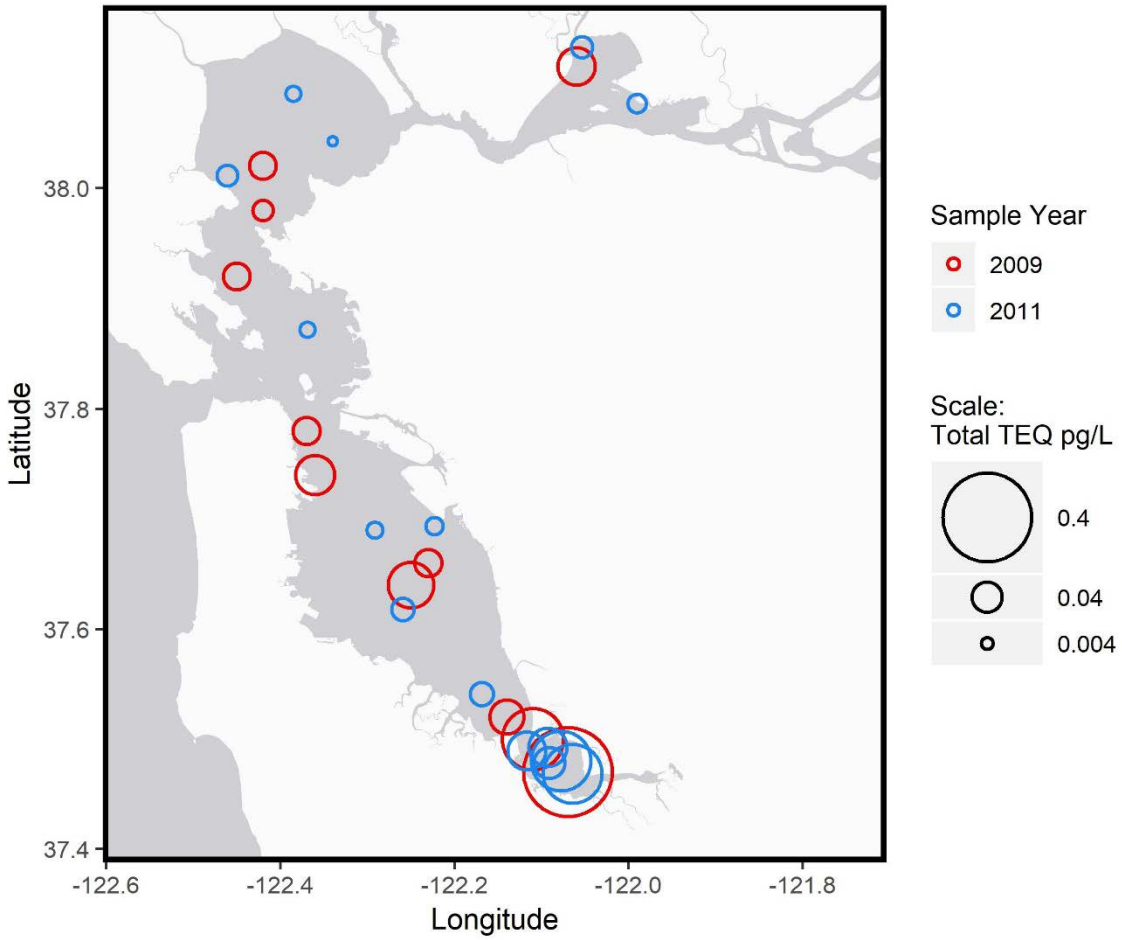

Figure 3-11. Dioxins TEQs in surface water (~1m depth) collected by the RMP in units of pg/L. Results are for total fraction samples (dissolved and particulate analyzed together, or analyzed separately and added). Colors indicate the year each sample was collected. Bubble area is proportional to concentration (legend indicates scale, e.g., the highest concentration is ~0.4 pg/L).

Water concentrations showed more variation than surface sediment concentrations, in large part due to variations in suspended sediment among different locations and sampling events. A comparison of whole water dioxins against suspended sediment concentration (Figure 3-12) showed a fairly strong correlation (Spearman's rho = 0.86, $p < 0.001$), suggesting dioxins in the water column are largely partitioned to suspended sediment. For samples with SSC < 150 mg/L, the relationship is nearly linear, with a significant correlation ($R^2 = 0.84$, $p < 0.001$) and a slope of 0.28 pg dioxins/mg SSC, which is roughly in the same range as ambient sediment concentrations, often around 0.2 to 0.3 ng/g dw for open Bay sites. The dioxins to SSC relationship shows some curvature, suggesting dilution or mixing with cleaner sediment sources at the highest SSC values.

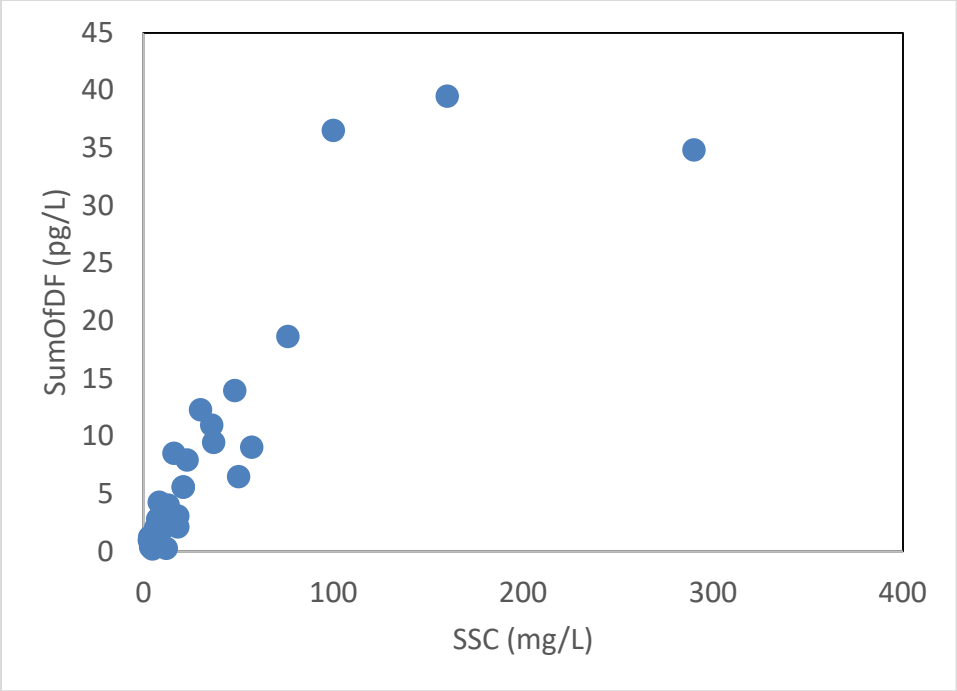

Figure 3-12. Plot of dioxins (Sum of DF) versus suspended sediment concentration (SSC) in RMP surface water. Total water dioxins and SSC were significantly correlated (Spearman's test, rho=0.86, $p < 0.001$), indicating strong association of dioxins with the particulate phase; for SSC < 150 mg/L the ratios of PCDD/Fs to SSC are similar to ambient sediment concentrations.

Correlation to PCBs

Although the primary sources of dioxins are not related to PCB use or disposal, both groups of compounds are anthropogenic, persistent, bioaccumulative, and toxic hydrophobic organic compounds with urban and industrial sources, so similarities in sources and environmental behavior may allow some degree of co-management. As an illustration of this, the sum of dioxins concentrations are plotted against the sum of PCBs (for the RMP 40 congeners) for RMP ambient sediment data (Figure 3-13). There is a noisy but very significant correlation (R^2= 0.29, $p < 0.001$) between the two groups. The regression slope indicates dioxins concentrations averaging 2% of those for PCBs. Analysis of Aroclor 1254 mixtures found only 0.0011-0.0039% PCDD/Fs (Kodvanti et al., 2001), so PCB mixtures are likely not a major source of dioxins found. However, given their co-occurrence in many sediments, some measures taken to reduce loads of sediment sources containing PCBs, such as greater implementation of urban "green infrastructure" may have some co-benefit in reducing dioxins loads.

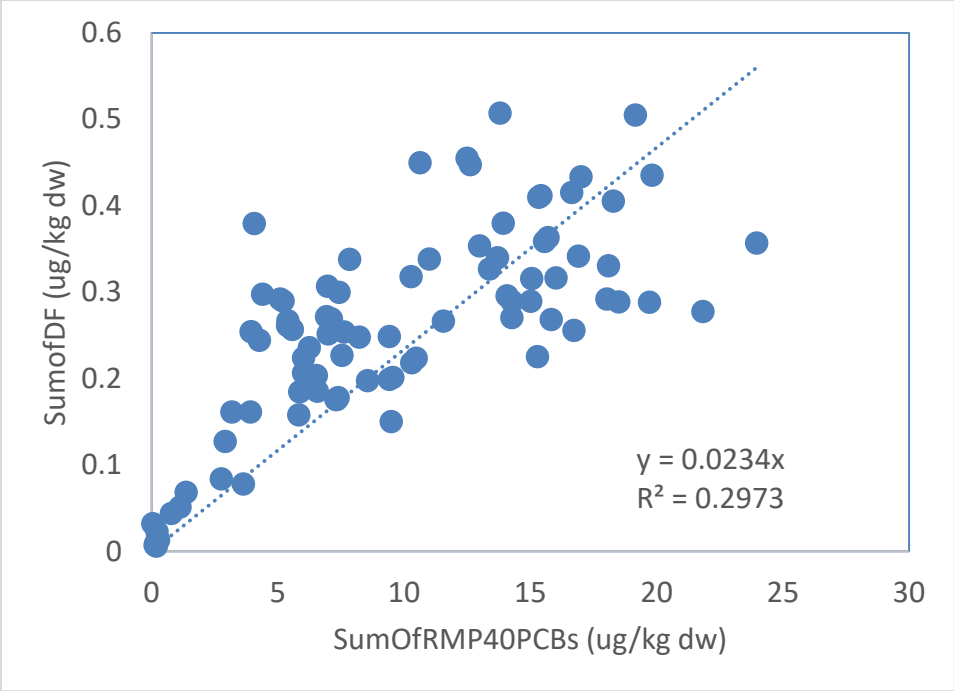

Figure 3-13. Linear regression of dioxins (Sum of DF congeners) to PCB (Sum of RMP 40 PCBs) concentrations in RMP ambient surface sediments. Total sediment dioxins and PCBs were significantly ($p < 0.001$) correlated.

