Regional Monitoring Program for Water Quality in the San Francisco Estuary

Contaminant Fate Workgroup: Five-Year Workplan

DRAFT

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SFEI Contribution XXX

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EXECUTIVE SUMMARY

The Regional Monitoring Program (RMP) Contaminant Fate Workgroup (CFWG) is concerned with the fate of pollutants after their introduction to the Estuary and links up to their subsequent biological exposure or effects. Much of the work under the CFWG to date has been on persistent particle-associated bioaccumulative pollutants for which total maximum daily loads (TMDLs) have been or are being developed, especially PCBs, for which a multi-box hydrodynamic and sediment mass balance model was developed. As TMDLs for other pollutants develop, some of them (especially other persistent hydrophobic organic compounds) may be examined using a similar mass budget framework through adjustments to the multi-box tool.

The focus of RMP fate studies will shift away from PCBs in the future as management priorities change and more pressing information needs are identified. Current management priorities, pollutants, and processes of interest to environmental managers and their current major uncertainties are briefly described, and roughly grouped into low, medium or high priority categories.

A five-year plan to address current priorities is described. One high priority need for better information is for mercury, where an approach focused on reducing total mass will result in little near-term change. There are currently large uncertainties in the distributions and transformations among mercury species, which greatly influence bioavailability and bioaccumulation. Mercury will be a primary focus of the CFWG in the near term, with studies to address the highest priority questions identified in the RMP Mercury Strategy. One study ("food web uptake"), with joint oversight by the CFWG and the Exposure and Effects Workgroup, will examine spatial and temporal patterns in uptake of mercury into the Estuary food web. Another study ("high leverage pathways") under the guidance of the CFWG will have the goal of identifying processes, sources, and pathways that contribute disproportionately to food web accumulation. The high leverage pathway study is being funded through a RFP for a two-year study in 2008 and 2009. In 2011, it is tentatively planned to shift emphasis more towards high leverage pathways, with the anticipation that the food web uptake study will have answered the major questions about spatial and temporal patterns in food web uptake. Other near-term needs include broader characterization of multiple legacy pollutant inventories in Bay sediments, being addressed through an ongoing sediment coring and analysis project, and developing conceptual and quantitative models for mercury and other pollutants as a framework for summarizing improvements in understanding.

Rough budgets and (annual resolution) timelines for planned CFWG studies and activities in the next five years are presented. As management needs evolve and conceptual models incorporate new information, this workplan will evolve in parallel to document and provide rationale for changes in priorities, and identify planned studies to address those needs for subsequent five-year periods.

INTRODUCTION

The Regional Monitoring Program for Traces Substances (RMP) is an innovative collaboration created in 1993 between the San Francisco Estuary Institute (SFEI), the San Francisco Bay Regional Water Quality Control Board (RWQCB), and the regulated discharger community. The mission of the RMP is to provide the information needed by policy makers, water quality managers, and the public to make decisions about stewardship of San Francisco Bay.

In 1997 the RMP underwent a Program Review concluding with the following recommendation: "Mass-balance inventories of contaminants should be developed which can, in turn, lead to models that attempt to account for the distribution, fate, and residence time of contaminants in the Bay." and "[Synthesis and interpretation] They are essential for converting raw data to information useful in decision making, for planning and adjusting future sampling, validating the quality of data, and for engaging creative scientists and managers in the monitoring process."

In response to the 1997 Review a Sediment Workgroup was formed to address questions regarding contaminant transport and fate in Bay sediments. The Contaminant Fate Workgroup (CFWG) was formed in 2002 to address the recommendations of that group regarding fate and transport processes in the ecosystem, with the Exposure and Effects Workgroup (EEWG) formed to address contaminant impacts on the ecosystem. Although the Sediment Workgroup focused on the fate of sediment-bound contaminants, the continuum of interactions among ecosystem components requires an understanding of those connections in order to effectively manage. The CFWG works with the Sources Pathways and Loadings Workgroup (SPLWG) as well as the EEWG to ensure that these intersections are not overlooked.

In August 2007 another RMP workgroup was formed to develop a program-wide strategy specifically for mercury. Mercury is one of the highest priority pollutants in the Bay, and was the first pollutant for which a TMDL was developed (Looker and Johnson 2004). Mercury is the first pollutant that is being treated in this manner in RMP planning. The Mercury Strategy Team has identified priorities for mercury work in the Program that will be described below.

The purpose of this workplan is to outline a strategy for the CFWG to address RMP objectives and management questions over the next five years, 2008 to 2012. In addition, this workplan presents a rationale for prioritizing the studies and tasks needed to address these objectives and questions. This plan will be revised and updated each year to reflect new findings and shifts in conceptual understanding and management priorities. This workplan presents CFWG activities conducted to date, current objectives and management questions, and priorities and activities planned for the next five years.

This document is provided to the CFWG for review and comment, incorporating input from managers and scientists on relative priorities, and fleshing out details of specific projects recommended for implementation, with products, timelines, and estimated budgets. We envision this workplan as a "living document" with periodic revision as studies by the CFWG and other RMP workgroups, or other groups locally and nationally, provide additional information to revise our conceptual thinking, approaches, and priorities.

MANAGEMENT CONTEXT

In the development of TMDLs and other plans to manage environmental pollutants, there are often large gaps in our knowledge: in the breadth and degree of contamination; the sources of pollutants; the transport or degradation processes that may ameliorate (or exacerbate) the problem in various areas; the effects of pollutants on biota. Although there is a need to take action despite these uncertainties, as we collect better information, these action plans can be continually modified to address the most pressing needs in a cost-effective manner.

The CFWG helps ensure that the work of the RMP related to fate studies is scientifically sound and relevant to management needs for attaining water quality standards. Two general topics covered by the CFWG that are critical to TMDL development are 1) forecasts of patterns of ecosystem impacts based on a quantitative understanding of fate and transport processes (i.e., fate models); and 2) the linkage of sources and pathways of pollutants with impacts.

Although much of the attention and investigation to date has largely paralleled the TMDL approach focusing on single contaminant mass balances, future investigations may follow other approaches; however, relevance to specific management needs (e.g. choosing among potential control actions, predicting results expected from those actions) should always be made clear. To this point, products and tasks in the CFWG have focused on the fate of PCBs in the Estuary, although some of the processes (e.g. sediment resuspension and erosion) important to the understanding the fate of one type of pollutant are often applicable to other pollutants.

IMPORTANT BAY CONTAMINANT FATE WORK TO DATE

Table 1 lists some of the many studies have contributed to our understanding of pollutant fate in the Estuary, including both pollutant-specific and general fate and transport processes.

The development of a simple, one-box mass budget model for PCBs began under the guidance of the RMP Chlorinated Hydrocarbon Workgroup (Davis and Yoon 1999), was completed as a technical report in 2002, published (Davis 2004), and then revised (Connolly et al. 2005, Davis et al. 2007). The revised one-box model has been used in development of the PCB TMDL (SFBRWQCB 2007). A special study developing a PCB food web model (Gobas and Wilcockson 2003) was also a project reviewed by the workgroup used in the PCB TMDL. The CFWG has also provided review and oversight for application of the one-box model to other pollutants (e.g. PAHs (Greenfield & Davis 2005), legacy pesticides (Leatherbarrow et al. 2003)) and will review and provide input on further mass balance exercises including budgets for PBDEs currently in draft (Oram et al., draft) and potentially for methylmercury or other contaminants.

Subsequent projects still underway include the multi-box PCB model (currently in draft, Oram et al. 2008), an expanded food web model (Gobas and Arnot 2005), and a sediment coring study (AMS & SFEI 2005). Since the formation of the Clean Estuary Partnership (CEP), the CFWG has provided review for projects conducted jointly by the RMP and the Clean Estuary Partnership (CEP), such as the multi-box model. Although reducing new sources and loadings of contaminants to the Estuary is an important goal, in some cases, understanding the processes by which historical contaminants are distributed and redistributed in the Estuary from both current and legacy sources may be critical for reducing biological exposure and effects (e.g., mercury, PCBs, and other contaminants with large legacy pools).

The one-box model for the various contaminants noted above was a greatly simplified representation of the complex interactions of a very heterogenous and dynamic Estuary. Nonetheless, the model was useful in identifying major influences on the loads and fate of contaminants in the Estuary. Because hydrophobic organic contaminants, such as PCBs and OC pesticides, are frequently associated with sediment particles, the one-box model was most sensitive to parameters affecting sediment fate and transport: depth of the sediment mixed layer; average sediment contaminant concentrations used; and the initial mass of the sediment contaminant pool, a product of contaminant concentrations and total sediment mass defined by the mixed layer depth (Davis 2004).

Several features of the Estuary were not captured in the one-box model, in particular differences among segments including: residence times in the water column and sediments in different segments of the Estuary; spatial distribution of contaminant inputs throughout the Estuary; erosion and deposition of sediments and associated cycling of contaminants within the Estuary; and potential rapid export of PCB inputs to the open ocean under high flow conditions. Despite these limitations, a one-box model was a useful tool for organizing available information, identifying data gaps, and developing conceptual understanding of ecosystem processes in the Estuary.

