Technical Report

of the Sources, Pathways and Loadings Workgroup

March 2001

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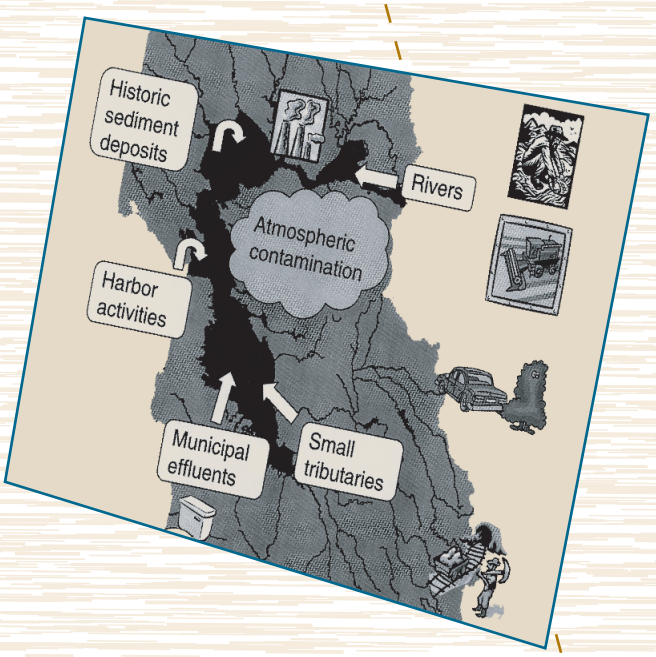

Preface

This report documents the activities of the RMP Sources, Pathways, and Loadings Workgroup in 1999. More comprehensive and detailed assessments of some of the topics presented, especially the mercury discussion and aspects of the PCB discussion, were completed in 2000. While this report is still a good introduction to these topics, the reader is also referred to the following publications for more recent and detailed information:

San Francisco Bay Regional Water Quality Control Board. 2000. Watershed Management of Mercury in the San Francisco Bay Estuary: Draft Total Maximum Daily Load Report to U.S. EPA. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

Davis, J.A. 2001; Draft Report: A PCB Mass Budget for San Francisco Bay. San Francisco Estuary Institute, Richmond, CA.

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I. Introduction

The revised RMP objectives developed in 1998 include an objective that has established a new direction for the RMP: "describe general sources and loading of contamination to the Estuary." As stated by the Five Year Review Panel (Bernstein and O'Connor 1997), this objective provides a functional connection between the RMP and efforts to identify, eliminate, and prevent sources of pollution. The Sources, Pathways, and Loading Workgroup (SPLWG) was formed to produce recommendations for incorporating collection, interpretation, and synthesis of data on general sources and loading of trace contaminants to the Estuary into the RMP. This Report takes the first step toward meeting the new sources and loading objective by establishing priorities for modifying the present design of the RMP. Developing an optimal design of RMP elements to characterize sources and loading will require an iterative process that periodically evaluates newly synthesized or generated information. It is envisioned that the SPLWG will continue to guide the RMP as information gathering, sampling design, and evaluation of results of field sampling proceed over the next several years.

The Five Year Review Panel (Bernstein and O'Connor 1997) concluded that recommendations for modifying the RMP should be based on: 1) RMP data and data from other continuing and historical studies; 2) mass balance models developed to guide redesign; and 3) a clear linkage of the design with RMP objectives and management questions. This approach was followed by the Workgroup.

The Workgroup was comprised of local experts with extensive experience in loading and cycling of trace elements and trace organics in the Estuary (Table 1).

Table 1. Members of the SPLWG.

Russ Flegal	U.C. Santa Cruz
Andy Gunther	Applied Marine Science
Tom Mumley	San Francisco Bay Regional Water Quality Control Board
Kim Taylor	San Francisco Bay Regional Water Quality Control Board
Khalil Abu–Saba	SFEI/San Francisco Bay Regional Water Quality Control Board
Jim McGrath	Port of Oakland
Stefan Seum	Port of Oakland
Trish Mulvey	Friends of the Estuary
Jim Kuwabara	USGS
Dave Tucker	City of San Jose
Jim Scanlin	BASMAA
Tom Hall	EOA
Daniel Rourke	City and County of San Francisco
Tom Grovhaug	Larry Walker Associates
Pam Tsai	EPA/SFEI
Rainer Hoenicke	SFEI
Jay Davis	SFEI

The Workgroup met three times in early 1999, and also communicated a great deal via email in 1998 and 1999. The Workgroup provided guidance to SFEI staff, which performed various information gathering activities. The tasks performed by SFEI were: 1) reviewing literature on priority contaminants, 2) identifying local datasets that could be used in evaluating contaminant loading to the Bay, 3) assessing existing information relative to RMP objectives and management questions, and 4) coordinating the activities of the Workgroup. This report is the product for tasks 1, 3, and 4. Summary information on local datasets, the product for task 2, is presented in Appendix 1.