MQ3. What is the dioxins reservoir in Bay sediments and water?

The persistence of dioxins in the environment means that past releases may present or contribute to current or future exposure. This section of the report addresses the management question regarding the remaining dioxins inventory in the environment.

Open Bay water and sediment dioxins inventories

The similarity between ambient surface sediment dioxins concentrations and ratios of dioxins to suspended sediment mass in the water column suggests that the previous mass budget conceptual model, with sediment and water column dioxins exchanging in a pseudo-steady state, is a reasonably simplified approximation of transport and fate processes. Wetland cores collected in 2005-2006 (Yee et al. 2011) and later analyzed for dioxins showed a gradient in dioxins concentrations (Figure 3-14), with higher concentrations in subsurface sections. However, subtidal Bay sediment cores often had dioxins more uniformly distributed in the top 20 cm (Figure 3-15), aside from lower concentrations in deep pre-industrial layers. The near surface core sections were often similar to or at slightly lower concentrations than averages from nearby RMP Status and Trends monitoring stations (small x marks in the figure). Thus the previous conceptual model of a fairly well-mixed “active” surface sediment layer is apparent in many subtidal cores. This deep mixing may prolong the time to recovery of the Bay from dioxins contamination, as existing contaminated sediments can be mixed to the surface and continue to affect biota until buried below a zone of biological activity.

The more recent monitoring under the RMP Dioxins Strategy has greatly increased the amount of available data on surface sediment and water dioxins concentrations. The area-weighted mean ambient sediment sum of dioxins congeners concentration from RMP sites is 0.25 ug/kg dw, with a median concentration of 0.26 ug/kg dw (Table 3-2). Corresponding mean and median

sums of TEQs (substituting zero for NDs) are both 0.0021 ug/kg dw respectively. These results (2008-2011 data plotted in Figure 3-7) are roughly in line with values used for estimating sediment inventories in the 2004 CMIA using USEPA Environmental Monitoring and Assessment Program dioxins data, with median concentrations of around 0.3 ug/kg dw for the sum of dioxins congeners. Using the same assumptions as in the previous CMIA for the Bay surface area, mixed layer depth, and bulk sediment density, the resultant dioxins inventory in the top 15 cm of subtidal sediment using the mean concentration in open Bay sediments is approximately 22 kg, equivalent to an inventory for sum of TEQs of 0.17 kg.

The area-weighted mean water concentration for the sum of dioxins congeners is 3.4 pg/L, with a median of 2.8 pg/L, yielding a total dioxins inventory using the mean in the water column of about 0.015 kg. Similar to the case for sediments, the sums of TEQs are about two orders of magnitude lower, with a mean of 0.029 pg/L and a median of 0.019 pg/L, equivalent to a water inventory of about 0.00011 kg TEQ using the mean Bay concentration and total Bay volume. Given the small mass in the water column relative to the inventory in the sediment (the latter six orders of magnitude larger), export via tidal advection will only slowly decrease ambient sediment concentrations, even without new loads being added to the Bay.

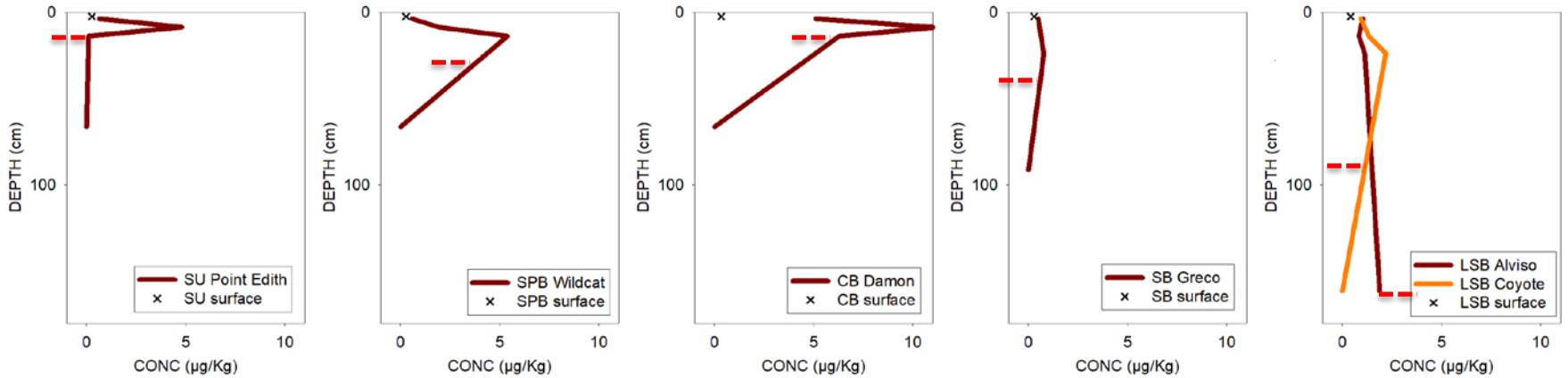

Figure 3-14. Depth profiles of dioxins in wetland sediment cores. Short red dotted line indicates maximum depth of detected ^{137}Cs (1950s). In wetland cores, surface concentrations have decreased from past peaks (~1970s, midway to the surface from 1950s impacted sections).

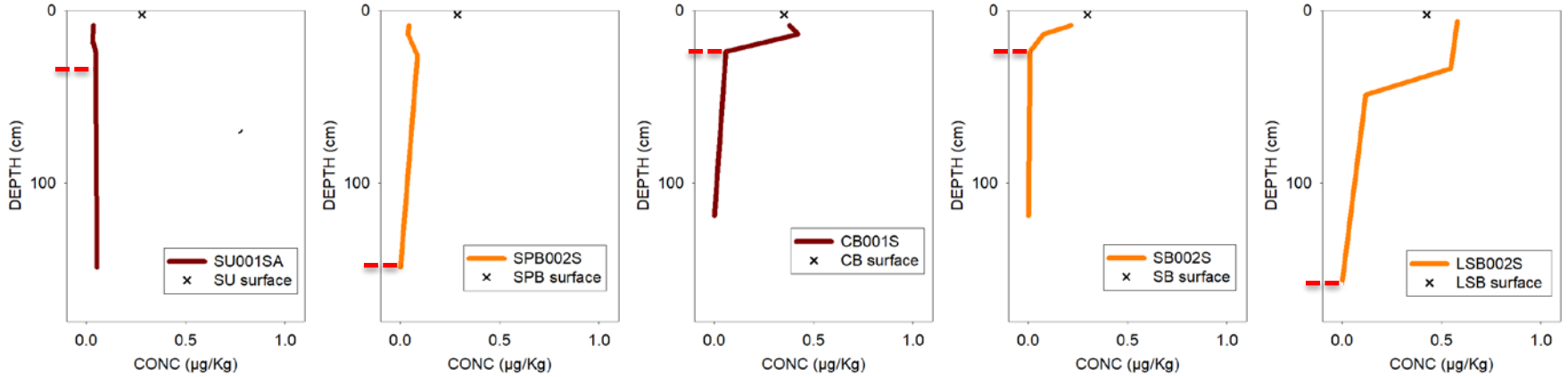

Figure 3-15. Depth profiles of dioxins in subtidal bay sediment cores. Short red dotted line indicates maximum depth of detected ^{137}Cs (1950s). In subtidal cores (note lower scale), surface concentrations are often similar to or higher than sections from ~1970s, suggesting mixing and dilution of continued inputs and/or redistribution from more contaminated nearshore areas.

Table 3-2. Mean and median dioxins sum of congener and sum of TEQ concentrations for RMP data.

	Count	Mean Sum DF	Median Sum DF	Mean TEQ DF	Median TEQ DF
Sediment (ug/kg dw)	89	0.25	0.26	0.0021	0.0021
Water (pg/L)	37	3.4	2.8	0.029	0.019

Port and marina dioxins inventories

The distribution of dioxins based on the DMMO data suggests that sediment in ports and marinas and other nearshore areas (< 250 m from the nearest shoreline) represent a different stratum from the open Bay samples collected by the RMP. Using GIS, we estimated the total area of the port and marina areas to be approximately 21 km^2. This total area collectively is larger than the open water area of LSB. Although many of the smaller ports and marinas are for pleasure boats, which are not likely large sources of dioxins and other industrial chemicals or by-products, over half of these locations are adjacent to former military facilities or urbanized areas that are or were industrialized in the period around World War II and later. When we consider these port and marina areas separately from the other sites in the DMMO database, mean and median dioxins concentrations were generally higher for the port areas versus outside of those areas (Table 3-3).

Similarly, near-shore areas in the DMMO database showed higher median and mean concentrations than open Bay areas (over 4x difference in means, 2x in medians), even relatively stronger than differences for port versus non-port areas. This suggests that much of the dioxins gradient is from terrestrial sources or loading pathways to near-shore environments, not necessarily due to sources inside of ports from maritime traffic. However, the relatively enclosed nature of many port areas helps ensure that many of the contaminants they receive are less readily dispersed.

An estimate of dioxins mass in port and marina areas (assuming a similar 15 cm mixed depth as in the open Bay) using the mean dioxins and TEQ values in the DMMO data yields an inventory of 1.3 kg dioxins and 0.0058 kg TEQ, about 6% and 3% of the overall Bay inventories, respectively. Although these masses do not represent a very large addition to the Bay dioxins inventory overall, it suggests that these port and nearshore areas, accounting for only 2% of the subtidal Bay, are disproportionately impacted by contamination. Similar to the conceptual model for PCBs, there may be opportunities for more focused management through discouragement of consumption of fish from these highly impacted areas and focus on reductions of incoming loads. Recovery may be slow given the legacy of contaminants already released and the enclosed nature of many of these locations, but without load reduction, recovery will likely take even longer.

Table 3-3. Mean and median sum of dioxins congener and sum of TEQ concentrations for DMMO data for areas inside of ports and marinas versus outside, and near-shore (< 250 m) versus more distant areas. Areas in ports and marinas, or near-shore, had higher average and median dioxins concentrations.

Location	Count	Mean Sum DF	Med Sum DF	Mean TEQ DF	Med TEQ DF
Non-Port	143	0.41	0.21	0.0021	0.0010
Port	58	0.81	0.31	0.0037	0.0019
Non-Shore	67	0.16	0.12	0.00084	0.00046
Shore (< 250 m)	134	0.71	0.28	0.0034	0.0018

SECTION 4: CURRENT SOURCES AND EXPECTED TRENDS

In addition to the current inventory of dioxins discussed in the previous section, understanding the ongoing and likely future inputs are critical to evaluating the expected trends and potential management of a pollutant, highlighted in this management question from the RMP Dioxins Strategy.