The RMP conducted a literature review to understand the dominant factors and uncertainties influencing fate and transport of sediment-associated contaminants in the Estuary (Leatherbarrow *et. al.* 2005). The objectives of the literature review were two-fold: to provide an overview of available information on the long-term fate of particle-associated contaminants and their transfer between sediment and biota; and to recommend future studies to address current data gaps. Major findings of the report are summarized below:

- Particle-associated contaminants are widespread throughout the Estuary, but spatially heterogeneous; many contaminants are typically higher in southern segments of the Estuary than in the northern reach and higher on the margins of the Bay than in deep channels. Areas of relatively high sediment contamination often coincide with areas of high concentrations in top consumers, such as sport fish and piscivorous birds.
- Data from a few depositional sites in the Estuary indicate that concentrations of ‘legacy’contaminants are highest at depths where sediment was deposited during periods of peak usage. Large-scale erosion or dredging of buried sediment in such areas could potentially exacerbate water quality and food web uptake problems.
- Bathymetric studies indicate that northern and southern areas of the Estuary are gradually eroding. As previously depositional areas of the Estuary continue to erode, release of sediments with high subsurface maximum concentrations may prolong water quality problems and exposure of contaminants to sensitive food web components.
- The depth of the actively mixed sediment layer exchanging with the water column greatly influences the long-term fate of persistent contaminants in the Estuary. The mixed sediment layer is highly variable throughout the Estuary and is in the range of

approximately 3 to 50 cm. Time scales for contaminant dispersion in the top 15 to 25 cm of sediment have been measured on the order of 60 to 100 days.

An initial PCB food web model (Gobas and Wilcockson 2003) was later revised to better address contaminant transfer and uptake into wildlife and humans (Gobas and Arnot 2005). Based on concentrations of PCBs in sediment and water, the model estimated concentrations of PCBs in select species, such as seals, birds, and fish residing in the Estuary. Sport fish, such as shiner surfperch, white croaker, and jacksmelt, are commonly caught and consumed by fishers and were therefore included to evaluate potential exposure to humans. A food web model was used for estimating the PCB concentrations in sediment and water column needed to achieve an adequate safety margin for wildlife and human exposure.

To address the limitations of one-box models, the RMP has collaborated with USGS on a multi-box model for San Francisco Bay, coupling a 51-segment tidally averaged salinity box model of San Francisco Bay previously developed by Uncles and Peterson (1995, Figures 1 & 2) with a sediment-transport module (Lionberger and Schoellhamer, 2003) linked to a model of contaminant partitioning and transformation processes. The multi-box model is better able to mirror the differences in contaminant and sediment loading rates and ambient contaminant distributions found among Bay segments due to its ability to capture finer spatial resolution. The model has been coded and tested over a range of input parameters, with model documentation and uncertainty analysis reports (Tetra Tech 2007, Oram et al. 2008) completed, and the final technical report scheduled for completion in early 2008.

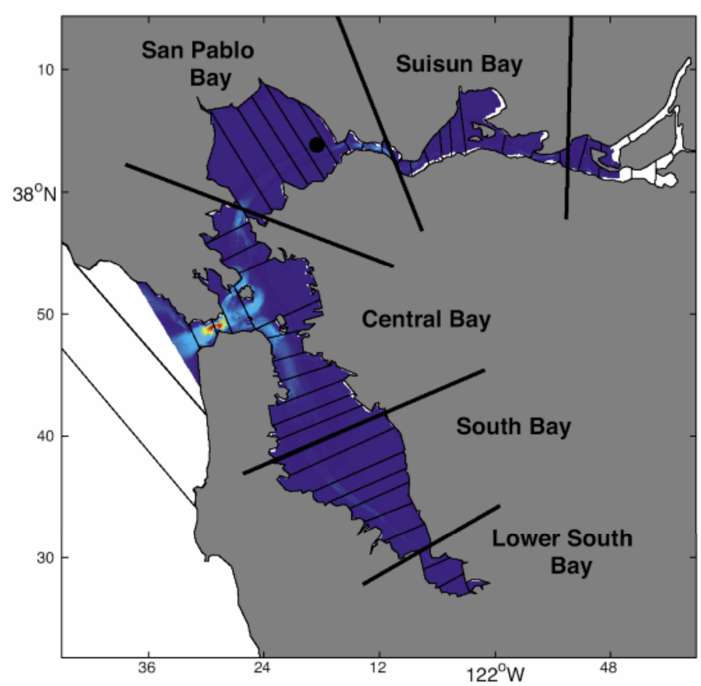

Figure 1: Schematic map of San Francisco Bay illustarting model boxes (Uncles and Peterson, 1996) and bay segments. The dot (●) indicates the location of the sediment core.

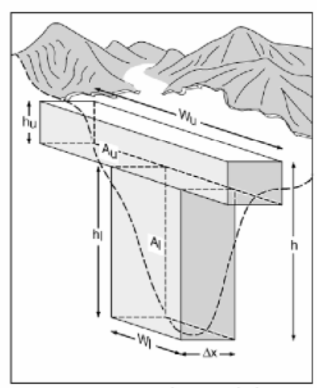

Figure 2: Sample model cross-section illustrating upper and lower boxes (Uncles and Peterson, 1996).

Testing of the one-box model revealed the sensitivity of its response to several parameters for which there was high uncertainty, in particular the sediment mixed layer depth, which affects the size of the sediment pool which may exchange with the water column, and the sediment contaminant distribution with depth, which determines the mass of contaminant in the system. Although model parameters were set using the best available information at the time, the availability of detailed information on contaminant distributions with depth for only a few sites in the Estuary constituted a major data gap. Large differences in mixed layer depth among various sites and studies in the literature review also highlighted the need to characterize or estimate this parameter for different areas of the Estuary.

More representative data are needed for these parameters in the Estuary, regardless of whether the one-box, multi-box, empirical, or other models are applied. CFWG has previously recommended the collection of additional field data (particularly cores) to determine the distribution of contaminants with depth, providing information on mixing of surface and deeper sediments. These data are also critical to the verification of the multi-box model results. An initial sediment coring field sampling campaign was undertaken in the summer/fall of 2006. Core samples from 17 sites (11 in the Bay, 6 in wetlands fringing the Bay) were collected and are currently being analyzed. Radiodating is expected to be complete by first quarter 2008, with chemical contaminant analyses completed in mid 2008. The results will be used to quantify the vertical distribution of measured pollutants in the sediments and the ages of those sediments to better understand and verify expectations of sediment processes such as mixing and deposition or erosion in various areas of the Estuary. Eleven cores in the Bay are a substantial addition to the data previously available on sediment core contaminant distributions in the published and gray literature, but are unlikely to constitute a representative sampling of the various Bay segments. Additional core data will likely be needed in the future, with appropriate numbers and locations of future coring to be determined based on outcomes of the current work.

OBJECTIVES AND MANAGEMENT QUESTIONS ADDRESSED

RMP Objectives and Management Questions

The overarching goal of the RMP is to **provide information needed to support management decisions.** In concert with the development of a comprehensive five-year plan for the RMP (of which this document represents one component), the objectives and management questions that guide the Program are currently being revised. The current draft RMP objectives and management questions are shown below, with questions that are pertinent to the CFWG shown in *italics*. (These objectives and questions are still undergoing revision, and their format and organization may change, but the subject areas identified are not likely to change significantly.)

Objective 1. Describe spatial patterns and long-term trends of pollutant concentrations in the Estuary

1.1 Do pollutant spatial patterns and long-term trends indicate particular regions of concern?

1.2 Are management actions effective in reducing pollutant exposure in the Estuary?

Objective 2. Project future impairment

2.1 What patterns of impairment are forecast for major segments of the Estuary under various management scenarios?

2.2 Which contaminants are predicted to increase and potentially cause impairment in the Estuary?

Objective 3. Describe sources, pathways, loading, and processes leading to pollutant-related impairment in the Estuary

3.1 Which sources, pathways, and processes contribute most to impairment?

3.2 What are the best opportunities for management intervention for the most important pollutant sources, pathways, and processes?

3.3 Are management actions effective in reducing loads from the most important sources, pathways, and processes?

Objective 4. Characterize the potential for adverse effects on humans and aquatic life due to pollution of the Estuary ecosystem

4.1 Which chemicals have the potential to adversely effect humans and aquatic life and should be monitored?

4.2 What potential for adverse effects on humans and aquatic life exists due to pollutants in the Estuary ecosystem?

4.3 Are management actions effective in reducing the potential for adverse effects on humans and aquatic life due to Bay pollution?

Objective 5. Provide monitoring information for comparison to regulatory guidelines and for establishing regulatory guidelines

5.1 What percentage of the Bay is impaired?

5.2 What is the percentage and degree of impairment in each Bay segment?

5.3 What are appropriate guidelines for protection of beneficial uses?

Objective 6. Effectively communicate information from a range of sources to present a comprehensive picture of the sources, distribution, fate, and effects of pollutants and beneficial use attainment or impairment in the Estuary ecosystem.

RMP work overseen by the CFWG focuses on developing forecasts under various scenarios (Objective 2) and linkages of contaminant loads from various sources and pathways to ecosystem impacts (Objective 3).