At the beginning of the study, the Regional Board provided a prioritized list of contaminants to help focus the efforts of the Workgroup (Table 2). The activities and objectives of the SPLWG overlapped considerably with other recent or concurrent efforts on these contaminants, including the RMP Chlorinated Hydrocarbon Workgroup, the RMP Registered Pesticides Workgroup, the Regional Board's mercury strategy, the South Bay TMDL project, and USGS research on selenium. In order to avoid duplication of effort, the SPLWG focused on synthesis of information on PAHs and trace elements, and relied to a large extent on the Chlorinated Hydrocarbon Workgroup for synthesis on PCBs, the Registered Pesticides Workgroup for most of the synthesis on organophosphate pesticides, the Regional Board's synthesis on mercury, the TMDL synthesis on copper and nickel, and work in progress by USGS on selenium. The SPLWG chose not to include TBT, chlordanes, and DDT in this written assessment due to limited time and budget.

Table 2. Prioritized list of contaminants considered by the SPLWG.

Contaminant	Priority
PCBs	Top
PAHs	High
OPs	High
Hg	Medium
Se	Medium
Cu	Medium
Ni	Medium
TBT	Medium
Ag	Medium
Cd	Medium
Chlordanes	Low
DDT	Low

"Sources" were defined by the Workgroup as activities leading to the release of contaminants into the environment, such as combustion of gasoline in a car engine or application of a pesticide to an agricultural crop. Sources are distinct from "pathways", which include the routes through which contaminants enter the Bay, such as urban runoff, local tributaries, or municipal effluents (Figure 1) pathways are sometimes misconstrued as sources. The Workgroup agreed that information gathering efforts should include both sources and pathways, since we are concerned both with the mass loading to the Bay and how contaminant inputs can be reduced. Loading is the rate of mass input (kg/day) of a contaminant to the Estuary. The analysis presented in this report is a first step, considering only the mass loading of contaminants and not the chemical forms of inputs and potential to accumulate in sensitive organisms. Further analyses to understand the food web accumulation potential of different inputs will be essential for effective management.

This Report summarizes the recommendations of the SPLWG (Section III) and provides a formal justification for the recommendations (Section II). The justification is presented in the form of a contaminant-by-contaminant summary of the state of knowledge regarding overall mass budgets for the Bay and the magnitude of loading from individual sources and pathways to the Bay.

In addition to producing recommendations pertaining to sources, pathways, and loading of the priority contaminants, the SPLWG also developed more general recommendations for modifying trace metal monitoring in the RMP to better meet the objectives of the program. Findings and recommendations regarding trace metal monitoring in the RMP are presented in Appendix 2.

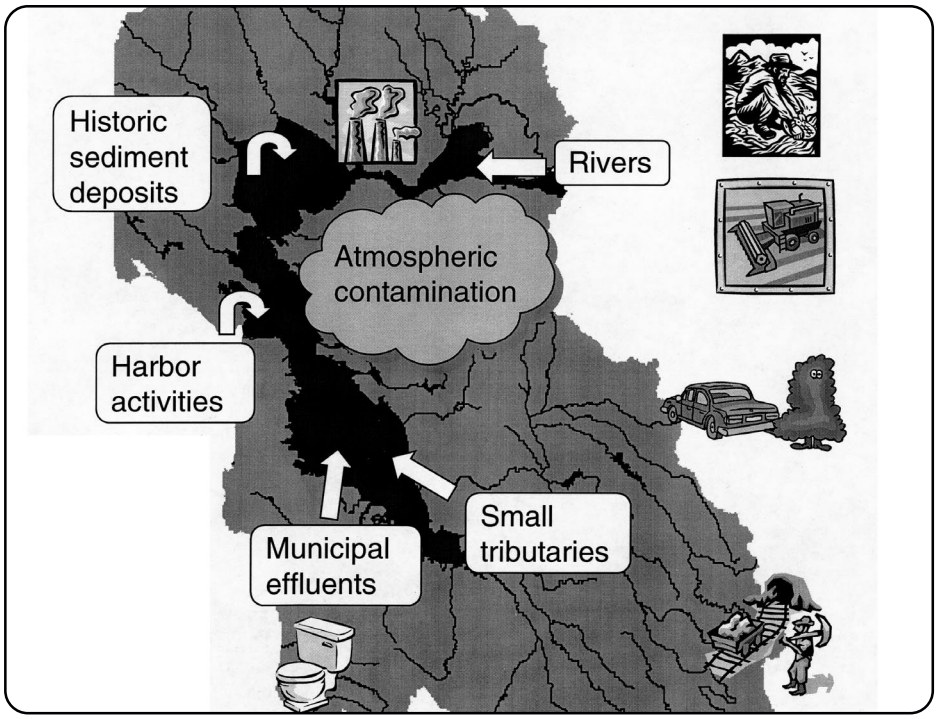

Figure 1. Illustration of sources, pathways, and loadings of contaminants to the Estuary. Sources (gold and mercury mining, agriculture, industry, automobiles, municipal wastewater) are shown as pictures. Pathways (rivers, small tributaries, historic sediment deposits, harbor activities, atmospheric deposition) are shown as text. Loadings are indicated by arrows.