MQ5. What is the relative contribution of each loading pathway as a source of dioxins impairment in the Bay?

Point source emissions from facilities such as incinerators and smelters were previously thought to be the largest sources of dioxins, but few such sources remain in Northern California. Smaller dispersed sources such as yard burning and vehicle emissions, remaining at levels more similar to those in the past, were expected to exceed those from point sources nationally (Peek et al. 2002), so a similar trend is expected locally given disappearance of many of the large point sources.

Regardless of their original (“true”) sources, dioxins are expected to enter San Francisco Bay through relatively few pathways:

- municipal and industrial point discharges;
- water flows from the Central Valley and other local watersheds;
- direct atmospheric deposition; and
- exchange with buried sediment.

In the previous CMIA, a simple mass budget model considered sediment exchange in a single well-mixed box, which appears to be a reasonable approximation for the open Bay, based on the similarity in sediment concentrations in most Bay segments in RMP Status and Trends monitoring, as well as their similarity to DMMO data from open-water areas. However, based on the near-shore concentration gradients seen in the DMMO data and the few wetland cores taken for the RMP, it may be more appropriate to treat the dioxins inventory in ports and other near-shore areas as a more discrete compartment, rather than assuming it is well-mixed and rapidly exchanged with open Bay sediment. The presence and persistence of the near-shore gradient itself illustrates that sediments in these compartments are not rapidly interchanged, and/or that there are ongoing sources. Ongoing loads may input sediments that are more contaminated than current concentrations in the open Bay, but less contaminated than

sediments already captured in near-shore areas. The decreases in concentration from past peaks in many wetland cores suggest that the inputs to the near-shore areas have already decreased somewhat, and also that older contaminated sediments have not been completely mixed or exported out of many such near-shore locations. Continued resuspension and exchange of more-contaminated near-shore sediments with less-contaminated sediments from the adjacent open waters would result in net export of dioxins to the open Bay.

Thus exchange with near-shore areas might be better modeled as external dioxins loads, similar to stormwater and wastewater inputs. Although rough bounds of exports from these margin, marina, and port areas might be explored (e.g., 10% of inventory exported per year is likely too high, as that would suggest half-lives of less than a decade for these inventories and the gradients should largely disappear. Conversely, 0.1% exported annually would maintain gradients but contribute negligibly to the overall Bay mass loading budget), such exercises would be largely speculative. As mechanistic models of hydrologic and sediment processes improve, it may be possible to more explicitly model these exchange and transport processes, but this is beyond the scope of our current capabilities.

Table 4-1. Loading pathways and inventories of dioxins for all of San Francisco Bay: Estimated g TEQ/year loads, and open Bay water column and sediment (top 15 cm) inventories (from Gervason and Tang 1998, Connor et al., 2004, Allen and Yee 2012, and this report).

Loads (g TEQ/year)	Gervason and Tang 1998	Connor et al. 2004	Allen and Yee 2012
Local Watersheds	5.1	5.1	8.9
Delta Watershed		0.88	3.4
Atmospheric Deposition	1.2	1.2	16.7
POTW Effluent	0.13	0.67	0.67
Refinery Effluent	0.004	0.019	0.019
Other Effluent		0.019	0.019
Total	6.4	7.9	30
Inventories (g TEQ)		Connor et al. 2004	This report
Water		0.23	0.11
Sediment		160	170

Watershed Sources

Inputs of dioxins from watersheds (both local watersheds and the Delta), including stormwater were though to represent the largest loads to the Bay (Connor et al., 2004). However, atmospheric deposition is currently thought to be the largest pathway (Allen and Yee, 2012) of dioxins (Table 4-1). There is considerable uncertainty in loading estimates for both pathways.

Estimates of loading for local watersheds and the Delta have increased since the 2004 CMIA report, with more samples collected at a number of watersheds (Gilbreath and,McKee, 2015, McKee et al., 2017) to reduce the data gap previously identified. This increase in estimated loads is not due to an increase in actual sources and loads, but rather largely due to the insufficient representativeness of the data in previous studies used to estimate regional loads.

Uncertainty in runoff loads arises because discharges from watersheds and storm drains are temporally and spatially heterogeneous. Calculations of “average” loads are thus highly dependent on the locations and period sampled.

Although there may be individual sites of dioxins contamination within each watershed that could be remediated, it is likely that the majority of contamination is widespread from atmospheric deposition to the watershed and lower level legacy contamination distributed throughout the surrounding region. The significant correlation between dioxins and PCB concentrations in RMP sediment samples suggests that they may share similar source areas and/or transport and fate processes (e.g., slow degradation, preferential partitioning to solids), so some management actions taken for PCBs, such as wider implementation of green infrastructure, may be beneficial for dioxins. Individual storm drains or smaller tributary loads might be captured or treated in some cases if particularly contaminated areas are identified. However, removal of PCBs in building materials and other actions taken to remove specific PCB original or “true” sources will have more limited benefit for dioxins, given the low content of dioxins in PCB technical mixtures.

Atmospheric deposition

Atmospheric deposition behaves as a non-point source on a watershed scale and is difficult to measure directly, so estimates are generally derived from total air concentrations combined with particle size distributions and modeled settling and diffusion rates. A collaborative project by the BAAQMD, the California Air Resources Board, and USEPA (California Ambient Dioxins Air Monitoring Program (CADAMP)) that monitored urban sites around the Bay for five years (2002-2006) provided the data for our most recently revised atmospheric deposition estimates (Allen and Yee 2012). The new estimates were about ten-fold higher than estimates used in the 2004 CMIA and 1998 SFBRWQCB staff reports, which used no local data to estimate deposition. Similar to the case for watershed loads, the higher atmospheric deposition relative to past estimates is not due to an increase in actual sources and loads, but due to the insufficient representativeness of the data used in previous estimates. Given the disappearance of various local point sources, past load estimates likely should have been yet higher than current new estimates.

There were some concerns raised about the potential for additional dioxins inputs into the Bay from the October 2017 forest fires in Sonoma and Napa counties. The final report for the CADAMP monitoring effort (STI, 2010) examined the concentrations at a monitoring site in Southern California during a large wildfire event in October 2003. The site was approximately 10-20 km from those fires, and directly downwind for several days during the event. Two samples collected in that time period had dioxins concentrations about double those seen the same months in 2002 when only small fires were burning, while samples had around the same maximum furans concentrations in both years. Even within very close proximity to the fires, atmospheric total dioxins only doubled in concentration, so fires > 20km away, such as those in Sonoma and Napa, are likely to have had a much smaller impact on the Bay.

A speculative order-of-magnitude estimate was made to assess the North Bay fires as a possible dioxins source to the Bay. A review of dioxins from biomass combustion (Zhang et al., 2016), compiling information from several other studies (Table 4-2), listed emissions averaging 25 ng TEQ/kg fuel or less, with most of the results averaging below 3 ng TEQ/kg fuel. Three

North Bay fires (Atlas, Nuns, and Tubbs) burned about 59,000 hectares of forest. To estimate the total mass of forest burned, we used the United Nations Food and Agriculture Organization estimates of average North American forest aboveground biomass as 95 metric tons per hectare.Assuming an emission factor at the median of the studies in Table 4-2 (2 ng TEQ/kg fuel), the total dioxins released by the fire would have been about 11 g TEQ.

These total forest fire emissions would represent a substantial portion of the 30 g TEQ annual loading to the Bay, *if* they were to deposit to the Bay in a single year. However, a large portion of these emissions would be expected to be carried through the air out of the local watershed, and even for that portion depositing in local watersheds, any deposited to pervious surfaces would see only a fraction transmitted via runoff into the Bay in any given year. Assuming about 10% of the total is transmitted to the Bay in this first year (30% of emissions remaining local, 30% of that depositing onto impervious surfaces), the impact of a 1 g TEQ increase in load is likely minor and difficult to measure, an increase of about 3% of the total average annual load. Nonetheless, the upper range emissions estimates presented are about ten times higher (from Zhang et al., 2016, the EPA Open Burning Test Facility method for Oregon and North Carolina are 15 and 25 ng TEQ/kg fuel, respectively), so potentially some events could register a greater impact. Crude order-of-magnitude calculations such as these may be useful to explore whether particular sources could have an impact. More accurate quantitation would require ambient air measurements from these specific fires and more sophisticated handling of atmospheric transport and deposition specific to wildfire processes, a task beyond the scope of this review.

Table 4-2. Emission factors for PCDD/Fs from forest fires (from Zhang et al., 2016)

Table 4 Emission factors for PCDD/Fs from forest fires

Source	Experimental approach	n	Mean emission factor (ng TEQ/kg fuel)	Range (ng TEQ/kg fuel)	Reference
Forest biomass, France	Chamber tests	5	10.5	1.02–25.9	[114]
Forest biomass, France	Chamber tests	5	0.8 (dl-PCBs)	0.23–2.34	[114]
Forest biomass, Oregon	EPA's OBTF	3	15	1–56	[115]
Forest biomass, North Carolina	EPA's OBTF	4	25	14–47	[115]
Forest biomass, USA	EPA's OBTF	27	2.9[a]	0.2–13.2[a]	[117]
Duke forest	Field	4	0.52	0.4–0.79	[118]
Duke forest	Field, over brick hearth	4	0.59	0.18–1.2	[118]
Duke forest	EPA's OBTF	6	0.75	0.27–1.2	[118]

n number of tests, *OBTF* Open Burning Test Facility

[a] These values originally were reported on a carbon basis and converted to total biomass by multiplying with ½ (biomass on a moisture and ash-free basis roughly contains 50 % Carbon)

Effluent sources

Municipal and industrial (refinery and other industry) effluent discharges were among the better-characterized loading pathways in the 2004 CMIA, and they represented a moderately small component of the overall load so recent efforts have not focused on improving these estimates since the prior report.

With the updated information collected (most notably the ten-fold higher estimate of the atmospheric deposition loads), we can revisit the projections for the expected future (rather than observed or current/past) long-term fate for dioxins in the Bay.

MQ6. What future impairment is predicted for dioxins in the Bay?