PRIORITY CONTAMINANTS AND FATE ISSUES

The contaminants of primary interest for the CFWG are in large part defined by the needs of local management agencies. Most of these are already included in the National Toxics Rule and California Toxics Rule lists, with legacy and/or ongoing inputs previously or currently resulting in impairment of various beneficial uses or other impacts on the San Francisco Estuary. There is also a need to proactively identify emerging contaminants, which are the focus of the Emerging Contaminants Workgroup (newly formed in 2006) and may be included in subsequent versions of the CFWG workplan as information gaps and questions specific to new contaminants are identified.

Some contaminants of concern to the CFWG have been investigated by or in concert with the Clean Estuary Partnership (CEP), which was largely concerned with collecting information for the rationale and development of water quality attainment strategies for various Bay contaminants, in particular with respect to current and planned TMDLs. This resulted in development of a set of Conceptual Model/Impairment Assessment reports for a number of pollutants of concern: diazinon, dioxin, legacy pesticides, mercury, PCBs, and selenium, available in draft or final form via the CEP website (http://www.cleanestuary.org).

Pollutants

Current pollutants of interest to the RMP and local environmental managers are listed below by relative priority, which will evolve and be revised over time as major uncertainties are addressed or new effects are found and priorities change. Issues and uncertainties specific to each of these pollutants are also discussed below.

High- TMDLs developed, active management /bans

The most intensive efforts are being taken towards reducing loads and impacts of the following contaminants, with environmental concentrations well above target criteria, and TMDLs developed or near completion.

PCBs-

Production and new applications of PCBs have been banned since 1979, but legacy inputs and their very long persistence cause them to remain an ongoing concern. There are no truly new sources, but ongoing transport from soils and sediments in watersheds and failing equipment still in use may provide continued loadings to the Estuary.

Implementation actions recommended by the TMDL (Hetzel, 2007) provide some general guidance for potential future CFWG study efforts. Information needs listed in the PCB TMDL for San Francisco Bay are largely related to improving quantitation of various loads (largely covered by the Sources Pathways and Loads Workgroup, SPLWG), but the TMDL staff report also identifies other critical data needs: *"Data and other information are needed to assess both the progress toward attainment of the numeric fish tissue target and to inform the adaptive implementation of the TMDL. Dischargers will therefore be required to support the following studies to fill critical data needs. "*

Needed study areas mentioned in the TMDL staff report include the following:

1. PCBs mass budget modeling and food web model improvements
2. Rate of natural attenuation of PCBs in the Bay environments

Many specific elements within the same study areas were identified in the PCB CMIA. Some of the most critical needs mentioned include:

1. The subsurface inventory of PCBs in different parts of the Bay;
2. The historic trajectory of recovery on regional and local scales
3. Present trends in concentrations in sport fish and other integrative indicators of interannual variation in food web PCBs;
4. The loss of PCBs and sediments to the ocean through the Golden Gate; and
5. *In situ* degradation rates of PCBs.

Data gaps and possible studies to address them identified in the PCB CMIA are included here as Appendix Table 1. Information needs with high priority for TMDL and/or technical understanding, with high uncertainty, and highly feasible are the highest priorities. Needs listed under "Processes" in the CMIA are most directly relevant to the CFWG, but other topics are also integral to the understanding of PCB fate in the environment.

Thus far, PCBs have received the greatest attention and allocation of resources for RMP contaminant fate studies. Although there will continue to be great interest and concern about PCBs in the Bay, further focus on PCBs will mainly be on model refinements that might be extrapolated to other contaminants.

Mercury (Hg)

There was a large legacy input of Hg from mining activities, as well as ongoing (potentially growing in some media like air) inputs; only a small fraction of total loads are present as the most bioaccumulative methylmercury (MeHg) form (typically <1% of total Hg in the Estuary, Figure 3), with no apparent correlation between total Hg and MeHg.

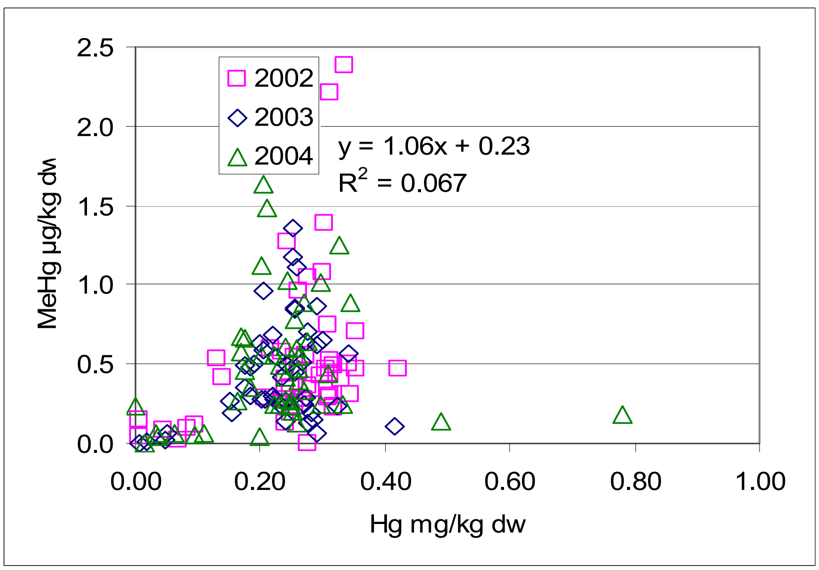

Figure 3. MeHg vs total Hg in San Francisco Bay Surface (0-5cm) sediments

Similar to the PCB TMDL, in addition to load reductions, the San Francisco Bay Mercury TMDL staff report (2006) recommends that dischargers *"Conduct or cause to be conducted studies aimed at better understanding mercury fate, transport, the conditions under which mercury methylation occurs, and biological uptake in San Francisco Bay and tidal areas."*

Many of the same approaches would apply to Hg as they would for PCBs, although MeHg, rather than total Hg, is the primary parameter of interest when considering biological impacts. *In situ* production and removal processes of MeHg complicate understanding and prospects for management; small and moderate changes in total Hg loading may show little or no short- or mid-term effect. Thus an added area of interest for MeHg (but not for PCBs) is in relative rates of (Me)Hg transformation from different sources

Because PCBs and total Hg are largely bound to particles in the aquatic environment, modeling efforts tracking sediment movement such as the one-box and multi-box models will perform reasonably well in tracking the major masses of these contaminants. However, unlike PCBs, the persistence of MeHg is days to weeks, rather than months to years. Also unlike PCBs, MeHg degradation pathways are reversible; *in situ* production of MeHg from

Hg in the Estuary likely constitutes a major proportion of mercury that enters the food web. Numerous factors that differ on small spatial and temporal scales (DOC, pH, DO, sulfate/sulfide redox) influence the methylation and demethylation rates of MeHg. Although on global or regional scales, lumped parameter models (e.g. McCleod & McKone 2006) may suffice to approximate large scale system response (with temporal and spatial variations averaging out), variations in MeHg found in biota on Bay segment or smaller scales are not effectively captured, as our current understanding of these transformation processes are not yet sophisticated enough to use predictively.

Mercury priorities

The RMP Mercury Strategy Team has developed a specific set of questions for this top priority pollutant. The strategy for providing the information most needed by managers is to address these questions in the order presented.

1. Where is mercury entering the food web? (paraphrase of RMP MQ 1.1)
2. Which processes, sources, and pathways contribute disproportionately to food web accumulation? (RMP MQ 3.1)
3. Can we do anything about these high-leverage processes, sources, and pathways? (RMP MQ 3.2)
4. What effects can be expected from management actions? (RMP MQ 2.1)
5. Will total mercury reductions result in reduced food web accumulation? (a form of RMP MQ 2.1)

Some of these same information needs have been identified in the CEP's Hg CMIA and are included as Appendix Table 2.

Question 1 is most directly answered through monitoring accumulation of MeHg in the food web. Biomonitoring efforts such as the RMP Small Fish Study (Table 2) provide direct measures of exposure and indications of the areas (and potentially time periods) of greatest concern, which may be useful in identifying localized sources or other processes leading to increased exposure. Food web monitoring to evaluate spatial and temporal trends is primarily the purview of the RMP EEWG, but the information derived is reviewd by the CFWG to prioritize potential areas to focus other study efforts.

Question 2, identifying specific processes, sources, and pathways that most contribute to (Me)Hg accumulation and potential impacts (e.g., in sport fish and sensitive wildlife species) will help in developing strategies to manage Hg contamination, a primary focus of the CFWG over the next five years. This approach provides some hope (but no assurance) for reducing Hg impacts in a decadal time frame, versus strategies focused primarily on reducing total Hg in the Bay, expected to take on the order of 100 years or more (Looker & Johnson 2004) given the existing mass already in place.

One step toward identifying or narrowing down potential high leverage Hg processes, sources, and pathways may be through a methylmercury mass budget. Another step taken in late 2007 was the issuance of a request for proposals soliciting special studies (up to $200,000 over 2 years) to investigate these factors. The CFWG will be involved in reviewing and selecting among these studies, and in guiding the final study scopes and designs to ensure that they meet management needs.

Moderate –TMDLs / restrictions planned, or (re)evaluating priority

PBDEs-

Two PBDE formulations (penta- and octa- mixes) have been banned in California, but there is continued use/release of the deca- mix, which can degrade to some lower brominated isomers. Legacy releases of octa- and penta- mixtures are likely to contribute the majority of lower brominated congeners in the near term. Biological effects thresholds are still being studied, but tissue PBDE levels have doubled in a short span for some species of concern. There is some evidence of leveling or decreases for some congeners in the environment, possibly resulting from timely management action (e.g. the ban of some mixtures), dispersion, and degradation processes, which are typically faster than for PCBs.