II. Review of Information on Sources and Loading

a. PCBs

Conceptual Model and Mass Budget Considerations

A conceptual model and mass budget for PCBs in the Bay was developed by SFEI under the guidance of the Chlorinated Hydrocarbon Workgroup. The mass budget model is discussed in more detail in the "Technical Report of the Chlorinated Hydrocarbon Workgroup" and will be discussed in full detail in a forthcoming SFEI technical report.

The objectives of the mass budget modeling effort were to estimate inputs of PCBs to the Bay and the response time (rate of change in concentrations under different management scenarios) of the Bay for PCBs. A one-box model was developed for the whole Bay as a first step in understanding the PCB mass budget. The use of a modeling framework developed by Mackay *et al*. (1994) and further refined by Gobas *et al*. (1995, 1998) was recommended by the Workgroup. Figure 3 illustrates the processes included in the model. Extensive data on PCB concentrations in the Bay generated by the RMP, the Bay Protection Program (Hunt *et al*. 1998), and other programs were used as input for the model.

Information obtained from the mass budget model provides valuable context for interpreting the magnitude of potential loadings to the Bay. PCB losses from the Bay could be estimated using the RMP database on sediment and water concentrations. The total loss rate is an important benchmark. If the magnitude of PCB inputs is comparable in magnitude to the total loss rate, then concentrations in the Bay would not be expected to decline. If inputs are lower than the total loss rate, then declines would be expected, with more rapid declines depending on just how much lower the inputs are.

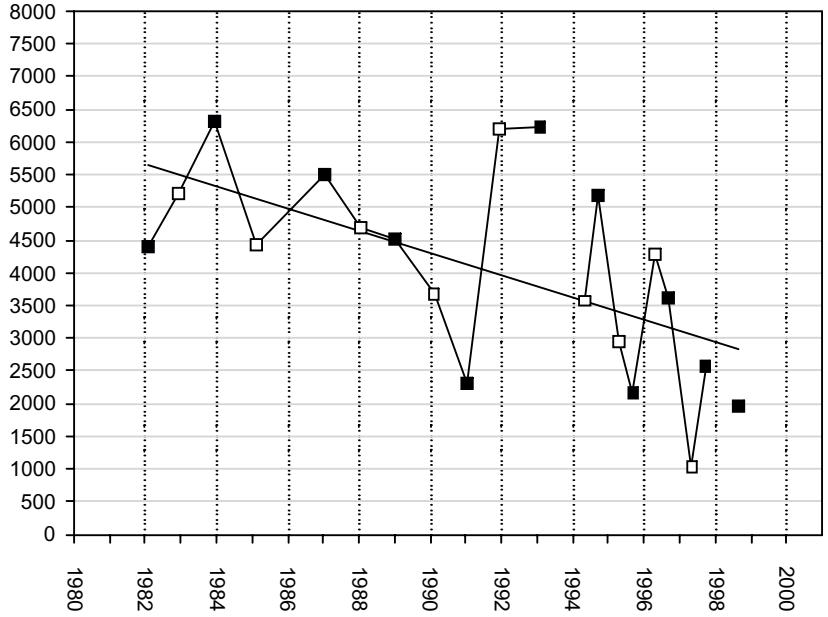

Figure 2. PCB concentrations in transplanted mussels at Yerba Buena Island, in ng/g lipid. Data from the State Mussel Watch (SMW) Program for 1980-1993 (sum of Aroclors) and the RMP for 1994-present (sum of congeners).