The updated information on loads and ambient concentrations of dioxins in the Bay suggest moderate adjustments to the predicted fate in the Bay, with loads currently estimated to be at the upper end of the range used for exploring the sensitivity of the mass budget model to various parameters in the 2004 CMIA. The new data also illustrate some limitations in the conceptual and quantitative accuracy of the one-box model

The current load estimate is about three-fold higher (within the 10-fold higher and 5-fold lower range of loads relative to baseline explored then) and the estimated initial inventory about equal to the previous baseline case. The increase in estimated load is not due to a temporal increase in actual or expected loads, but rather due to the inclusion of studies of measured loads from more representative local watersheds, as well as better local data on ambient air concentrations to estimate direct atmospheric deposition. The previous mass budget estimated that the Bay would be roughly near its pseudo-steady state with the earlier (lower) load estimates and similar ambient concentrations. If no other parameters were changed, the recent load estimates (3x higher than in the 2004 report) would result in the mass budget model suggesting a 1.5-2x higher final steady state concentration than seen in the current ambient open Bay data.

However, the dioxins trends in fish data and concentration profiles in subtidal cores do not suggest that ambient concentrations have increased appreciably in the recent decades as would be suggested by the simple mass budget model. The downward trends seen in South Bay fish (versus insignificant trends elsewhere) are evidence of the oversimplification of the one-box mass budget model, as that model would predict that trends would not differ between segments. The gradients in dioxins away from shoreline and port areas are additional evidence of the oversimplification of the model; loads entering the Bay from tributaries or other pathways around the margins are only gradually being spread to the wider Bay.

In addition to the oversimplification of modeling the Bay as a uniform box, there are numerous parameters in the mass budget model with high degrees of uncertainty, such as the exchange between water and sediment, dioxins degradation rates in sediment, and others, so the mass budget model is more useful as an illustrative conceptual model rather than as an accurate quantitative predictor. Additional information has not drastically changed expectations of a slow decline for dioxins concentrations for the Bay, but has provided more representative data for refining our current state of knowledge, which is important if we wish to develop more accurate quantitative models of long-term fate.

SECTION 5: DIOXINS TRENDS

Given the reductions in most ongoing dioxins sources projected nationwide by the USEPA (Peek et al., 2002) and borne out locally by the disappearance of large-scale waste incinerators and other major point sources, we would expect a continued downward trend in ambient dioxins in all environmental matrices. This is directly addressed by one Dioxins Strategy question, regarding observed rather than predicted trends.

MQ4. Have dioxins loadings/concentrations changed over time?

The bulk of efforts taken towards improved dioxins data collection under the RMP Dioxins Strategy occurred over a relatively short time period, 2008-2012. Given the short interval (and consequently likely small net change) and small total number of samples collected (a few dozen in each year for any given matrix), these efforts would not likely be able to detect small or modest changes in ambient conditions.

Even if samples are taken over a longer time span (i.e., with a larger total number of samples collected, and a larger net change to detect), comparability of measurements across time presents a challenge, particularly for analytes like dioxins, which are often not detected or are near their detection limits. The analytical variation (and frequent non-detects) in quantitation of such low concentration pollutants is one major source of uncertainty, as the statistical methods and substitution methods for non-detects used will affect trend detection. Differences in analytical methods among labs (if different labs measure in different time periods), or even within labs (with minor or major changes in staff, instruments, and operating and reporting procedures) may also obscure real trends, or create analytical artifacts appearing as trends.

Synoptic measurement of archived samples collected over a long period may help overcome some potential artifacts of inter-lab or intra-lab method differences for detecting trends, but may experience challenges of sample availability (e.g., if archived material is previously used up by other needs, unless some is specifically reserved for retrospective analyses) or usability (e.g., due to degradation with extended storage). EPA Method 1613 suggests hold times of up to a year for solid frozen matrix samples (< -10ºC), but notes no “demonstrated maximum holding time,” which would typically be needed to detect long-term trends. Nonetheless, dioxins are a problem in large part because they are persistent in the environment under ambient conditions, so degradation under frozen storage can be expected to be slower. In addition, older samples would likely be more degraded than newer ones, which would present a problem if environmental concentrations were stable; the greater degradation of older samples would create an apparent increasing trend. Fortunately, the trend in dioxins is expected to be downward based on reductions in sources, so the net effect would likely at worst be somewhat reduced apparent trends, by reducing the apparent baseline starting concentration in older samples. Furthermore, given that degradation rates under ambient conditions are likely to be higher than during frozen storage, stored sample degradation is unlikely to create artifacts that would fully eliminate or reverse real declines in the environment.

The limited data from wetland cores also provide evidence of past trends at specific locations. Similar to the case for samples in frozen storage, dioxins in older deeper sediments are likely to have undergone more degradation than newer sediments *in situ*, so apparent trends might be reduced relative to actual changes in loads and ambient concentrations. In the worst case, a seeming increasing trend could result if new sediments are introduced at a constant concentration. Despite this possibility, most wetland sites showed concentrations greatly decreased from peaks in the not too distant past (occurring typically at depths within the top 20 cm of sediment, less than 50 years ago), consistent with actions taken to reduce known dioxins sources in industrial processes and by-products. However, similar to the management history for PCBs, the most impactful “low hanging fruit” of management actions may already have been taken, so future declines will be slower and more modest, and thus more difficult to detect.

Subtidal cores do not show any decrease from past peaks in the subsurface sediments, with most cores nearly uniform, aside from lower concentrations only in deep pre-industrial sediments. This suggests mixing processes occurring faster than changes in loading, smearing out any changes, or a relatively small proportion of the dioxins loads introduced in near-shore areas getting exported to the open Bay in any given time. These fate processes likely vary by site, with both mixing and slow export to the open Bay occurring in some places.

Although open Bay sediments have not been measured for a long enough period to detect changes in surface sediment concentrations, fish dioxins concentrations in South Bay (but not other areas) indicate a decreasing trend which is in line with decreases in sediment concentrations seen at some near-shore sites. Lower South Bay generally has higher sediment concentrations than most of the rest of the Bay, and most of its area is very near shore, so

distinctions between near-shore and open water areas were less apparent. Nearly all resident biota would be impacted by concentrations in both areas.

SECTION 6: CONCLUSIONS AND FUTURE NEEDS

The RMP Dioxins Strategy management questions developed following the 2004 CMIA report provide a useful framework for considering the various information needs for evaluating and managing dioxins risk. Although as noted in Section 2 of this report, dioxin-like PCBs contribute more to TEQs due to their overall greater concentrations, dioxins alone (i.e., in the absence of PCBs) may cause negative impacts and thus are of interest. The subsequent work conducted under the RMP Dioxins Strategy from 2008 to 2014 has addressed some of these questions.

MQ1. Are the beneficial uses of San Francisco Bay impaired by dioxins?
Based on fish tissue concentrations, the beneficial use of commercial and sport fishing continues to be impaired by dioxins. Fish tissue concentrations are variable among periodic sampling events, but nearly all are above the screening value. USEPA adjustments to risk targets would place the Bay even further from an unimpaired state, if they were adopted by the state of California.

MQ2. What is the spatial pattern of dioxins impairment?
Dioxins in Bay water are strongly correlated to SSC, indicating association primarily with a suspended particulate phase, and estimated concentrations on particulates are largely in the same range as bed sediment concentrations in the open Bay. Sediment concentrations in turn are similar among open water Bay sites, but are occasionally much higher in nearshore sites, particularly for some dredged sites reported to the DMMO. This suggests loads discharged from the land are poorly transported and dispersed from shore, evidenced by the strong gradients seen in some DMMO data, but much stronger transport and mixing occurs once in open water areas, seen in the fairly uniform RMP ambient sediment data. Biota monitoring indicates insignificant spatial differences in most species, with only shiner surfperch showing significant evidence of inter-site differences. This may be reflective of the occasionally high dioxins concentrations in near-shore sites, which would have greater effect on species like shiner surfperch that feed primarily in and around shoreline areas.

MQ3. What is the dioxins reservoir in Bay sediments and water?
The inventory of dioxins in sediment is much greater than that in water, regardless of whether we assume a 5 cm or 25 cm mixed sediment layer. The DMMO dataset provides interesting supplemental information for sediments; these concentrations are occasionally much higher than in RMP ambient samples. The ports and marinas dioxins data reported to the DMMO accounts for 2% of the Bay surface area, but they consist of an inventory of up to 6% more dioxins (and 3% of dioxins TEQs) as compared to the estimated mass for the open Bay. Although much of the sediment reported in the DMMO database has already been redistributed to the wider bay during dredge material disposal activities, the pattern of concentrations suggests there may be opportunities for more focused management actions and risk reduction, reducing exposure to local biota, while also reducing eventual export to the wider Bay.

MQ4. Have dioxins loadings/concentrations changed over time?
Dioxins concentrations in cores collected from wetland and subtidal Bay sites in 2005-2006 provided clear evidence of changes in dioxins over time. For all cores in which the bottom sections were from pre-industrial times, surface or near-surface sections were always higher in dioxins than the bottom sections. Although the subtidal cores were usually fairly uniform in their surface layers, suggesting extensive mixing, the wetland cores were more stratified and many showed surface dioxins concentrations greatly reduced from past peaks. Thus major actions

taken several decades ago to reduce dioxins loads and sources appear to have had positive effect, at least in some of these near-shore locations. The smaller difference in both subtidal and wetland cores between current near-surface concentrations and pre-anthropogenic background suggest that continued decreases may be slower, more modest, and more difficult to observe, especially at a Bay-wide scale. Although much of the biota monitoring was conducted only after the major changes in ambient concentrations had occurred, significant declines in dioxins concentrations in biota for South Bay provide some indication of continued improvement. Continued monitoring of biota, combined with periodic monitoring in either cores or in archived surface sediment samples (particularly from fixed/repeat monitoring sites) would be useful in verifying a continuing decline in loads (e.g., as opposed to changes primarily in the food web from climate change or invasive species for example). However, such efforts should be made at a fairly low intensity (long intervals between analyses), due to expectations of very slow and modest decline (no significant declines in fish tissue concentrations in North and Central Bay, and fairly uniform concentrations only moderately higher than pre-industrial background in many subtidal cores); obtaining sufficient power to detect a small decline with much certainty would require analysis of a prohibitively large number of samples.

MQ5. What is the relative contribution of each loading pathway as a source of dioxins impairment in the Bay?