Dioxins/Furans-

Although there are few data on PCDD/F distributions in water and sediment media in San Francisco Bay, concentrations in fish tissue are above recommended thresholds. Better information on distributions, sources, degradation rates and other loss pathways would be needed to characterize and manage this risk. Although limited data for the Bay suggest dioxin-like PCBs contribute ~80% of total toxic equivalents (TEQs), dioxin/furan contributions to TEQs alone are 5 times higher than the screening value and present their own sources and management considerations that are different from those for PCBs.

Selenium-

There are ongoing Se inputs from the Central Valley and local watersheds, and high tissue concentrations persist in some species despite greatly reduced loads from refinery sources. This raises questions of which forms and loads of selenium are most critical to bioaccumulation, and highlights a need to understand ecosystem processes that transform selenium to bioaccumulated forms. Like MeHg, selenium can undergo rapid biologically-mediated transformations in the environment, with large differences in bioavailability and uptake rates among the different forms. USGS (Luoma and Presser, 2004) and other researchers (Cutter & Cutter, 2004, Meseck & Cutter, 2006) have modeled transformations and relative biouptake rates of various Se forms; site-specific characterization of Se speciation will be needed to understand relative risk from Se at different locations. Projected changes in loadings of particular Se species might then be applied in a model to examine potential results of management actions.

PAHs-

Studies suggest sublethal effects at much lower concentrations than established toxicity thresholds; increasing watershed urbanization and continued increases (per capita and population level) in petroleum fuels use raise concerns. Large uncertainties in sources and loads and degradation rates lead to large uncertainties when estimating mass balances (Greenfield 2004), which limit our current ability to quantitatively predict future trends and impacts of potential management actions. Lab estimates under realistic environmental conditions or field measures of degradation pathways and by-products are needed to better constrain modeling efforts.

Current use pesticides-

Episodic toxicity in urbanized streams and proximate receiving waters are often attributed to current use pesticides; previously diazinon and chlorpyrifos, now largely supplanted by pyrethroids. The shift to more hydrophobic pyrethroids increases the importance of sediment fate to understanding impacts of current use pesticide fate and transport. A major issue is that regulatory restriction of a pesticide with demonstrated adverse side effects often leads to replacement by other pesticides, until their negative impacts are found, in an ongoing cycle. Generalized models of water and sediment transport, combined with chemical-specific partitioning and degradation parameters may allow us to address emerging pesticide issues as use patterns change. Tracking evolving use patterns and loads is to be done under review of the ECWG and SPLWG, after which questions of ecosystem fate (e.g. partitioning and degradation rates) for particular compounds will arise for examination under the CFWG.

Pharmaceuticals and personal care products (PPCPs)-

There is much interest in potential effects of PPCPs, but there is currently little information on environmental distribution, and documentation of effects has largely been in lab settings. Similar to pesticides, the first challenge is establishing the nature and extent (under the ECWG & SPLWG) of environmental risks posed by particular compounds, after which specific questions about ecosystem fate can be addressed under the CFWG. Generalized water and sediment transport models combined with compound specific parameters (e.g., partitioning, degradation rates) will allow predictions of PPCP fate.

Low –under control/low priority under status quo

Although less intensive efforts are being made to reduce loads of the following contaminants, if ongoing monitoring shows lack of progress, additional intervention and study may be required to reduce loads, data gaps, and uncertainties.

Organochlorine pesticides (OCPs)-

Organochlorine pesticides have been banned for most uses since the ~1970-1980s, although there may be continued inputs from legacy deposits in watersheds and the Bay. Biological effects are likely to decrease over time as these legacy deposits continue to degrade and disperse, but there is potential utility for OCPs as calibration data for hindcast modeling efforts applied to water and sediment transport models. If OCPs do not continue to decrease as would be predicted from their banning and estimated degradation rates, finding unaccounted sources will likely be the highest priority. However, reexamination of predicted degradation rates may be warranted as well.

Trace metals (Cu, Ni, Ag, As, Cd Cr, Pb, Zn)-

Some of these are decreasing with changes in uses and source control (e.g., no more Pb in gasoline, Ag in photo processing). Although many of these metals have ongoing inputs that may increase slightly (e.g., increasing Cu in brake pads), concentrations are currently below regulatory effects thresholds. Sediment transport in the Bay combined with watershed loading predictions will allow projections of future concentrations for these elements. Improved speciation models (e.g., the EPA Biotic Ligand Model) in the future could also allow better prediction of local speciation and likely biological impacts without extensive and expensive site-specific water effects toxicity testing.

- General Fate and Transport Processes

Although questions about factors influencing Hg fate in the Bay will command much CFWG attention in the near future, information applicable to multiple contaminants will continue to be important as we work to develop better understanding of current and emerging pollutant issues. A general framework for examining these is via RMP MQ 2.1:

What patterns of impairment are forecast for major segments of the Estuary under various management scenarios?

Sediment core analyses-

The multibox PCB model has highlighted the influence of the depth profile of sediment pollutant deposits and processes on recovery of the Bay from persistent, particle-associated pollutants. The erosional sedimentation regime in the Bay further heightens the importance of pollutants at depth. Present information on depth profiles is still extremely limited (profiles from 2 cores are available for organics, and a few more for mercury and other metals), though additional RMP coring work is currently in progress that will provide data from another 17 cores. For an estuary as heterogeneous and dynamic as San Francisco Bay, additional cores will be needed to provide a reasonable basis for forecasting the recovery of each segment of the Bay. Continued coring is therefore included as another primary element of the five-year plan.

Multi-pollutant modeling-

Continued application and refinement of predictive models is another high priority activity for the next five years that will support development of forecasts. The one-box or multi-box framework that has been developed for PCBs can be applied to other pollutants, particularly where there is slow or irreversible transformation, and where the primary processes are partitioning and transport, with biouptake largely modeled as a partitioning process. Thus PCBs, OCPs, PBDEs, PAHs, dioxins, and other persistent hydrophobic contaminants can share a common model, with adjustments to account for differences in parameters such as octanol-water partition coefficients, air-water partitioning, and degradation rates. These box models can be used as extended conceptual models or as screening tools for potential problem contaminants, identifying major information gaps in a semi-quantitative manner. As sufficient information is obtained, more detailed evaluations of a pollutant may be applied to box models as was done for PCBs.

Such mass balance approaches can also work with some of the trace element contaminants, presuming the major biological concern is with the total mass of that element, rather than with any particular species. If all the mass of an element is interconvertible within the time scale of management action and desired observed response, then tracking total mass balance may also be suitable despite transformation and speciation, assuming these processes are uniform over the spatial and time scales of interest.

However for elements such as Hg and Se mentioned previously, transformations are relatively rapid compared to residence times of total masses, and in the case of Hg, the most biologically active form typically constitutes such a small and variable portion of the total mass that parameters other than the total mass are likely to play a major role in its fate and biouptake. For these contaminants, studies refining our understanding of factors affecting speciation and transformation processes leading to exposure of sensitive species are far more important than efforts to refine tracking of total masses.

ALTHOUGH SITE-SPECIFIC DIFFERENCES IN FOOD WEB STRUCTURE ALSO INFLUENCE EXPOSURE OF SENSITIVE SPECIES, THERE ARE FEWER APPARENT CONTROL ACTIONS (E.G. INVASIVE SPECIES CONTROL, WETLAND HABITAT RESTORATION DESIGN) THAT MIGHT BE CONSIDERED TO DIRECTLY MANAGE THESE FACTORS.

FIVE-YEAR PLAN FOR RMP FATE STUDIES

Specific Questions to be Addressed in the Next Five Years

Two top priorities to be addressed by the CFWG in the next five years are briefly described below and will be addressed in more detail later in this section. A major focus for the CFWG is to obtain better information to manage the Hg problem in the bay, expressed in the Mercury Strategy Team management question:

Which processes, sources, and pathways contribute disproportionately to food web accumulation of mercury?

A critical step towards reducing mercury impairment of beneficial uses is to identify sources and pathways that contribute most to impairment ("high leverage sources"). Impairment is caused by the net production and accumulation of methylmercury by biota, so a focus on reducing methylmercury sources, pathways, and processes holds some hope for reducing impairment in a 10- or 20-year time frame, in contrast to strategies to reduce total mercury in the Bay requiring 100+ years(Looker & Johnson 2004).

It is unclear what would be the best approach to identify high leverage sources, and it is also unclear whether they could be reduced. A number of possible studies have been discussed, and the RMP has issued a RFP to solicit potential studies to fund. A major role for the CFWG is to develop an optimal course of study, recommending, selecting from among, and/or revising proposed studies to best investigate these high leverage mercury sources.

A less pollutant-specific focus is contained in the more general RMP management question:

What patterns of impairment are forecast for persistent, particle-associated pollutants for major segments and the Estuary as a whole under various management scenarios?