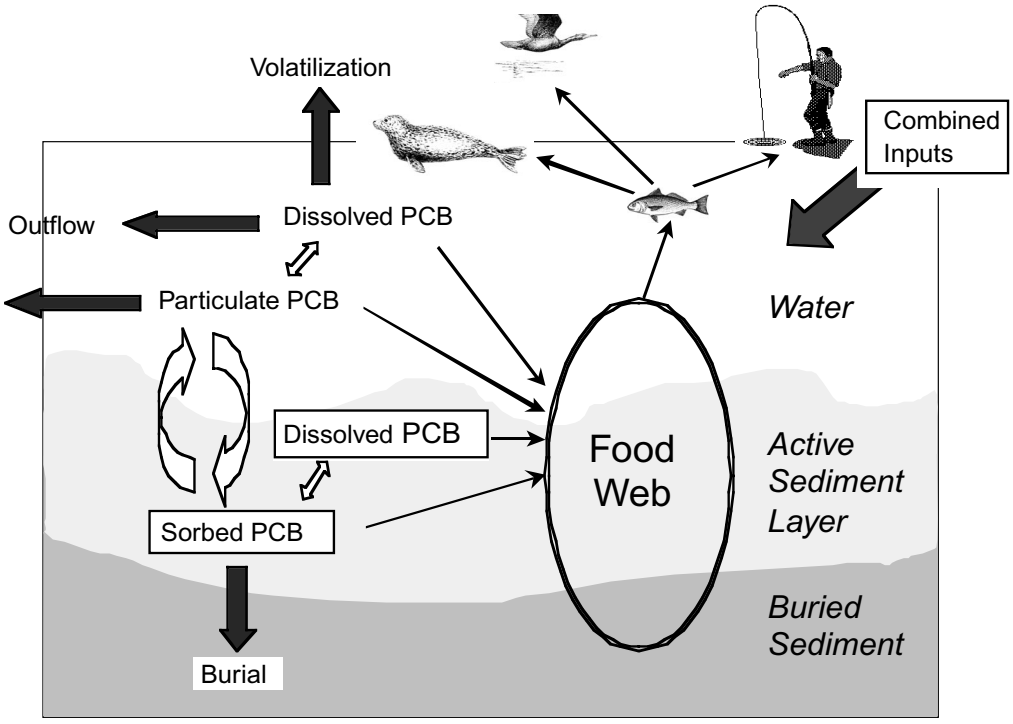

Figure 3. PCB pathways in San Francisco Bay.

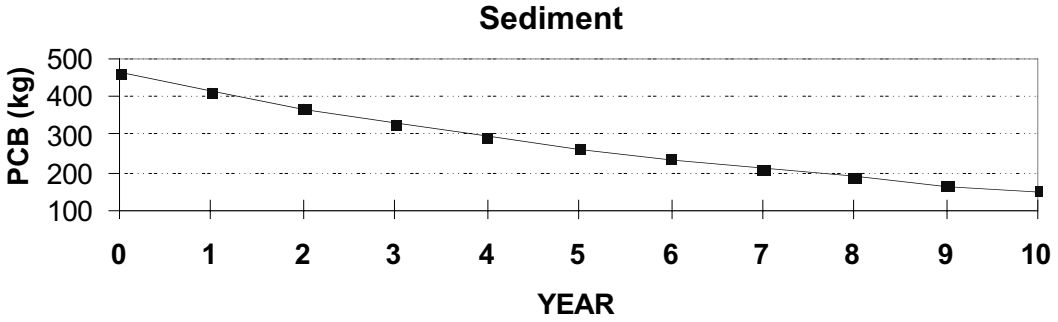

Figure 4. Predicted change in PCB mass in Bay sediment assuming no loading of PCBs and using best estimates of all input parameters.

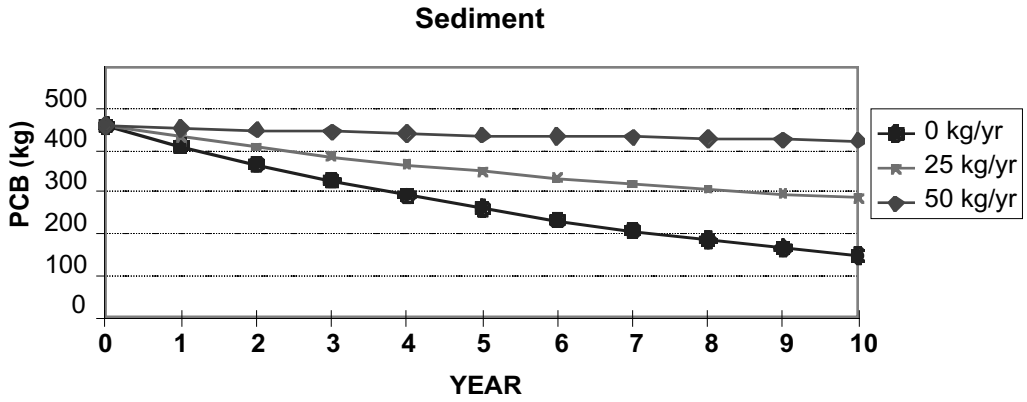

Figure 5. Predicted change in PCB mass in Bay sediment assuming different levels of loading of PCBs and using best estimates for all other input parameters.

Important pathways for PCB loss from the Bay include outflow through the Golden Gate, burial in deep sediment, and volatilization (Figure 3). Approximately 20 kg/yr are estimated to leave the Bay via each of these pathways. Degradation probably has an insignificant effect on the budget. Losses from the Bay are therefore estimated to total approximately 60 kg/yr.

The mass budget model could also be used to estimate the response time of the Bay for PCBs - the length of time needed for the Bay to respond to changing PCB inputs. Using the best available estimates of each input parameter for the model, if external loads to the Bay were completely eliminated, the total mass of bioavailable PCBs in the active sediment layer (which accounts for 98% of the total mass of PCBs in the Bay) would be predicted to decrease from approximately 450 kg to approximately 150 kg over a 10 year period (Figure 4). The model indicates that loads of 25 - 50 kg/yr could significantly delay reductions in the mass of bioavailable PCBs in the Bay (Figure 5).

The best long term time series on trends in PCB concentrations indicates that PCBs declined slowly from 1982-1998, falling by about 50% in this 16 year period (Figure 2). Assuming the other input parameters have been estimated accurately, this rate of decline would suggest that inputs during this period were on the order of 25 kg/yr.