Stormwater runoff and atmospheric deposition were among the least well-quantified loads to the Bay at the time of the 2004 CMIA, and special studies undertaken by the RMP have revised and improved these estimates. Our new estimate of annual loads is about three-fold higher than in the 2004 CMIA, with a slight majority of loads now expected from atmospheric deposition. Continued CARB and BAAQMD efforts to reduce particulate emissions such as restrictions on new fireplace construction, and efforts to reduce overall emissions from transportation sources may also help reduce dioxins loads to the Bay. Further information should be gathered from these agencies on the replacement of diesel buses with electric buses, and on the improvements required by diesel trucks, as well as any reduction in fireplace construction. This information would be of use in the interpretation of the trends in atmospheric loadings of dioxins to the Bay. Although a crude estimate for the Napa and Sonoma wildfires in 2017 suggests likely a small input to the Bay, future wildfires occurring nearer the Bay may yield larger short-term impacts similar to the two-fold increase in atmospheric dioxins seen in CADAMP monitoring in 2003 in a Southern California site near a wildfire. The CADAMP air dioxins data in the Bay Area are fairly old (circa 2002-2006), so updated air data would be important for evaluating atmospheric deposition loads in the future. Likewise, continued monitoring of watershed loading may be beneficial but challenging for detecting loading trends due to the climate-dependent episodic nature of watershed discharge. Strategies for accounting for these factors are currently being explored for PCBs, so lessons learned from those efforts may also be useful for dioxins.

MQ6. What future impairment is predicted for dioxins in the Bay?

Sources of dioxins are expected to continue decreasing locally due to past and current management efforts towards reducing atmospheric sources and emissions (e.g., the cessation of most local major point sources, and local and state air quality agency actions to restrict and reduce future smaller non-point sources), so the actual quantitative observed impacts (e.g., additional cancer cases per population or other human or wildlife health effects) are likely to decline, even if the estimated risk thresholds or regulatory standards are further tightened and make impairment relative to targets appear worse. Continued monitoring of fish tissue concentrations, the primary driver of the impairment determination, is needed to assess the current status of the system at any given time, as well as possibly indicate any trends. Given the evidence of higher concentration of dioxins in near-shore sediments, consideration should also be given to collecting near-shore fish, sediment, and possibly water dioxins concentrations in

conjunction with the near-shore PCBs studies in the future. These data would help determine the role of local versus general sources of loadings of dioxins to the Bay, and therefore may help determine whether management actions would result in load reductions. Eventually, updated models of PCBs will be needed to incorporate data gathered in the near-shore study. As such, it would be an efficient use of limited monitoring funds to collect dioxins data during these studies. The food web model should also eventually include avian species that integrate PCBs and dioxins spatially. Dioxins concentration data should continue to be collected in eggs in conjunction with the near-shore and regular RMP monitoring.

Overall, it appears that dioxins will be a pollutant impairing beneficial uses in the Bay for a long time to come, with recovery likely to be slow, and progress modest on a Bay-wide scale unless interventions beyond load reductions are taken. As noted before, it is important to monitor dioxins in the long term to track status and progress, most particularly in fish tissue, which is most directly tied to the impairment listing.

Through a combination of focused and more widespread management action, dioxins impairment could be reduced on a faster timeframe than monitored natural attenuation. If there are near-shore sites that are more highly contaminated, they may indicate past or current localized sources or pathways of higher dioxins loading. Therefore, measurement of dioxins in select dredging projects or study locations, particularly for sites near the shore (e.g., < 250 m) and with previously measured high dioxins concentrations nearby, should be considered. Although dredged material is often moved offsite, it is unknown whether the original source remains in the landscape, so ongoing measurement and reporting of dioxins data in near-shore studies can be useful in identifying potential localized upland and watershed sources for additional focused characterization and possible management.

Similarly, for more widespread and lower level contamination across the urban landscape, the general correlation between PCBs and dioxins suggest that even if their sources are not coincident, their persistence, and environmental partitioning and transport behaviors are similar enough that some of the approaches to manage PCBs, such as increasing the extent of green infrastructure, will have collateral benefits for dioxins.

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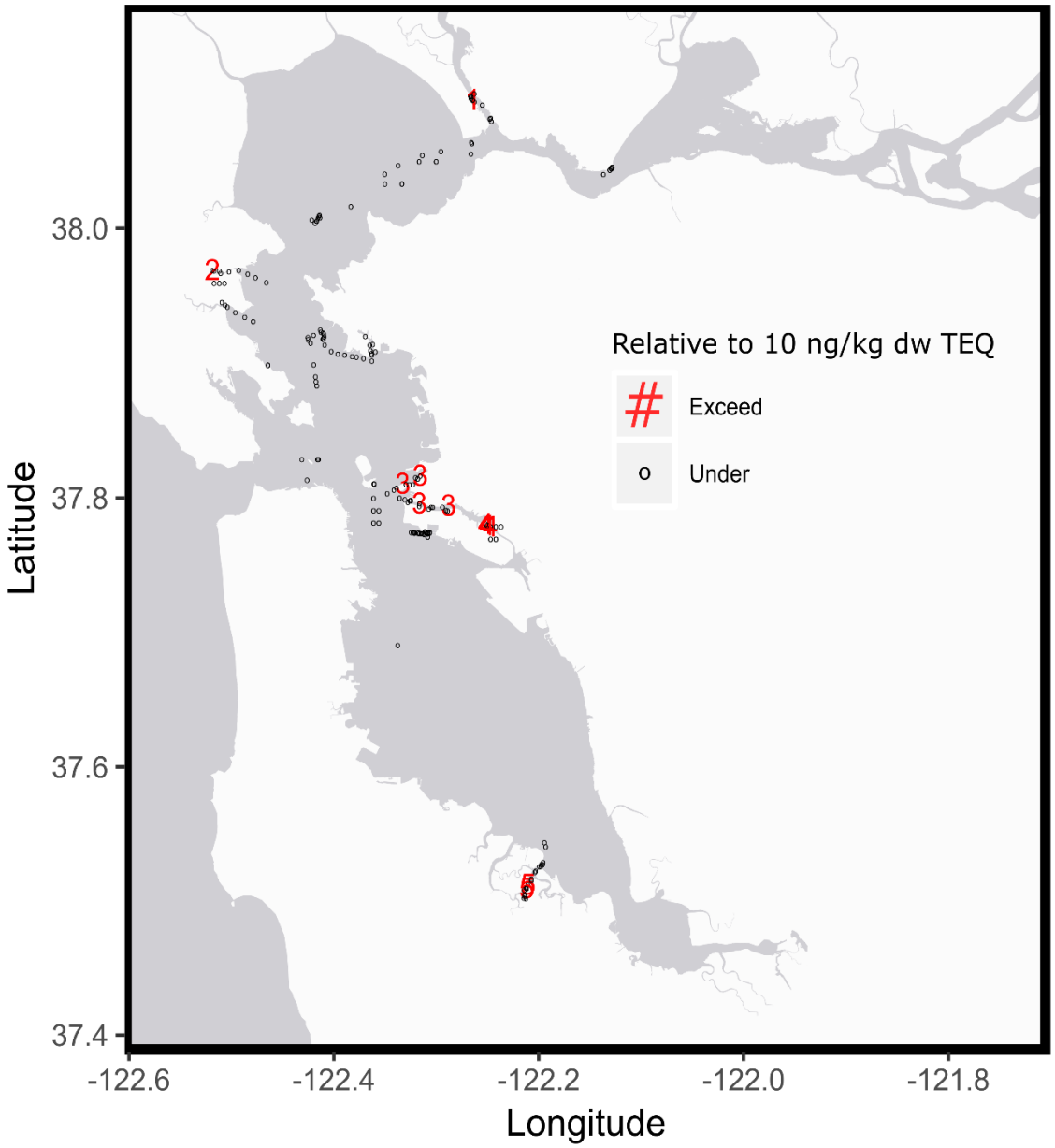
APPENDIX A: DMMO DIOXINS DATA



SampleNumber	StudyName
1	Mare Island Shipyard 2009
2	San Rafael Channel Final Report 2010
3	Port of Oakland Berths 22-26,33,57/59,67/68 2015
4	US Coast Guard Island Integrated Support 2014
5	Port of Redwood City 2015
o	Sites <10 ng/kg dw TEQ

Figure A-1. Dioxins TEQs in samples in the DMMO database. Large red numbers indicate studies with samples exceeding the DMMO bioaccumulation testing TEQ threshold of 10 pg/g dw in sediment. Small black circles indicate samples with concentrations below the threshold.

Table A-1. Dioxins in Sediment Samples in the DMMO Database. Samples grouped by study (alphabetically sorted). Individual samples with TEQs exceeding the DMMO Bioaccumulation Testing threshold of 10 pg/g dw are highlighted in red shaded cells.

StudyName	StationCode	TEQ pg/g dw
Alameda Point Channel 2011	DU1	0.17
Alameda Point Channel 2011	DU2	0.21
Alameda Point Channel 2011	DU3	0.37
Alameda Point Channel 2011	DU4	0.19
Alameda Point Channel 2011	DU5	0.29
Alameda Point Channel 2011	DU6	0.4
Alameda Point Channel 2015	DU1	1.58
Alameda Point Channel 2015	DU2	1.75
Alameda Point Channel 2015	DU3	2.45
Alameda Point Channel 2015	DU4	1.99
Alameda Point Channel 2015	DU5	2.68
Alameda Point Channel 2015	DU6	2.9
Alameda Point Channel 2015	DU7	1.77
Alameda Point Channel 2015	DU8	1.68
Alameda Point Channel 2015	DU9	2.6
Alameda Point Entrance Channel 2008	EC	0.75
Alameda Point Entrance Channel 2008	MC	0.71
Alameda Point Entrance Channel 2008	Ref Site	0.59
Alameda Point Entrance Channel 2008	SF-11	0
Alameda Point Entrance Channel 2008	TB1	0.72
Alameda Point Entrance Channel 2008	TB2	0.61
Alameda Point Entrance Channel 2008	WC	0.54
Bel Marin Keys North Lagoon 2006	NL1	0.35
Bel Marin Keys North Lagoon 2006	NL2	0.37
Bel Marin Keys North Lagoon 2006	NL3	0.45
Bel Marin Keys North Lagoon 2006	NL4	0.37
Bel Marin Keys North Lagoon 2006	PC	0.1
Chevron Long Wharf 2015	BSA/B-1/B-2	1.43
Chevron Long Wharf 2015	DU-1/2	4.11
Chevron Long Wharf 2015	DU-3/4	0.98
Chevron Long Wharf 2015	DU-5/A/B	1.76
Chevron Long Wharf 2015	SF-11	0.07
Kiewit Infrastructure West Bulkhead Approach 2015	KIW	2.58
Kiewit Infrastructure West Bulkhead Approach 2015	SF-9	2.56
Larkspur Ferry Terminal 2015	DU1	3.47
Larkspur Ferry Terminal 2015	DU2	2.57
Larkspur Ferry Terminal 2015	DU3	1.07
Larkspur Ferry Terminal 2015	DU4	1.18
Larkspur Ferry Terminal 2015	DU5	1.45
Larkspur Ferry Terminal 2015	DU6	0.7
Mare Island Dry Dock Berth 12 and Barges B/C 2015	DU1	4.69
Mare Island Shipyard 2009	DU1	2.91
Mare Island Shipyard 2009	DU2	1.25
Mare Island Shipyard 2009	DU3	13.42
Mare Island Shipyard 2009	DU4	2.7
Mare Island Shipyard Dry Dock 2014	MI-DU1	1.09