The multibox PCB model highlighted the influence of pollutant depth profiles on recovery of the Bay from persistent, particle-associated pollutants. The erosional sedimentation regime in the Bay further heightens the importance of pollutants at depth. Pollutant depth profile data are currently limited, though additional RMP coring work is currently in progress. For a heterogeneous and dynamic estuary like San Francisco Bay, more core data will be needed to provide a reasonable basis for forecasting the recovery of each segment. Continued coring is included as a substantial part of the five-year plan.

Continued application and refinement of the multi-box model for developing forecasts is another high priority activity for the next five years. The multibox framework that has been developed for PCBs could be applied to other pollutants, either as a rapid screening tool to evaluate pollutants on a gross scale, or for more detailed evaluation such as was performed for PCBs.

Specific near-term (five-year) studies to address these questions, planned or underway, and other potential studies (to be considered as resources become available or as priorities adjust), are described below.

Current Studies

General Fate and Transport

Near-term priorities for CFWG projects include projects currently underway, including in particular the coring studies and multibox modeling efforts mentioned previously. These studies are not tied to understanding of particular contaminants, but are valuable to a general understanding of Bay hydrodynamics and sediment transport.

Sediment Contaminant Distributions and Dating (MQ 1, 2)–

Existing coring data sets (Hornberger, Venkatesan, and Fuller, 1999, C. Conaway, UC Santa Cruz, pers. Comm., Marvin-DiPasquale, 2003) are not expected to be representative of the Estuary in general and thus are of limited usefulness for understanding Estuary-scale processes. Collection of these sediment cores will provide valuable information on vertical profiles of contamination in wider areas of the Bay; and data on sediment mixing, accumulation, and burial rates to characterize regional variation. This characterization study is of very high priority, given the limited data and assumptions on which much of the forecast modeling currently rests. Utility of coring data is not tied to any particular fate and transport model, and if sufficiently distributed and representative, can be used in either mechanistic or empirical models. Completion of this project is anticipated in late 2008.

Multi-Box Modeling (MQ 2)–

The ongoing development of a multi-box model in cooperation with USGS improves on the spatial resolution of the simple one-box-model previously used to predict the long-term fate of PCBs, PAHs, and OC pesticides. This overcomes limitations in the one-box model, which treats all sediment inputs, regardless of size or location, as being immediately uniformly redistributed throughout the Estuary ecosystem. The multi-box model is better able to predict spatial differences in contaminant distribution along the transect of Bay segments, although the model design cannot yet capture lateral variations (across the Bay spine) and shows some artifacts resulting from optimization based on net sediment accumulation. A three-dimensional model may overcome some of these limitations, with the priority of such a project to be determined by future management needs. Completion of the current multi-box model is a high priority and anticipated for early 2008.

Outflow through the Golden Gate-

At present, the USGS does not measure the suspended sediment concentration at the Golden Gate due to the high flows that occur at the Bridge and the difficulty of maintaining equipment at this site. As a result, we do not have a very good understanding of the sediment flux out of the Estuary. A special study proposed in 2006 and currently underway is examining the feasibility of an alternative using satellite imagery to generate first order estimates of Golden Gate outflow during major discharge events. This project is scheduled for completion in March 2008.

Probable Future Work

Concepts for future work that should be considered by the CFWG include some studies addressing specific chemical contaminants, and others examining general transport processes. Also included below are some notes about information gaps, for which studies have not yet been planned or proposed.

General Fate and Transport

Sediment Contaminant Distributions and Dating (MQ 1, 2)–

Completion of the current coring project is expected in late 2008, but more data are needed in the future to get more "representative" distributions for other areas of the Bay. A possible design would be piggybacking on the RMP S&T sediment cruise, coring 1-2 randomized sites on an annual basis. Such a distributed effort would also benefit radiodating efforts for measuring short-lived isotopes in more core sections, given limited staff and equipment at many labs preventing quick turnaround for large numbers of samples. The proposed five-year plan (Table 2) includes funding for continued sampling every other year to further characterize depth profiles of high priority pollutants. The alternating-year approach will allow for an adaptive approach, with evaluation of results from each round of sampling prior to the next round.

Multi-Box Screening Modeling (MQ 2)–

The multi-box model framework developed for PCBs can be applied to perform screening-level (semi-quantitative) evaluations of pollutant patterns and trends in the Bay and project potential impacts of management action. This effort would assist in identifying the major uncertainties in estimating the environmental fate of various contaminants (e.g., if uncertainties in load calculations, partitioning, or exchange between Bay regions are more critical) and better constraining model parameters shared in common among contaminants (e.g., watershed sediment loading rates, sediment mixed layer depth, net sedimentation rate). The product of this work would be estimates of the environmental fate of current and emerging contaminants in San Francisco Bay in a way that will help managers prioritize efforts. The proposed five-year plan allocates $40,000 toward this effort in 2008, and an additional $25,000 in 2010 and 2012 to screen additional pollutants.

Possible Future work

Mercury

A top priority for the near future is to identify high leverage processes, sources, and pathways contributing to Hg impairment. The proposed five-year plan (Table 2) allocates significant funding toward addressing these questions. Although it is probable that some variant of at least one of these studies will be implemented, the best studies selecting or combining from among these or others to address local mercury management questions have not yet been decided. An initial two-year allocation of $200,000 is proposed for 2008 and 2009, with data analysis and reporting in 2010, and more funding later for additional or other work.

As information on the first mercury management priority question (where is Hg entering the food web?) becomes clearer, more of the future funding might be directed to addressing any specific problem areas or processes identified through biomonitoring. Although the EEWG has primary oversight in the design and review of biomonitoring efforts, additional oversight by the CFWG can help guide development of the monitoring efforts and subsequent process studies to ensure that the most critical factors are examined.

The CFWG has recommended that RMP develop a Request for Proposals (RFP) to solicit the best potential projects to address these questions. The Mercury Strategy Team has worked with RMP staff in developing an RFP, distributed in December 2007 to various investigators in the Hg research community. Some of the ideas that have been put forth prior to issuance of the RFP are described below, but other ideas not previously considered might also arise form the RFP process.

Given the wide range of possible studies and the major data gaps in many aspects of our understanding of Hg processes, criteria for selection of appropriate studies are described in the RFP language: *"The proposals should explain how the proposed work addresses the overarching RMP goal of providing information needed to support water quality management decisions. Studies that have the potential to support decision-making more directly or in the nearer-term will be more valuable to the RMP."*

Because additional funding is allocated to address these questions in future years, the priority for the 2008-9 round of proposals is to fund "no regret" studies, to provide information required by environmental managers in the near-term, regardless of potential outcomes of other studies underway or planned. Proposals will be reviewed by the CFWG and rated for 1) applicability to management needs, 2) technical feasibility, and 3) likelihood to achieve stated objectives with the proposed scope.

RMP staff, with the CFWG and the selected principal investigators, will work to revise the initial proposals in developing final scopes of work for these projects to ensure they best meet management needs. The selected revised proposals (with finalized scopes of work and budgets) will be presented to the RMP Technical Review Committee for approval in March 2008.

Methylmercury mass balance-

One approach is to consider MeHg rather than total Hg in a mass balance model, addressing the contribution of various MeHg sources to impairment (MQ 3.1) and potential changes under various management scenarios (MQ 2.1). Data gaps and the importance of interconversion rates become explicitly important in such an exercise. Although uncertainties around various possible inputs are quite large (e.g., wetlands can be net sources or sinks at different times, Stephenson et al., 2007), a mass balance model can provide an indication of the scale of uncertainties, allowing prioritization of particular inputs that most need better quantification. Any mass balance model would need some estimates of *in situ* methylation/demethylation rates to account for imbalances in loading and discharge rates from receiving waters.

Relative availability of Hg from different sources for methylation -

This addresses areas of possible management intervention to reduce MeHg production (MQ 3.2). Such a study would focus on factors affecting the availability of inorganic Hg (elemental or ionic) to methylating bacteria; this could be approached through a number of methods. One approach is lab or field studies of methylation rates using Hg inputs from various sources, and isolates or mesocosms of methylating organisms. Surrogate measures of available mercury have been proposed, ranging from chemical reduction (by $SnCl_2$, Hammerschmidt & Fitzgerald, 2006), to sequential extractions (water/acid/base, Bloom et al., 2003), which would need to be correlated to MeHg concentrations or production rates to establish their relevance to biological methylation pathways. Experiments of this type are proposed in Chapters 4 of the CEP mercury conceptual model (Tetra Tech 2006). Challenges to conducting and interpreting such studies are in differences relating laboratory/mesocosm to actual field conditions.

Given that MeHg is a small proportion of total Hg, reductions in some key highly available sources may result in better short and mid-term responses than just addressing total Hg loads. Studies have shown large differences in methylation rates between newly deposited Hg and other sources, and the Water Environment Research Foundation (WERF) has funded a literature review to compare the relative bioavailability of various Hg sources (in large part concerned about relative methylation rates for wastewater compared to other sources). This topic is a very high priority for stakeholders, because depending on whether or not all Hg is created equal (within the time frame of recovery plans), appropriate management responses to minimize future biological Hg impacts will differ greatly.