The model also provided a means of quantitatively assessing the importance of historic sediment deposits. Large masses of persistent, particle-associated contaminants are bound up in Bay sediments. This sediment pool continually supplies contaminants to the benthic and pelagic food webs of the Bay. The size of this pool is directly related to the response time of the Bay. The size of the sediment pool is indicated in the model by the "depth of the active sediment layer": the average depth of the layer of sediment that is actively exchanging with the water column and supplying contaminants to the food web. For an active layer of 15 cm, the

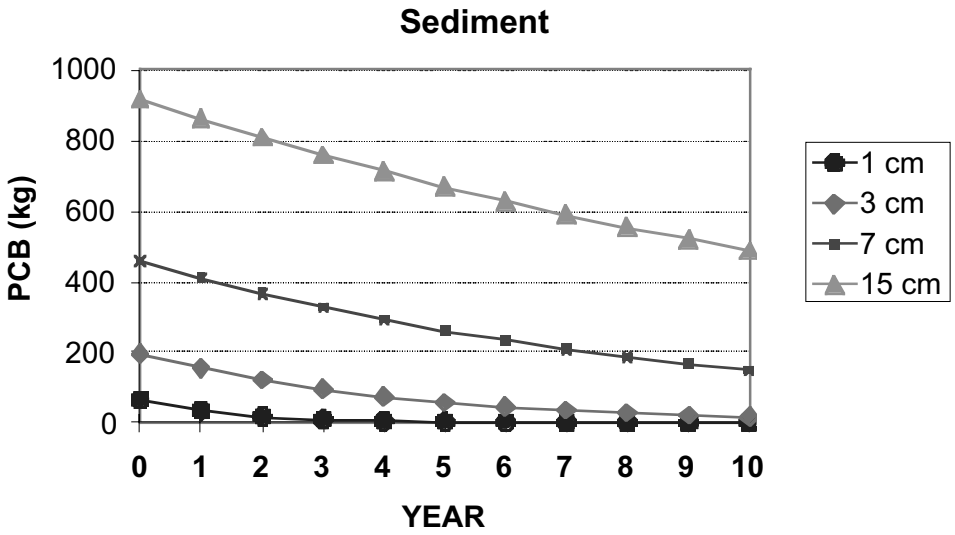

Figure 6. Predicted change in average PCB concentration in Bay sediment assuming different values for depth of the active sediment layer, no external loading of PCBs, and using best estimates for all other input parameters.

decline in PCB mass in sediment over a 10 year period in the absence of loads to the Bay is predicted to be 44%, for an active layer of 7 cm a 67% decline is predicted, and for an active layer of 3 cm a 90% decline is predicted (Figure 6). The "best" estimate of a 7 cm active layer is based on data gathered by USGS for one sampling area in Richardson Bay (Fuller *et al*. 1999). A Baywide average active sediment depth is difficult to estimate because of the spatial and temporal heterogeneity of Bay sediment and benthic biota, the very limited data available, and the abstract nature of the concept. More information on this parameter is clearly needed in order to understand response times for PCBs and other particle-associated persistent contaminants in the Bay.

It should be understood that the estimates produced by the model are crude approximations. The model is based on estimated values of Baywide annual averages of many input parameters that are often uncertain and highly simplified characterizations of complex features and processes in the Bay. A more detailed treatment of the uncertainty of the model, along with detailed information on assumptions, equations, and input parameters, will be provided in the full report.

In the context of understanding PCB loading to the Bay, a mass budget model provides several benefits. First, boundaries on the magnitude of continuing PCB input to the Bay can be established even in the absence of reliable empirical data on loading. Such boundaries are essential to understanding the importance of loading from individual pathways. Second, the influence of continuing inputs on response times can be evaluated. Third, the importance of historic sediment deposits can be quantified. Although the model estimates are uncertain, this uncertainty can be reduced as better information becomes available. The modeling exercise also provides the benefit of identifying parameters for which improved estimates would yield the greatest improvement in understanding of PCB loading and fate in the Bay.

Sources, Pathways, and Loading

The PCB mass budget modeling led to the conclusion that inputs probably existed in order to explain the slow decline in PCBs in the Bay from 1982-1998. Changing PCB fingerprints (congener ratios) observed in RMP water sampling (Jarman *et al*. 1997) provide additional evidence of continuing "fresh" inputs to the Bay. For example, Central Bay samples in July 1996 had a distinct fingerprint of Aroclor 1248, especially at Red Rock (BC60) and the Golden Gate (BC20). The lower chlorinated congeners found in Aroclor 1248 would not be expected to persist in the

Bay over the long term, nor would the fingerprint of a specific Aroclor be expected to be distinctly apparent after years of mixing in the Bay.

Uses and Sources of PCBs

The persistence of PCBs and their widespread use in the watershed combine to further suggest that PCBs are continuing to enter the Bay. Due to their resistance to electrical, thermal, and chemical processes, PCBs were used in a wide variety of applications (e.g., in electrical transformers and capacitors, vacuum pumps, hydraulic fluids, lubricants, inks, and as a plasticizer) from the time of their initial commercial production in 1929 (Brinkmann and de Kok, 1980). In 1979, a final PCB ban was implemented by the U.S. Environmental Protection Agency, prohibiting the manufacture, processing, commercial distribution, and use of PCBs except in totally enclosed applications (Rice and O'Keefe, 1995). However, a significant amount of the world inventory of PCBs may still be in place in industrial equipment (Rice and O'Keefe, 1995).