Mare Island Shipyard Dry Dock 2014	MI-DU1	0.84
Mare Island Shipyard Dry Dock 2014	MI-DU2	0.83
Napa River Federal Navigation Channel 2015	NRC-2015-1	3.22
Napa River Federal Navigation Channel 2015	NRC-2015-2	1.7
Napa River Federal Navigation Channel 2015	NRC-2015-3	1.61
Phillips 66 Richmond Marine Terminal 2014	P66	2.38
Phillips 66 Sediment Characterization 2016	P66	0.25
Port of Benicia Terminal (AMPORTS) 2016	ABT	1.16
Port of Oakland Berths 22-26,33,57/59,67/68 2015	B22-26	11.51
Port of Oakland Berths 22-26,33,57/59,67/68 2015	B33	11.49
Port of Oakland Berths 22-26,33,57/59,67/68 2015	B57-59	11.51
Port of Oakland Berths 22-26,33,57/59,67/68 2015	B67-68	11.66
Port of Oakland Berths 22,25/26/57/59,60/63 2012	B22	2.97
Port of Oakland Berths 22,25/26/57/59,60/63 2012	B25-26	2.04
Port of Oakland Berths 22,25/26/57/59,60/63 2012	B57-59	1.81
Port of Oakland Berths 22,25/26/57/59,60/63 2012	B60-63	1.93
Port of Oakland Berths 23,30/32,35/37,55/56 2014	B23	2.35
Port of Oakland Berths 23,30/32,35/37,55/56 2014	B30/32	1.53
Port of Oakland Berths 23,30/32,35/37,55/56 2014	B35/37	1.37
Port of Oakland Berths 23,30/32,35/37,55/56 2014	B55/56	0.69
Port of Oakland Berths 60-63 2016	B60/63	5.26
Port of Oakland Brths 23/24,30/32,35/37,55/56 2011	B23/24	1.05
Port of Oakland Brths 23/24,30/32,35/37,55/56 2011	B30/32	0.39
Port of Oakland Brths 23/24,30/32,35/37,55/56 2011	B35/37	0.13
Port of Oakland Brths 23/24,30/32,35/37,55/56 2011	B55/56	0.59
Port of Redwood City 2015	DU1	8.65
Port of Redwood City 2015	DU1	13
Port of Redwood City 2015	DU2	9.95
Port of Redwood City 2015	DU2	15.6
Port of Redwood City Marina & F-Dock 2013-14	F	3.16
Port of Redwood City Marina & F-Dock 2013-14	MA	6.69
Port of Redwood City Marina & F-Dock 2013-14	MB	8.14
Port of Richmond Terminals 7 and 8 2016	PR-DU1	0.56
Port of Richmond Terminals 7 and 8 2016	PR-DU2	0.49
Richmond Inner Harbor 2015	RIH-2015-1	1.45
Richmond Inner Harbor 2015	RIH-2015-2	2.45
Richmond Inner Harbor 2015	RIH-2015-3	1.87
Richmond Inner Harbor 2015	RIH-2015-4	2.18
Richmond Inner Harbor 2015	RIH-2015-5	2.46
Richmond Inner Harbor 2015	SF-10-2015	0.32
Richmond Outer Harbor 2015	ROH-1	0.59
Richmond Outer Harbor 2015	ROH-2	0.88
Richmond Outer Harbor 2015	ROH-3	0.75
Richmond Outer Harbor 2015	ROH-4	0.41
Richmond Outer Harbor 2015	SF10	1.74
San Rafael Channel Final Report 2010	SF-10	0.22
San Rafael Channel Final Report 2010	SF-11	0
San Rafael Channel Final Report 2010	SRC-1	0.49
San Rafael Channel Final Report 2010	SRC-2	0.13
San Rafael Channel Final Report 2010	SRC-3	0.04

San Rafael Channel Final Report 2010	SRC-4	0.28
San Rafael Channel Final Report 2010	SRC-5	0.35
San Rafael Channel Final Report 2010	SRC-6	2.4
San Rafael Channel Final Report 2010	SRC-7	5
San Rafael Channel Final Report 2010	SRC-7	0.82
San Rafael Channel Final Report 2010	SRC-8	6.1
San Rafael Channel Final Report 2010	SRC-8	10.21
Schnitzer Steel Industries Terminal Berth 2015	SS	2.41
US Coast Guard Island Integrated Support 2014	CGI-1-4	9.69
US Coast Guard Island Integrated Support 2014	CGI-1-4	21.18
US Coast Guard Island Integrated Support 2014	CGI-1-4	0.17
US Coast Guard Island Integrated Support 2014	CGI-1-4	0.13
US Coast Guard Island Integrated Support 2014	CGI-1-4	0.02
US Coast Guard Island Integrated Support 2014	CGI-1-4	0.45
US Coast Guard Island Integrated Support 2014	CGI-5-8	3.32
US Coast Guard Island Integrated Support 2014	CGI-5-8	18.06
US Coast Guard Island Integrated Support 2014	CGI-5-8	0.02
US Coast Guard Island Integrated Support 2014	CGI-5-8	0.14
US Coast Guard Island Integrated Support 2014	CGI-5-8	0
US Coast Guard Island Integrated Support 2014	CGI-5-8	0.07
US Coast Guard Island Integrated Support 2014	CGI-9-12	0.02
US Coast Guard Island Integrated Support 2014	CGI-9-12	0
US Coast Guard Island Integrated Support 2014	CGI-9-12	0.01
US Coast Guard Island Integrated Support 2014	CGI-9-12	3.2
US Coast Guard Island Integrated Support 2014	CGI-9-12	14.17
USACE Oakland Entrance Channel 2008	O	0.58
USACE Oakland Entrance Channel 2008	PC	0.59
USACE Oakland Inner and Outer Harbors 2008	OI1	0.56
USACE Oakland Inner and Outer Harbors 2008	OI2	0.38
USACE Oakland Inner and Outer Harbors 2008	OO1	0.4
USACE Oakland Inner and Outer Harbors 2008	OO2	0.37
USACE Oakland Inner and Outer Harbors 2008	PC	0.59
USACE Oakland Inner Harbor Channel 2010	OAK-1	0.01
USACE Oakland Inner Harbor Channel 2010	OAK-2	0.01
USACE Oakland Inner Harbor Channel 2010	OAK-3	0
USACE Oakland Inner Harbor Channel 2010	OAK-4	0
USACE Oakland Inner Harbor Channel 2010	OAK-5	0.06
USACE Oakland Inner Harbor Channel 2010	OAK-6	0.31
USACE Pinole Shoal Channel 2009	PIN-AM-1	0.01
USACE Pinole Shoal Channel 2009	PIN-AM-2	0.04
USACE Pinole Shoal Channel 2009	PIN-AM-3	0.03
USACE Pinole Shoal Channel 2009	PIN-AM-4	0.03
USACE Pinole Shoal Channel 2009	SF-10	1.21
USACE Pinole Shoal Channel 2009	SF-9	0.64
USACE Pinole Shoal Channel 2010	AM-1	0.37
USACE Pinole Shoal Channel 2010	AM-2	0.04
USACE Pinole Shoal Channel 2010	AM-3	0.08
USACE Pinole Shoal Channel 2010	AM-4	0.05
USACE Pinole Shoal Channel 2010	RM-1	0.01
USACE Pinole Shoal Channel 2010	RM-2	0.07

USACE Pinole Shoal Channel 2010	RM-3	0.02
USACE Pinole Shoal Channel 2010	SF-10	0.58
USACE Pinole Shoal Channel 2010	SF-9	0.46
USACE Redwood City Harbor 2011	RED-1	3.77
USACE Redwood City Harbor 2011	RED-2	3.43
USACE Redwood City Harbor 2011	RED-3	3.73
USACE Redwood City Harbor 2011	RED-4	4.29
USACE Redwood City Harbor 2011	RED-5	6.17
USACE Redwood City Harbor 2011	RED-6AM	4.07
USACE Redwood City Harbor 2011	RED-7AM	5.14
USACE Redwood City Harbor 2014	RED-1	3.29
USACE Redwood City Harbor 2014	RED-2	2.19
USACE Redwood City Harbor 2014	RED-3	2.82
USACE Redwood City Harbor 2014	RED-4	3.3
USACE Redwood City Harbor 2014	RED-5	2.78
USACE Redwood City Harbor 2014	RED-6	3.59
USACE Redwood City Harbor 2014	RED-7	5.81
USACE Redwood City Harbor 2014	SF-10	2.07
USACE Richmond Inner/Outer Harbors 2008	RIH-1	0.49
USACE Richmond Inner/Outer Harbors 2008	RIH-2	0.83
USACE Richmond Inner/Outer Harbors 2008	RIH-3	0.56
USACE Richmond Inner/Outer Harbors 2008	RIH-4	0.51
USACE Richmond Inner/Outer Harbors 2008	RIH-5	0.89
USACE Richmond Inner/Outer Harbors 2008	RIH-6	3.18
USACE Richmond Inner/Outer Harbors 2008	ROH-1	0.19
USACE Richmond Inner/Outer Harbors 2008	ROH-2	0.29
USACE Richmond Inner/Outer Harbors 2008	ROH-3	0.3
USACE Richmond Inner/Outer Harbors 2008	ROH-4	3.78
USACE Richmond Inner/Outer Harbors 2008	SF-10	0.67
USACE Richmond Inner/Outer Harbors 2008	SF-11	0
USACE Richmond Outer Harbor 2012	ROH-1	0.18
USACE Richmond Outer Harbor 2012	ROH-2	1.26
USACE Richmond Outer Harbor 2012	ROH-3	0.36
USACE Richmond Outer Harbor 2012	ROH-4	0.97
USACE Richmond Outer Harbor 2012	SF-10	1.1
USACE San Bruno Shoal Channel 2016	SBS-2016	1.04
USCG Yerba Buena Island 2011	A	4.06
USCG Yerba Buena Island 2011	A	4.54
USCG Yerba Buena Island 2011	B	3.86
Valero Benicia Refining Co 2008	DU1	0.52
Valero Benicia Refining Co 2008	DU2	0.46
Valero Benicia Refining Co 2008	DU3	1.54
Valero Refinery Terminal 2012	DU1	0.19
Valero Refinery Terminal 2012	DU2	1.33
Valero Refinery Terminal 2012	DU3	0.68
Valero Refinery Terminal 2015	DU1	2.52
Valero Refinery Terminal 2015	DU2	3.04
Vallejo Ferry Terminal 2011	VFT	0.24
Vallejo Marine Terminal 2015	VMT-DU1	1.67
Vallejo Marine Terminal 2015	VMT-DU2	1.86