MeHg degradation pathways and rates-

This information helps to "project future impairment" (MQ 2.1) via a process for MeHg to "leave" the Estuary and thus a possible opportunity for management intervention (MQ 3.2). Knowledge of degradation rates is needed to understand MeHg distributions, as a low MeHg concentration in the environment could arise from a low loading/production rate with low turnover, or high loading and production rates with rapid degradation (high turnover). If little/nothing can be done to control MeHg production and release rates, approaches to maximize degradation might be an alternative management technique on smaller scales in specific environments.

Hg isotope source signatures-

The use of stable isotope signatures to may help identify key sources for Hg ultimately methylated and bioaccumulated (MQ 3.1). Preliminary work has shown differences among different geologic Hg sources and fractionation through abiotic and biological processes, which might help identify dominant sources and pathways of Hg loading and MeHg production and uptake. If bioaccumulation of Hg in indicator species occurs with predictable (or negligible) enrichment of specific isotopes from a source signature, particular Hg sources most impacting these species could be identified. It is currently unknown whether different Hg sources in the Estuary or organisms of one receptor species from different areas of the Estuary have distinctive isotope signatures, information needed to establish the utility of this approach.

Other Possible (Lower Priority) Fate Studies

If the CFWG can conduct additional work after the top priorities are addressed, the following studies are some possibilities that can be considered (in no particular order).

General Fate and Transport

Sediment Flux Studies (MQ 3.1)-

Much of the work examining sediment flux of contaminants use flux boxes or lab incubations (e.g., Topping et al., 2004), which allow diffusive transport, groundwater advection, and bioturbation, but by design (isolating a patch of sediment) cannot capture advective forces causing sediment re-suspension and porewater exchange The inability of typical flux measurement methods to account for water column exchange with the sediment needed to obtain mass balance on some contaminants (Tetra Tech, 1999) illustrates this limitation. Better flux estimates are a moderately high priority, given the large contribution from sediments posited in mass balances for many contaminants.

Bathymetric Surveys (MQ 2)-

In the late 1980s and early 1990s, the USGS conducted comparative bathymetric analysis of long-term erosion and deposition in San Pablo and Suisun Bays (Jaffe et al. 1998, Cappiella et al. 1999). More recently, a similar analysis was completed for South Bay by the USGS (Foxgrover et al. 2004), although the latest data used are still from the 1980s. Updated bathymetric data, coupled with sediment coring studies, could identify and describe areas of potential concern inhabited by sensitive species. A new bathymetric survey of the South Bay is currently in progress as part of the South Bay Salt Pond Restoration Project. The current multibox model is optimized to match net sedimentation rates between the latest two bathymetric surveys in each segment, so updated surveys would make projections more tuned to current sedimentation trajectories. This information is of high importance, but given the scale and expense of these efforts, additional studies will largely depend on the needs of other agencies (e.g. NOAA) for bathymetric data.

Bed Sediment Dynamics (MQ 2)–

As part of the RMP, the USGS has collected continuous data on suspended sediment in the water column at several locations in the Estuary; but little is known about bed sediment dynamics and transport. Studies that evaluate bed sediment dynamics and transport will further our understanding on cycling and residence times of sediment and persistent contaminants in the Bay. Data on sediment mixing from radiotracers (Fuller et al., 1999) and introduced chemical tracers (Leahy et al., 1976) can be used to confirm or refine model predictions. Given that modeled bed dynamics properties are constrained in large part by a need to generate realistic net sedimentation rates and water suspended sediment concentrations, sensitivity analyses of the current model should be examined first to test model response to a realistic range of possible parameter values.

Mercury

Me/Hg sediment-water exchange processes (MQ 3.1)-

These are potentially a key pathway for MeHg introduction into the aquatic food web. Although the movement of Hg (and MeHg to an extent on short time scales) in bulk sediment can be addressed through modeling of sediment transport, the exchange of MeHg from sediments, where it is produced, to the water column, where it is accumulated by many of the biota of interest, remains a major data gap. The CEP mercury conceptual model proposes experiments such as flux chamber studies to collect this information (Chapter 5), but notes possible/likely small-scale temporal and spatial variability as a challenge to extrapolation, and other limitations of flux chamber measurements were noted previously. Other sediment flux measurement or estimation methods would therefore be needed.

Factors influencing MeHg uptake rates and assimilation efficiency (MQ 3.1, 3.2)-

Water column parameters such as DOC and phytoplankton density and changes in food web structure potentially could also affect MeHg uptake rates. These types of studies are most directly relevant to the Exposure and Effects Workgroup, but the CFWG should be aware of any efforts on this front and incorporates these factors into models as needed.

PCBs

Modeled hot spot loads (MQ 3.1)-

Although most of the information needs listed in the PCB TMDL for San Francisco Bay are related to improving quantitation of loads (addressed by the SPLWG), one category of these sources, contaminated hotspots within the Bay, will likely require detailed site characterization and modeling on a small spatial scale to estimate the inventory of contamination and loading rates. In-Bay PCBs contaminated sediments will be remediated according to site-specific clean-up plans, and information on those inventories and loads will likely be developed as part of the site clean-up plan, rather than through the RMP. However, information developed from these local efforts should inform Bay-scale efforts to track loads and contaminant fate.

Dioxin-like PCBs characterization (MQ 3.1, 4.1)-

Based on existing data for the region, dioxin-like PCBs are generally larger contributors to fish tissue TEQs than PCDD/Fs. A portion of the TEQ risk might be addressed through the PCB TMDL, if the dioxin-like congeners are included in monitoring and modeling efforts. However, there have not yet been formal proposals to include more of the dioxin-like PCBs (particularly of PCB 126, with the highest TEF) in RMP monitoring.

In-situ PCB degradation rates (MQ 2.1, 3.2)-

One of the major uncertainties in the multi-box model is the PCB degradation rate used in the model. Several approaches to addressing this question are possible, ranging from reviews of the literature, to laboratory or field (microcosm/mesocosm) studies.

PCB transport model refinements (MQ 2.1)

Information on sediment characteristics and processes (under "General Fate and Transport") are integral to the understanding of the long term fate of PCBs and other sediment associated contaminants, and are already included as a high priority for general contaminant transport so therefore are not included here. Additional refinements could include congener-specific modeling (the current multi-box is calibrated on a single congener), which would require associated input data such as congener-specific loads, degradation rates, and partitioning constants.

PBDEs

Degradation/transformation (MQ 2.1, 3.2)-

Penta and octa PBDE mixes have only recently been banned in California, but there is continued use/release of the deca mix, which can degrade to less brominated isomers. If penta and octa isomers persist much longer than projected from current data on loading and degradation rates, in addition to increased loading studies (under the SPLWG), reexamining degradation rates and/or estimates of conversion rates of deca- isomers to other forms may help explain continued persistence of these compounds in the environment.

Selenium

Speciation/partitioning measurements (MQ 3.1, 4.1)-

The USGS selenium bioaccumulation model (Luoma and Presser, 2000) requires concentrations of various dissolved and particulate species of Se as inputs to calculate the assimilation rate of aquatic consumers such as bivalves. RMP currently only measures dissolved and total Se, without examining speciation. A pilot study investigating Se speciation at various locations in the Bay would provide the information needed to estimate uptake rates using the USGS model. Understanding changes in speciation and uptake rates at various locations at different times of year will also be critical to understanding the risk posed to resident (e.g. sturgeon) and transient (e.g. migratory birds) biota in the Estuary.

Mass balance model (MQ 2, 3)-

With a large proportion of total selenium in the dissolved phase, the multi-box model may be a suitable tool for tracking total Se, although the relevance of total Se to biological effects is unclear at this point. Where concentrations of particular species do not behave conservatively, transformations between forms of Se will need to be added to any models to address this. A two compartment mass balance (equivalent to the RMP "one-box" model with one water and one sediment compartment for the whole Bay) was used for the CEP CMIA report on selenium (Abu Saba and Ogle, 2005), so inter-segment differences in Se loads and transport processes were also not captured. As a Se TMDL is developed, a multibox mass balance exercise for relevant Se species may rise in priority.

Dioxins/Furans

Quantitative environmental distribution (MQ 1)-

Information gaps on dioxin-like compounds are currently driven primarily by limited quantitative data in various environmental matrices. The dioxin CMIA report for CEP (Connor et al., 2005) utilized what little local data there was in a one-box model to project future distributions under various loading assumptions. Once more quantitative data for various locations and matrices are obtained for the Estuary, decisions can be made on whether additional study of the fate and transport processes of dioxins is needed.

PAHs

Degradation and loading rates (MQ 2)-

Application of a one-box model to PAHs revealed the sensitivity of the model to PAH degradation rates and the high uncertainty in those rates derived from available literature (Greenfield and Davis 2004). That study recommended reducing uncertainty in those estimates before attempting to develop more refined mass balance models. Another major uncertainty is the range of possible loading rates (~5x difference between maximum and minimum estimates), which would be addressed by studies of the SPLWG. The priority of studying PAHs will rise if a TMDL is developed.

Current use pesticides, PPCPs

Identifying target compounds (MQ 4.1)-

Given little information available on environmental distribution of current use pesticides and PPCPs, first priorities are to choose appropriate compounds to target and to find them in ambient environments. Once these pollutants are found at relevant concentrations potentially affecting biota and potential sources identified, efforts should be applied to understanding their fate and transport. Currently, no PPCPs meet those criteria, but data on pyrethroids may be improving (in quantity and quality) to the point that their environmental processes can and should be tracked concurrent with efforts to reduce their inputs.