Of the 1.5 billion pounds of PCBs that were produced, about 5%, or 8 million pounds, are estimated to still be in use, mostly in electrical transformers (Brandon Carter, USEPA, personal communication). Pacific Gas and Electric (PGE), one of the primary historic users of PCBs in the Bay Area, has essentially eliminated use of PCB capacitors and transformers, but does still have a large amount of equipment containing PCB residues as a contaminant (parts per million concentrations) from the production process (Victor Furtado, PGE, personal communication). Many other industries also used PCBs in many other applications. A recent initiative by USEPA has used information voluntarily provided by industries to compile an inventory of PCBs still in use. Leakage from or improper handling of such equipment has led to widespread PCB contamination of industrial areas. A significant portion of the Bay shoreline and watershed is industrialized, and PCB contamination has been identified at many sites in the watershed.

PCB Pathways

Mass budget studies in other aquatic ecosystems have identified tributary inputs, atmospheric deposition, and effluent discharges as the primary pathways of PCB loading (Marti and Armstrong 1990, Mackay *et al*. 1994, Pearson *et al*. 1996, Nelson *et al*. 1998). These same categories are the primary potential pathways to the Bay. The Workgroup divided tributary inputs into inputs from the major rivers (the Sacramento and San Joaquin rivers) and small tributaries (including storm drains) that flow directly into the Bay. The relative importance of each major pathway in the overall PCB budget for the Bay is summarized in Table 3.

Historic Sediment Deposits

Historic sediment deposits represent one of the most important pathways for contaminant entry into the Bay food web. Nearly all of the mass of PCBs in the Bay (98%) resides in the sediment, and continued resuspension of this material due to the dynamic sediment/water interface in the Bay is a primary reason for the slow decline of PCBs in the past 20 years. Historic sediment deposits are similarly important for all of the priority contaminants in the Bay that are predominantly particle-associated.

The mass budget model provided a means of quantitatively assessing the importance of historic sediment deposits. Historic sediment deposits have a strong influence on the response time of the Bay for persistent, particle-associated contaminants such as PCBs, as discussed above under "Conceptual Model and Mass Budget Considerations". The deep mixing of Bay sediments causes the Bay to respond slowly to changes in contaminant inputs (Figure 6). Based on observations on sediment cores in Richardson Bay, Fuller *et al*. (1999) estimated that 82% of a 1-year pulse input of contaminated sediment would remain in the mixed layer (30 cm deep in their study) of sediment 20 years after deposition.

The most urgent information need relating to historic sediment deposits is an improved understanding of the active sediment layer. Little has been done to evaluate average mixing depths in the Bay. A variety of sources of existing information (e.g., data on the depth of the

Table 3. Significance of pathways of priority contaminants in the Regional Monitoring Program.

	Historic sediment deposits	Small tributaries (including storm drains)	Direct atmospheric deposition	Sacramento and San Joaquin Rivers	Effluent discharges	Harbor activities including dredging
PCBs	Significant	Possibly significant	Possibly significant	Possibly significant	Probably minor	Probably minor
PAHs	Significant	Probably significant	Probably significant	Possibly significant	Probably minor	Probably minor
Registered Pesticides	Probably minor	Probably significant	Minor	Significant	Probably significant	Minor
Mercury [A]	Significant	Probably significant	Possibly significant	Significant	Probably minor	Probably minor
Selenium	Probably minor	Probably minor	Not significant	Significant	Significant	Probably minor
Copper	Significant	Possibly significant	Probably minor	Possibly Significant	Probably Minor	Possibly Significant
Nickel	Significant	Possibly significant	Probably minor	Significant	Probably Minor	Probably minor
Silver	Significant	Probably minor	Probably Minor	Significant	Probably Minor	Probably minor
Cadmium	Probably Minor	Possibly significant	Probably Minor	Possibly Significant	Probably Minor	Probably minor

[A] Evaluation of the significance of mercury inputs must also consider where methylation is occurring in the Estuary.