Vallejo Marine Terminal 2015	VMT-DU3	0.24
WETA Central Bay O&M Facility 2012	WETA-DU1	1.1
WETA Central Bay O&M Facility 2012	WETA-DU1	0
WETA Central Bay O&M Facility 2012	WETA-DU2	1.89
WETA Central Bay O&M Facility 2012	WETA-DU2	0.1
WETA Richmond Ferry Terminal 2016	RFT-DU1	4.73

APPENDIX B REVIEWER COMMENTS/RESPONSES

Frank Gobas comments:

The Dioxin Synthesis Draft Report by Yee et al. (2018) is another fine effort by SFEI which evaluates information on the fate of dioxins in SFB that were considered information gaps in the 2005 Conceptual Model/Impairment Assessment report for dioxin.

Before making this report more generally available, I would suggest the following revisions:

1. Change the title. It sounds like a chemistry project.

Done

2. Tighten up the language. Without prior knowledge of the subject matter and familiarity with the spoken lingo, it is difficult to follow.

Provided description/definition of first uses of acronyms and other jargon

3. I agree with the conclusion that dioxin will be impairing beneficial uses in the Bay for a long time to come. The conclusion that there is a slow recovery (l. 33 p. 30) is not supported by the data (Fig 2-1), most of the core data and the increase in loading estimates. I suggest rewording this to state that that there has been no statistically significant/detectable recovery to date and that a significant recovery is not expected to occur in a reasonable time frame unless management is undertaken. Perhaps, this what is meant but I read this a few times and I am not sure that that message comes through.

The increase in loading estimates is not a documentation of a real increase but rather an update of past likely underestimated loads (added notes in watershed loads and atmospheric dep, loads with greatest change over previous estimates). At least some of the nearshore (wetland) cores show some evidence of decrease from the historic worst cases, and for South Bay there is some evidence of change in shiner surf perch ($p<0.5$), but the change is not evident or significant everywhere as noted in the report

Also, I suggest that in the report, the time trend data are discussed in terms of the results of the one compartment model. If I remember correctly, the half-life time for dioxins in the Bay is about 20 yr or so. Given this half-life time, a two fold decline in the concentrations of dioxins in fish may be expected since 1994. Perhaps, the monitoring programs cannot detect such a change. If so, this should be stated. However, if the monitoring program can detect such a change, then it means that there are still on-going loadings into the Bay. One can even derive a load estimate from the model.

As noted previously, the South Bay shiner surfperch show significant decline. The report also notes numerous caveats on the quantitative accuracy of the one box model (e.g. estimated current loads should result in a steady state about 1.5-2x current ambient, and previous loads would have been higher yet, so many elements of the one-box are likely inaccurate).

p.3, l.31. I suggest removing the reference to the expectations that dioxins will decrease nationally from the report here and perhaps elsewhere as well. This paragraph is confusing because of this statement (which is not all that relevant). I suggest adding here, what data led to the main conclusion that dioxins will be impairing Bay uses for a long time.

Added a few sentences to Exec summary and report text clarifying basis for expecting slow recovery.

4. l. 31, p6. Concentrations of dioxins and furans IN WHAT?

Line removed

5. l. 35, p.6. I think that the oral slope factor is usually presented in units of kg.day/mg. It is used correctly though in equation 1. Also, add a reference here.

USEPA reference added

6. Note that TEQ screening levels are referred as 0.15 pg/g and later as 0.14 pg/g. Maybe correct or provide an explanation for the difference.

Fixed to 0.14 everywhere

7. p.9. It would be useful to refer here to Fig 2-1. I assume Fig 2-1 belongs to this analysis. The text refers to exceedances of the ATL, but the figure shows concentrations of TEQs in fish. I am a bit skeptical about the lack of a trend in the white croaker dioxin TEQs. There appears to be an increase in concentration. I suggest supporting this with some linear regression stats.

Fig 2.1 mixed data with different basis (whole body 2014, skin on fillets other years). Regressions added to section 3 after the fish bubble plots~p15. 1994 had few sites and thus spatially unrepresentative/biased, and regression on all other years (also excluding 2014, analyzed on wrong basis) showed no significant trend. Sun et al 2017 fish tissue report also found no significant trend on all bay croaker dioxin.

8. I suggest exploring the use of lipid normalized concentrations to deal with the difference in skin-on and skin-off filets.

Explored, and with paired Wilcoxon for sample year analyzed both skin on and off (2009) lipid normalized dioxin was always lower for skin on fillet (skin added more lipid than dioxin)

9. How Non-Detects are dealt with is crucial in the evaluation of any contaminant with concentrations close to the method detection limit. Rather than choosing one method for dealing with NDs, I suggest using 3 methods (i.e., ND=0, ND is not used at all and ND=1/2 the detection limit) and use the results of all three methods to interpret the combined data set.

Shown in new Fig 3-1. Negligible effect for fish tissues. For water noted that any substitutions other than 0 blow virtually all samples above criterion.

10. Add error to the slope in Fig 3-1.

We are not attempting to do anything with the slopes, main point was to show correlation. Especially with 3 substitution options it would get very busy.

11. l.9, p.12. Not sure what this means. You mean a drop of 2 fold over 14 years, or a 2-fold drop per year. The latter reduces concentrations by 67 times over 14 years. This would be more than significant. Numbers OK? You mean 0.05 yr-1?

Clarified to say two-fold decrease overall.

12. I suggest revisiting the two paragraphs on p.12. A p of 0.14 means that the hypothesis of the existence of a decline in concentration fails at the used confidence level. This means for us scientists that a trend was not observed.

Reworded throughout to not pay mind to observations of p>0.05

It would be nice to show the data in a temporal plot rather than in a bubble diagram which do not show time trends too well.

Have elected to not show plots as with too many variants (e.g. Table 3-1) plots would take a lot of space without much additional value.

Also, I suggest that the statistics are reported more robustly. This is an important component of the analysis. If indeed no statistically significant declines can be detected then this informs both on what is going on and the monitoring strategy that is followed.

The new table 3-1 summarizes the trends assessments aggregated/not in different ways, for different species.

13. Given the ground work presented in Fig 3-1, it would be expected to have the data in Figures 3-2 to 3-5 presented or interpreted in terms of TEQs. This would support the main conclusion of the report that dioxins still cause impairment. The criteria are presented in TEQs, but the figures are in pg sum of dioxins and furans. Given Fig 3-1 it should be possible to estimate concentrations in terms of TEQs and also include the error in this analysis, which is not small, judging from Fig 2-1.

Switched all map plots to TEQ basis.

14 I like the comparison with the results from the Ross study (add to the reference list). I suggest adding the data to the report, so that the results can be evaluated. Also, to make the data sets more comparable, it may be worthwhile to lipid normalize the concentration data and to use (if possible) similar units for concentrations as those used by Ross et al. Also, clarify what "trend" means.

Reanalyses done lipid normalized for all possibilities. All of our data are downloadable from SFEI site.

15. It would be good to see the data being referred to on p.16. Also, in my view at least, Fig 2-1 shows signs that concentrations of TEQ in one species are increasing from 1994 to 2015. Hence, the statement that there are no indications of upward trends may need to be dialed down a bit. The main point here is that the report suggests that concentrations of dioxins in fish and wildlife are going down, but the actual data presented in the report that are easily interpretable in terms of time trends do not support this. My suggestion is to stick more closely to a statistical interpretation of the data. The p values discussed are mostly above 0.05!

As mentioned before, Fig 2-1 a bit misleading because of spatially unrepresentative 1994, and 2014 analyzed whole body creating artifacts. Reduced to years spatially and tissue basis comparable, no trends were observed on the whole bay basis. There may be hints of South Bay change though (new Table 3-1)

16 In the discussion of the sediment data, I suggest that a reference point is provided. Perhaps, refer to sediment quality criteria. Perhaps, add a discussion on what the sediment say about impairment and time trends. Clarify the hypothesis that the sediment data are testing.

The main point of the sediment data is to representatively characterize that stratum. If it has to be stated as a hypothesis test, it would be that concentrations of dioxin in the Bay are uniform.

17. A depth of 0 m? Perhaps clarify further.

Reworded to indicate 0m from the sediment surface

18. l. 35, p. 21. Correlation between what? I am not sure that the very nice correlation says much about the contribution of local discharges. It simply says that dioxins partition predominantly in the suspended sediment fraction of the water. Revise the conclusion I suggest.

Restated as suggested.

19. An interpretation of the sediment core data on p. 26 in terms of time trends could be added.

Brief text added to caption to mirror statements in narrative

20. The statement in line 4-8 on p.27 that the mean and median sums of TEQs of 0.0021 ug/kg dw are roughly in line with values used for estimating sediment inventories in the 2005 CMIA using EMAP dioxin data, of around 0.3 ug/kg dw for the sum of dioxin isomers needs further explanation. Refer to Fig 3-6. Does fig 3-6 use the same data as the comparison being referred to here?

Indicated 2008-2011 data in Figure 3-7

21. What does the 22 kg on p. 27 refer to? Top layer of sediment? All of the sediments? Further details on the calculation would be useful here. Same for the water inventory. How the inventory is calculated is not entirely clear. Another question is how these inventories have changed over time.

Noted top 15cm for sediment, total Bay volume for water. Since concentrations are similar to 2000 data, inventories unchanged.

22. I welcome the discussion on p.29. The statement that it may be more appropriate to treat the dioxin inventory in ports and other near-shore areas as a more discrete compartment, rather than assuming it is well-mixed and exchanged with open Bay sediment makes sense. Perhaps add that this is being done with the PMU strategy.