Organochlorine pesticides

Multibox modeling (MQ 2)-

Following their ban for most uses, concentrations of OCPs are generally declining, and concentrations for many compounds are now below estimated effects thresholds. However, the ecosystem response to their bans may serve as useful calibration or validation data for hindcast modeling efforts.

Trace metals (Cu, Ni, Ag, As, Cd Cr, Pb, Zn)

Future trends and loads (MQ 2, 3)

Loads of many trace metals have been decreasing with changes in uses and source control, with Cu and Zn being possible exceptions due to increased vehicle use (Cu through changes in brake pad wear debris, Zn in tires with increases in per capita vehicle miles traveled). Zn is well below effects thresholds for the Bay, but Cu is sometimes near the California Toxics Rule water quality criterion (3.1 μg/L nor th of the Dumbarton Bridge). Changes in the Basin Plan increasing the water quality criterion (to 6.9 μg/L for Lower South Bay, 6.0-6.9 μg/L also planned for the rest of the Bay) to account for complexation by organic ligands in the water (via water effects ratios, WERs), will lessen the urgency of additional studies of Cu processes, but exceedances of triggers levels (~4.0-4.4 μg/L, above current concentrations but below the new criteria) set to prevent degradation will require studies of environmental processes, such complexation by organic ligands, effects levels for biota , and sediment cycling, in addition to more stringent source controls.

USEPA is currently developing (with contractor HydroQual) a Biotic Ligand Model for calculating metal ion toxicity in freshwater environments, using combinations of measured water quality parameters (pH, DOC, major cations) with metal concentrations to predict free metal ion activity. The model has not been applied to marine ecosystems yet, but such models may one day supplant static WERs (or at least simplify their derivation) for developing site-specific metals criteria. RMP data collected might prove useful for validating refining a marine BLM under realistic conditions in the future.

CFWG COORDINATION WITH OTHER STUDIES

There are many studies and programs within SFEI and other groups in the Bay Area and beyond that can provide data, ideas, and case studies to enhance the efforts of the CFWG. Examples include much of the work underlying CFWG efforts to date such as USGS bathymetric studies and modeling, NOAA-EMAP surveys, CEP CMIA reports, and monitoring and modeling efforts in other regions. Continued sharing of information and collaboration with these other efforts will help ensure that the best available science is applied to challenges of environmental management.

Although RMP workgroup titles delineate separate interest areas, the reality is that there is significant overlap between workgroups, as the interactions among ecosystem components are continuous rather than discrete. Thus while the SPLWG might primarily be concerned with flux from the sediment as a loading to the Bay water column, the CFWG needs to improve understanding of the interactive cycles that lead to the water and sediment contaminant distributions found. Similarly, while projects under the CFWG might focus on the physical and chemical parameters leading to bioaccumulation in the food web, the EEWG may focus on the effects of those contaminants to organisms at high trophic levels.

Although these interactions could be treated as "black box" inputs among different RMP components, deeper understanding of underlying assumptions and additional information shared through collaborative development can only enhance the science.

Integrative thinking can be facilitated through participation of RMP staff (particularly workgroup leaders) in multiple workgroups. Although periodically shared workgroup meetings might be a long-term goal, difficulties of meeting logistics (need for a large venue, coordinating schedules among many participants) largely preclude such an approach as a primary mechanism of interaction. However, shared review of study proposals and work products (reports and presentations) among groups for projects that straddle these interest areas represents an easy (and arguably necessary) opportunity for cross pollination.

ACKNOWLEDGEMENTS

We would like to thank all the workgroup participants over the past 5 years, who have helped guide and review RMP projects and products concerning contaminant fate, helping to ensure that the work is both scientifically robust and relevant to management. We would also like to thank the SPLWG, for critical loading data upon which the mass balance models are reliant, and the workplan structure from which we borrowed heavily.

TABLE 1. SELECTED CONTAMINANT FATE WORK IN SF BAY

REFERENCE	SPONSOR	OUTCOME/CONCLUSIONS
Abu Saba & Ogle 2005	CEP	Selenium conceptual model
Bessinger et al 2006	SFO	URS/Exponent 2d hydrodynamic model originally for SFO project
Connolly et al 2005		Tidal corrections to 1 box PCB model
Connor et al 2005	CEP	Dioxin conceptual model
Davis 2004, 2007 1-box PCB model	RMP	Recovery sensitive to initial pool and mixing depth
EOA/LWA 2005	CEP	Cu/Ni conceptual model for SFBay north of Dumbarton Bridge
Gobas & Arnot 2005	RMP	Expanded food web model
Gobas & Wilcockson 2003 Food web model	RMP	PCB fugacity model trophic transfer
Greenfield & Davis 1-box PAH model	RMP	Large uncertainties in degradation and loading rates
Jaffe et al 1998, Cappiella et al 1999, Foxgrover et al 2004	USGS	Bathymetric history Identified areas that were depositional or erosional in various time periods
Leahy 1976	USACE	deposition and mixing of sediments to > 20cm in <1 year
Leatherbarrow et al 2005 Literature review	RMP	Lit review, sediment contaminants generally higher in South Bay for multiple reasons
Leatherbarrow et al 2006 1-box organochlorine pesticide model	RMP	Bans and degradation have lowered OC pesticides
Lionberger & Schoellhamer 2003 51 box water/sediment transport model	USGS	Added sediment transport to Uncles & Peterson, calibrated to long term bathymetric change
Luoma & Presser 2000	USGS	Selenium bioaccumulation model
NOAA 1997 Literature Review	NOAA	Review of bay sediment contamination data to mid 1990s
Meseck & Cutter	2006	Se speciation model for North Bay
Oram et al 2006 Multi-box PCB model	RMP	Added contaminant transport to Lionberger & Schoellhamer water/sediment transport model
Oram et al 2006 one-box PBDE model	RMP	Distinct PBDE sources north and south bay
Oros & Werme 2005	CEP	PBDE conceptual model
Tetra Tech 1999	San Jose	Copper conceptual model
Tetra Tech 2006	CEP	Mercury conceptual model
Uncles & Peterson 1995 51 box hydrologic model	USGS	Tidally averaged model of salinity balance and hydrodynamic exchange
Venkatesan et al 1999 Organic contaminant profiles in SF Bay cores	USGS	Subsurface maxima found for some organic contaminants in cores from depositional areas

TABLE 2. FIVE-YEAR WORK PLAN FOR THE CONTAMINANT FATE WORKGROUP.

Activity	Funding	Tools / Products	2007	2008	2009	2010	2011	2012
*Workgroup meetings	RMP (Prog Mgt)	Power Point presentations / verbal communications	20	20	20	20	20	20
*External Coordination	RMP (Prog Mgt)	Attend key meetings hosted externally, review external reports						
*CFWG expert review and meeting attendance	RMP (Prog Mgt)	4 experts attend 2 meetings a year to provide independent comment	6	6	6	6	6	6
**5-year plan revisions	RMP (Prog Mgt)	CFWG meeting preparation, Written reporting	3	3	3	3	3	3
		Subtotal	**29**	**29**	**29**	**29**	**29**	**29**
Multibox Model (PCBs)	RMP/CEP (Data Integ)	Model refinement, report writing	20					
Golden Gate Outflow	RMP (P&SS)		8	40				
Sediment Coring Study	RMP/CEP (P&SS)	Sectioning, radiodating, contaminant analysis, report	27*(54)*	33*(67)*		100		100
Reactive Hg Study (UCSC)	RMP (S&T)	Lab extractions, data, report	40					
High leverage Hg Processes	RMP (P&SS)			100	100		150	150
MeHg Model Development	RMP (Data Integration)		25		25		25	
Multi-box multi-pollutant screening model	RMP (Data Integration)			40		25		25
Food Web Uptake of Mercury (Small Fish) (in EEWG 5-Year Plan)	RMP (S&T, P&SS)			150	150	150	100	100
		Subtotal	**120**	**183**	**175**	**125**	**175**	**125**
		Total	**149**	**212**	**204**	**154**	**204**	**154**

Table lists RMP funds contributed in $1000s *(CEP contribution in italics)*

APPENDIX TABLE 1: UNCERTAINTIES RELATING TO PCBs

DATA GAP (SOURCES & PATHWAYS)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	FEASIBLE	EXISTING WORK
High flow event river PCBs	Field sampling, modeling	High /med	High	Med	RMP Multi-box model
Dredging contribution to food web accumulation	Literature review, modeling	Low	Med	High	RMP Special Study
Magnitude of harbor stormwater loads	Field studies	High	Med	High	None
Effectiveness of harbor control options	Literature review, field studies	High	High	High	None
Direct and indirect atmospheric deposition rates	Field studies	Low	Low		
Rates of PCB volatilization	Field studies	Low	Low		
Redeposition of volatilized PCBs in the watershed	Modeling	Low	Low		
Local benefits of in Bay hotspot cleanup	Modeling, field studies	Med	High	High	Reg Bd, DTSC, USEPA
Regional hotspot influence	Modeling, field studies	Med	High	High	
Effectiveness of hotspot remediation (removal, burial, sequestration)	Literature review, field studies, adaptive implementation	Med	High	High	CEP Nearshore coring
Magnitude of stormwater loads from local watersheds	Field studies	High	High	High	RMP, SCVWD
Stormwater loads during high flows	Field studies	High	High	High	RMP, SCVWD
Effectiveness of stormwater control options	Literature review, field studies, adaptive implementation	High	High	High	SWRCB Prop 13, CEP 4.28
Attenuation of urban runoff loads with no action	Lit review? Marsh coring studies? Others?	High	High	High?	CEP coring study?
Stormwater sources and pathways	Literature review, field studies (storm drain surveys, building chronologies, loads from catastrophic events, etc.)	High	High	High	BASMAA, Prop 13
Buried Sediment erosion/deposition trends in the past 15 years	Comparative bathymetry	High	High	High	SBSP (South Bay only)
Accurate quantification of buried sediment loads	Modeling	High	High	High	RMP Multi-box
Effluent		Low	Low	High	