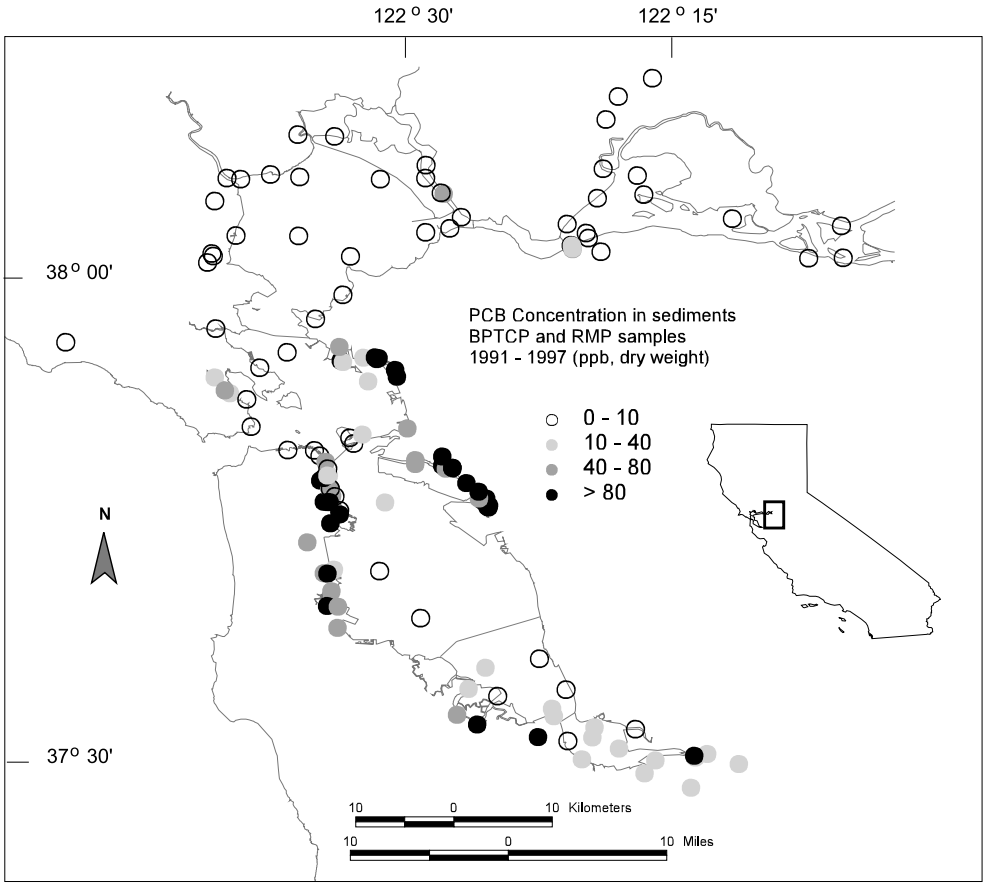

Figure 7. PCBs in Bay sediments measured in the BPTCP and RMP.

oxidized layer, estimated shear stresses) could be used to better understand this parameter. Additional measurements of sediment cores would be valuable.

Further refinement of the mass budget model could also improve our quantitative understanding of the influence of historic sediment deposits. One potentially important addition to the model would be consideration of resuspension of deeper, more contaminated sediments which occurs in portions of the Bay, large expanses of which are experiencing net erosion of sediments (Jaffe *et al*. 1998). Elaboration of the model from a one-box to a multi-box model may also improve its accuracy. A first step would be developing a separate model for South Bay.

Small Tributaries (Including Storm Drains)

Knowledge of PCB uses and monitoring data suggest that small tributaries (including storm drains) possibly represent a significant pathway for continuing PCB input to the Bay. Drainage from industrial areas with high PCB contamination potential would primarily enter the Bay via local tributaries. Sediment sampling under the Bay Protection Program (Hunt *et al*. 1998) and the RMP has frequently found high PCB concentrations at the points where local tributaries enter the Bay (Figure 7). A recent intensive survey of sediment contamination in San Leandro Bay has also found distinctly elevated PCB concentrations (300 - 500 ng/g dry weight) in surface sediments of three small tributaries to San Leandro Bay (Daum *et al*. 2000). Other very limited data on PCB concentrations in sediment of local creeks also indicate the presence of concentration gradients and suggest possible PCB transport to the Bay by small tributaries (BASMAA 1996). PCB contamination has been identified at many sites in the watershed, and

contaminated particles eroding from these sites would enter the Bay in runoff to small tributaries and storm drains. Overall, it is possible that small tributaries account for a large portion of the continuing PCB input to the Bay.

A sequence of analyses is needed to determine whether small tributaries are a significant pathway for PCB loading to the Bay. Further review of existing monitoring, chemical use, and land use data for local watersheds will help define the potential for inputs from specific drainage areas. Further development of a conceptual model describing PCB transport from local watersheds will be essential, and development of a land use-based models to estimate loadings will also be valuable. After existing data are thoroughly reviewed, field studies should be performed to determine whether or not specific small tributaries are a significant pathway. A sequence of field studies has been proposed that would identify small tributaries with the greatest potential loading and then quantify these loadings (see Recommendations).

Direct Atmospheric Deposition

Direct atmospheric deposition could be a significant source of PCBs to the Bay. The urban plume (Holsen *et al*. 1991, Simcik *et al*. 1997, Zhang *et al*. 1999) of the San Francisco peninsula would often sit right on the Bay, and local climatic conditions (fog, a turbulent air/water interface) could enhance air/water exchange of contaminants. Also suggestive of the importance of local atmospheric deposition are PCB concentrations in fish from San Pablo Reservoir that are comparable to those in Bay fish (OEHHA 1999) in spite of no known sources in the local watershed. Assuming a typical rainfall concentration of 1000 pg/L and a typical dry deposition rate of 10 mg m^{-2} yr^{-1} based on studies done elsewhere (Steve Eisenreich, Rutgers University, personal communication), wet deposition would be approximately 0.5 kg/yr and dry deposition would be approximately 10 kg/yr.