The statement that the presence and persistence of the near-shore gradient itself illustrates that sediments in these compartments are not readily interchanged is indeed a possibility, but it is also possible that there are on-going sources. The half-life times for the PMUs are likely shorter than for the Bay as a whole. If indeed concentrations in the PMU have not changed significantly, then there are still on-going sources that have not dissipated. A similar argument is presented in the following sentence. I suggest rewriting this section to provide a more balanced discussion using alternative explanations.

Revised partially. The wetland cores suggest that even if there are ongoing sources, they are not as severe as they once were. Places like the wetland cores sites might have had some losses from the highest concentration layers since their peak, but the mixing and throughput is not enough to erase/smear the signal to the extent seen in open bay cores. Nearshore locations like the wetland coring locations may see continuing sources (greater than open Bay ambient) but still also well below their historical worst exposures (partially captured and still in place, like seen in some of the wetland cores).

23. Clarify that Table 4-1 is for the Bay as a whole, not for particular sites.

Added for all of San Francisco Bay in caption

24. p. 30. It would be informative to know more about the increase in dioxin loads from local watersheds. The overall narrative of the report is that dioxin concentrations are declining but the load estimates here as well as the data in Fig 2-1 do not support this.

Clarified that the change from past is due to lack of representativeness in past data, not that loads are actually believed to have gone up. Noted in the first paragraphs of the watershed loads and atmospheric deposition sections, where the calculated loads have changed the most.

25. l.27-29 on p. 31 are unclear. It may be worthwhile to address MQ6 more directly. In essence, declines of concentrations of dioxins/furans in fish have not been observed (Fig 2-1). Loading estimates have gone up (p.32). Hence impairment will continue. Model estimates indicate that concentrations of dioxins in fish can be expected to decline at a rate of xx if external loadings cease and impairment would end after xx years. With continued inputs, the time frame to reach the point of impairment will be longer than that. Unless current loadings are reduced impairment will continue.

Declines in fish observed in some locations. Estimated loads have gone up, but past load estimates should have been higher yet. The model itself doesn't/can't capture the spatial difference in fish trends (decrease in S Bay, none elsewhere), nor the sediment concentration gradient away from shore/source areas, so we probably need a more spatially granular model to reconcile these differences,

26. P. 32-33, section 5. It is appropriate to discuss the challenges in establishing time trends. It is also good to state expectations for time trends. However, it is most important to report on the findings from this analysis discussed earlier, e.g. Fig 2-1. The last paragraph only discusses the wetland core data. However, the majority of core data (the bottom 7 on p. 26) do not show a decline in concentrations of dioxins over time. Only the top 3 do. This section needs to be revisited as the conclusions are not fully in line with the data and analysis presented.

Added discussion on fish trends (S Bay significant for lipid normalized, fig 2-1 is the crude source data for impairment assessment, which must be wet weight, and lumps all areas together, and excludes 1994 unrepresentative in site counts, and 2014 analyzed on wrong basis), and a section added on the subtidal core data.

27. l. 26 on p. 33. Refer to time trends.

Added a bit on lack of trend seen in the subtidal cores, and the lack of fish trend seen in North and Central Bay)

28. p. 24, l. 10-12. I suggest that the sentence “Thus major actions taken several decades ago to reduce dioxin loads and sources appear to have had positive effect.” is put into context with the other findings in this study. It appears to me that in certain locations there is evidence that actions had impacts, but not in other locations. The whole Bay?

Noted that the change is in “some locations”.Also that the difference to distinguish durther change (difference between current and pre-industrial concentrations) is smaller and thus likely difficult.

29. I do not see how the data in Table 4-1 are reflected in the response to MQ5 on p. 34. The main messages are that local watersheds are the main sources/pathway and that watershed loading estimates are going up.

Again, misunderstanding that the revised estimate changes due to better representativeness/improved data for calculation, not likely due to temporal change in loads. Have tried to make that clearer.

30. The emphasis in the response to MQ6 on p. 34 should be on the analysis of data presented in this synthesis study. I would remove the paragraph about the national expectations and add the rationale for the expectation of continued impairment.

Have emphasized the local lack of point sources and more recent air board actions rather than the national trends.

From: Christian, Elizabeth@Waterboards
Sent: Friday, October 26, 2018 4:19 PM
To: 'Jay Davis' <jay@sfei.org>; Feger, Naomi@Waterboards <naomi.feger@waterboards.ca.gov>
Cc: Don Yee <donald@sfei.org>; Mumley, Thomas@Waterboards <thomas.mumley@waterboards.ca.gov>; Lunde, Kevin@Waterboards <kevin.lunde@waterboards.ca.gov>; Brian Ross (ross.brian@epa.gov) (ross.brian@epa.gov) <ross.brian@epa.gov>
Subject: RE: Dioxin report

Hi Jay,

I talked with Brian Ross at EPA and we boiled down our concerns into the following areas:

- Fines normalization of sediment TEQ data vs. the DMMO bioaccumulation testing trigger (BT = TEQ of 10 pptr)

The DMMO doesn't normalize TEQ data to fraction of fines when comparing to the BT, so it would be helpful to have a map of non-normalized TEQs at a scale that makes it easy to see which regularly dredged sites have historically had TEQs < 10 pptr.

Appendix A added with Figure A-1 of site labels for locations with TEQ >10 pg/g dw non-normalized, and Table A-1 for all the DMMO data sorted by study and site, with samples with >10 pg/g highlighted.

- The discussion of "surface" vs. "non-surface" samples on page 20, lines 9-12 and in Figure 3-9 is confusing to us, and we'd like clarify how this applies to the DMMO sediment core data.

The surface and non-surface distinction is eliminated for DMMO data in Fig 3-9

From: Gravenmier, Josh [mailto:Josh.Gravenmier@arcadis.com]
Sent: Tuesday, October 30, 2018 9:00 AM
To: Bridgette DeShields <bdeshields@integral-corp.com>
Subject: RE: [PCB WG] RMP PCB/Dioxin Workgroup: Revised Dioxin Report; Urgent Input Requested on Multi-Year Planning forDioxin Special Studies

This is the compilation of my and Scott Bodensteiner' s comments.

- In Section 5 author states: "Similar to the case for samples in frozen storage, dioxin in older deeper sediments are likely to have undergone more degradation than newer sediments *in situ*, so apparent trends might be reduced relative to actual changes in loads and ambient concentrations." However, there is no discussion related to newly deposited sediments potentially emanating from resuspended sediments from a bedload previously buried in other areas of the Bay now eroding per USGS/RMP Status and Trends.

  More recent USGS studies have suggested that the net surplus of sediment in North Bay has already passed the tipping point and most areas are no longer net erosional with consequent increased clarity (and phytoplankton blooms noted by Jim Cloern).

  There is however some discussion of potential net movement from more contaminated nearshore areas to the open bay. E.g. the current p29: Continued resuspension and exchange of more-contaminated near-shore sediments with less-contaminated sediments from the adjacent open waters would result in net export of dioxin to the open Bay.

- No discussion on potential differences in sediment dioxin sources (e.g. adjacent shoreline vs. suspended sediments from other areas of Bay) attributable to variations in sediment transport and deposition in dredge areas with significantly lower elevations than most of the rest of the Bay.
  - In addition, it looks like the report links the DMMO sampling results from dredging sites specifically to near-shore sources of dioxins, but isn't is also possible that the sediment sampled during the dredge material

characterization is from dioxin that is from upstream sources on the newly deposited material and if so how would that impact the conclusions?

The loading and concentration data cannot, and we made no attempts to distinguish original true near-shore sources from pathways that discharge to the near-shore environments and have adjusted language to try and more explicitly clarify, e.g. p27:

"This suggests that much of the dioxin gradient is from terrestrial sources or loading pathways o near-shore environments, with transport and dilution processes moving away from shore, not necessarily due to sources inside of ports from maritime traffic."

- Would be nice to see what DMMO sites exhibited the small number of elevated dioxin concentrations in order to assess the context of the dredge events, i.e. location, dredge depth, shoal depth, dredge frequency, whether cores were vertically subsampled, etc.

Appendix A gives a brief indication of sites with higher concentrations. Queries of the DMMO database and other details in the respective project reports may help further elucidate particular factors in specific cases of high concentrations, a task beyond the scope of this report.

- Per previous comment, no significant discussion related to the sample/dredge frequency or core depth on dioxin concentrations in DMMO samples. Conclusion that port areas should be considered as a discrete compartment may be based on a small number of samples taken from some of the small number sites that do not dredge regularly (sometimes 15 years or longer in between episodes).

Added a sentence to note that the DMMO database is not exhaustive, including only data from select more recent projects. Potential causes of specific observed high concentrations would need to be a separate study for each site itself.

From J OHara comments

P4 line 3
Jon Konnan:Do we have evidence that localized sources still exist in local watersheds draining to the Bay?
J.OHara: I also have concerns with this sentence; seems like a bridge too far for this report. "May" isn't enough to bridge the gap IMO.

Revised sentence further. Rather than just may "It is unknown if"

P35line 19
JOhara: this statement should go no further than to say something like "and may help determine whether management actions would result in load reductions." Please don't jump from defining near-shore dioxin profiles to talking about management actions!
Used suggestion: "and may help determine whether management actions would result in load reductions."

P35 line 29-36

I don't see a basis for such a definitive statement. Even though it says "may", this reads like "can". What would the reservoir of dioxin have to be in upland sites, and how much would have to be removed/isolated, in order to actually see dioxin in the Bay reduce at a faster rate?

Ditto. Perhaps there is upland data I'm not aware of. Still, do you know it's likely? Or are you speculating that it's likely? See above.

Seems more scientific to say "we don't know whether and how much dioxin remains in the landscape, so…"

New wording:
Through a combination of focused and more widespread management action, dioxin impairment potentially could be reduced on a faster timeframe than monitored natural attenuation. If there are nearshore sites that are more highly contaminated, they may indicate past or current localized sources or pathways of higher dioxin loading. Therefore, measurement of dioxins in select dredging projects or study locations, particularly for sites near the shore (e.g., <250 m) or/and with previously measured high dioxin concentrations nearby, should be considered. Although in dredging, the material measured has been or will often be moved offsite, it is unknown whether the original source may remain in the landscape, so ongoing measurement and reporting of dioxin data in near-shore studies can be useful in identifying potential upland localized and watershed sources for additional focused characterization and possible management.