DATA GAP (PROCESSES)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	FEASIBLE	EXISTING WORK
Aggregate processes, reduction in uncertainty by specific studies	Uncertainty analysis	High	High	High	CEP – Tetra Tech
Burial/erosion over the past 15 years	Comparative bathymetry	High	High	High	SBSP (South Bay)
Projected burial/erosion	Model projections of impacts of wetland restoration, sediment budget	High	High	High	SBSP (South Bay)
Subsurface inventory of PCBs	Coring study	High	High	High	CEP/RMP
Erosivity of sediment	Field studies	High	Med	Med	None
Sediment mixing Representative models for each segment	Mixing studies (cores, isotope work, other approaches)	High	Med	Med	CEP/RMP (coring study?)
Outflow and tidal exchangeMagnitude	Field studies, modeling	High	High	Low	None
Degradation In situ degradation rates for the Bay for congeners	Field, microcosm, or lab studies	High	High	Med?	None
Sediment to Biota TransferSediment concentrations protective of beneficial uses	Food web modeling, site-specific bioaccumulation factors, associated field studies	High	High	High	CEP – Gobas and Arnot

DATA GAP (INVENTORY)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	FEASIBLE	EXISTING WORK
near shore concentration Representative average	Randomized sampling of near shore stratum?	Med	High	High	CEP/RMP
mass in watershed Accurate estimate of	Storm drain sediment sampling, targeted sampling of soils and sediments	Med	High	Med	Counties - storm drain sediment PCB surveys
Mass in Bay Accurate estimate of mass in subsurface sediments	Cores	Med	High	High	CEP/RMP

DATA GAP (SOURCES)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	FEASIBLE	EXISTING WORK
Past trendRecovery trajectory since PCB ban	Cores	Med	High	High	CEP/RMP
Present trends- Current rate of decline	Avian eggs	High	High	High	RMP
Current rate of decline	Bivalves	High	High	High	RMP
Current rate of decline	Sport fish	High	High	High	RMP

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APPENDIX TABLE 2: UNCERTAINTIES RELATING TO (Me)Hg

DATA GAP (SOURCES & PATHWAYS)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	UNCERTAINTY	FEASIBLE	EXISTING WORK	COMMENTS & CHALLENGES
Effectiveness of stormwater control options	Literature review, field studies, adaptive implementation	5	5	3	5	SWRCB Prop 13, CEP 4.28	Primary intended control knob
Magnitude of stormwater loads from local watersheds	Field studies	3 (totHg), 5 (MeHg)	3 (totHg), 5 (MeHg)	5	5	RMP, SCVWD	Large totHg input
Stormwater during high flows	Field studies	3 (totHg), 5 (MeHg)	3 (totHg), 5 (MeHg)	5	5	RMP, SCVWD	Loads may increase in nonlinear fashion, Just need a high flow year
Stormwater Sources and pathways	Literature review, field studies (storm drain surveys, building chronologies, loads from catastrophic events, etc.)	3 (totHg), 5 (MeHg)	3 (totHg), 5 (MeHg)	5	5	BASMAA, Prop 13	
Regional hotspot influence	Modeling, field studies	3	5	5	3/1?		MeHg modeling feasability low
Local benefits of hotspot cleanup	Modeling, field studies	3	5	5	5	Reg Bd, DTSC, USEPA	Fish may not be proportional to total Hg
Loads from harbor stormwater	Field studies	3	3	3	5	None	Relatively small mass
Effectiveness of harbor control options	Literature review, field studies	3	3	3	5	None	Relatively small mass
Buried Sediment erosion/deposition trends in the past 15 years	Comparative bathymetry	3	3	3	5	SBSP (South Bay only)	Potentially large influence on totHg, Just need bathymetry?
Accurate loads from buried sediment	Modeling	3	3	3	5	RMP Multi-box	
High flow event river loads	Field sampling, modeling	3	3 (totHg), 5 (MeHg)	5	3	RMP Multi-box model	how much immediate outflow- modeling easy but verification difficult
Effectiveness of hotspot remediation (removal, burial, sequestration)	Literature review, field studies, adaptive implementation	3	5	3	3	CEP Nearshore coring	If effectiveness measured by totHg change
Dredging contribution to food web accumulation	Literature review, modeling	1	1	3	5	RMP Special Study	Relatively small mass, characteristics similar to other sediment
Changing urban runoff loads with no action	Lit review? Marsh coring studies? Others?	1	1	3	5	CEP coring study?	Multi-box sensitivity to this unknown for totHg, A marsh core may work
Direct and indirect atmospheric deposition	Field studies	1	1	1	5	RMP AirDep, MDN	Load known, microbioavailability not.
Effluent loads		1	1	1	5		Load known, microbioavailability not.
Rates of volatilization	Field studies	1	1	3			

DATA GAP (PROCESSES)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	UNCERTAINTY	FEASIBLE	EXISTING WORK	COMMENTS & CHALLENGES
Convertability of Hg species	Extraction experiments, lab incubations	5	5	3	3?		Is all MeHg ultimately (~10-100yr) equivalent; lab availability may only approximate field
Origin of Hg in biota	Isotope signatures vs sources	5	5	5	3?		Signatures unknown, in biota and sources, but no lab artifacts
In situ production rates for MeHg	Field, microcosm, or lab studies	5	5	5	3?	None	Likely high temporal and spatial variability, but order of magnitude needed to ID control options
In situ degradation rates for MeHg	Field, microcosm, or lab studies	5	5	5	3?	None	A primary loss pathway, poorly known
Water/Sediment to Biota Transfer	Food web modeling, site-specific bioaccumulation factors, associated field studies	5	5	3	3	CEP – Gobas and Arnot	Possible high temporal and spatial variability, least uncertainty at primary producer or consumer
Methylation rates of different Hg sources	Incubation studies	3	5	5	5		Incubations can isolate source methylation potential, but subject to artifacts
Methylation rates of different Hg sources	MeHg isotope signatures	3	5	5	3?		isotopes might not be sufficiently distinct in some sources
Cofactors driving MeHg production	Field, microcosm, or lab studies	3	5	3	5	RMP?	Data already hint at importance of bacterial substrate
Burial/erosion over the past 15 years	Comparative bathymetry	3	3	3	5	SBSP (South Bay)	Total Hg load may be secondary (depending on convertability)
Projected burial/erosion	Model projections of impacts of wetland restoration, sediment budget	3	3	3	5	SBSP (South Bay)	Total Hg load may be secondary (depending on convertability)
Subsurface inventory of Hg	Coring study	3	3	1	5	CEP/RMP (coring study)	Potentially large influence on recovery, paucity of data
Erosivity of sediment	Field studies	1	1	1	3	None	Moderate influence in multi-box model = influence on total Hg but not MeHg
Sediment mixing Representative models for each segment	Mixing studies (cores, isotope work, other approaches)	1	1	3	3	CEP/RMP (coring study?)	Hg in upper layers often already uniform
Outflow and tidal exchange magnitude	Field studies, modeling	1	1	3	1	None	A total Hg loss pathway; Measurements at Golden Gate very challenging

DATA GAP (INVENTORY)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	UNCERTAINTY	FEASIBLE	EXISTING WORK	COMMENTS & CHALLENGES
near shore concentration average	Randomized sampling of near shore stratum?	3	5	3	5	CEP/RMP	Hg largely already more uniform
mass in watershed Accurate estimate of	Storm drain sediment sampling, targeted sampling of soils and sediments	3	5	3	3	Counties - storm drain sediment PCB surveys	Essential to understanding future inputs
Mass in Bay Accurate estimate of mass in subsurface sediments	Cores	3	5	3	5	CEP/RMP	Moderate influence on recovery, paucity of data

DATA GAP (TRENDS)	POSSIBLE STUDIES	TMDL PRIORITY	TECHNICAL PRIORITY	UNCERTAINTY	FEASIBLE	EXISTING WORK	COMMENTS & CHALLENGES
Recovery trajectory since mine closures	Cores	3	5	3	5	CEP/RMP	Only indicates totHg trends, long term erosion not a MeHg source
Current rate of change	Avian eggs	5	5	3	5	RMP	Indicator for long-term regional trends in selected food web components
Current rate of change	Bivalves, small fish	5	5	3	5	RMP	Indicator for interannual trends and spatial patterns, some unknown noise
Current rate of change	Sport fish	5	5	3	5	RMP	Noisy trend signal due to fish life history variation, but essential for evaluating impairment

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