These very crude estimates could be greatly improved by the measurement of PCB concentrations in local rainfall and local dry deposition rates of PCBs. Measurement of dry deposition downwind of industrial and military areas on the west side of the Bay would be particularly valuable. Inclusion of PCBs in the RMP Atmospheric Deposition Pilot Study would provide crucial information on this potentially significant pathway for PCBs.

Sacramento and San Joaquin Rivers

Potential sources of PCBs in the Central Valley include both areas with industrial development and hydroelectric power generation facilities (CVRWQCB 1987).

The Sacramento and San Joaquin rivers appear to transport masses of PCBs to the Bay that are possibly significant. RMP sampling has found typical concentrations of approximately 250 pg/L total (dissolved + particulate) PCBs at the river stations (BG20 and BG30). Combining this concentration with annual average Delta outflow yields an average annual mass load of 7 kg/yr.

This value probably underestimates loads from the rivers, since particle-associated contaminants such as PCBs are transported principally during runoff events early in the wet season and these short duration events are generally not captured by RMP sampling. One possible exception was in January 1997, when RMP water sampling coincided with a record runoff event. Using PCB concentrations and Delta outflow measured at this time, an instantaneous mass load of 19 kg/yr is obtained.

In spite of low concentrations and an apparently diluted signal of PCB contamination, events with high flows and sediment transport can still lead to significant mass loading from the Rivers. Loadings of 7 to 19 kg/yr could contribute substantially to the slow rate of decline observed for PCBs in the Bay.

Mass loading from the Rivers should be carefully estimated. Further analyses are needed to determine whether the rivers are a significant pathway for PCB loading to the Bay. Additional review of existing data on particle transport to the Bay during high flow periods is needed to produce more realistic estimates of possible PCB loading. If the need is indicated by review of existing data, field studies could be performed to better characterize PCB loading from the

rivers. Such studies would be technically challenging, and should be carefully designed with input from USGS and others with expertise in this area.

Effluent Discharges

PCB loading from effluent discharges are probably a minor component of the overall mass budget. Very few reliable data are available on trace organics concentrations in point sources. A few effluent samples were recently analyzed by the City of Palo Alto (Torke 1998) and concentrations ranging from 200 to 3000 pg/L were detected. If these concentrations are assumed to be typical of Bay Area POTW effluents in general, then these effluents are accounting for 0.1 to 2.0 kg/yr of PCB input to the Bay. There are very few reliable, quantitative data available on PCBs in effluents. An SFEI study is currently in progress that will provide very high quality data on effluent concentrations of PCBs and other trace organics. These data will allow a more precise estimate of loading from effluent discharges.

Vessels

Anecdotal information suggests that vessels could be a source of PCBs to the Bay. PCBs were used in paints on Navy vessels (Brandon Carter, USEPA, personal communication). Also, PCBs were used in equipment on ships. The Aroclor 1248 fingerprint found in Central Bay samples in July 1996 could have come from a vessel, as Aroclor 1248 was used in shipping (Steve Eisenreich, Rutgers University, personal communication). The total mass of PCBs entering the Bay from this source would be difficult to estimate, but is probably a minor fraction of the estimated 60 kg/yr total input to the Bay.

Harbor Activities (Including Dredging)

Harbor activities and dredging are essentially accounted for under the other pathway categories. Industrial harbors and shipyards often contain sediments with relatively high concentrations of PCBs (e.g., San Leandro Bay [Hunt *et al*. 1998] and Hunters Point [SFBRWQCB 1999]). These PCB residues can generally be attributed to inputs from small tributaries and storm drains or from maintenance of vessels, two categories already discussed above. Maintenance dredging and dredged material disposal either serve to redistribute sediments within the Bay (for in-Bay disposal), which doesn't affect a Bay-wide mass budget, or to remove sediment from the Bay (ocean or upland disposal), which represents a loss term in the mass budget. New work dredging, which could result in remobilization of older, more contaminated sediment, deserves consideration, but has not been included in the existing mass budget. In-Bay disposal could be dealt with in a multi-box model, with disposal at Alcatraz, for example, treated as an input to Central Bay. Harbor activities appear to have a minor influence on the overall PCB mass budget for the Bay, and could actually result in net removal from the Bay.

Estimation of the mass of PCBs released at in-Bay disposal sites would be an easy task. Comparing the disposal site releases to the other components of the mass budget would help place these releases in context.

While harbor activities are not a major component of the Bay-wide mass budget, they may still lead to increased PCB entry into the food web on a local basis.

Summary of Information Needs: PCBs

Due to the efforts of the Chlorinated Hydrocarbon Workgroup, a large body of research in other ecosystems, and the relatively predictable behavior of PCBs in aquatic ecosystems, a reasonable conceptual model and mass budget for PCBs in the Bay has been constructed. There remains, however, considerable room for improvement in the model. Overall, the most urgent pathway-specific information needs exist for loads from historic sediment deposits, local tributaries, the Sacramento and San Joaquin Rivers, and atmospheric deposition, which probably account for the majority of the total annual PCB input to the Bay.

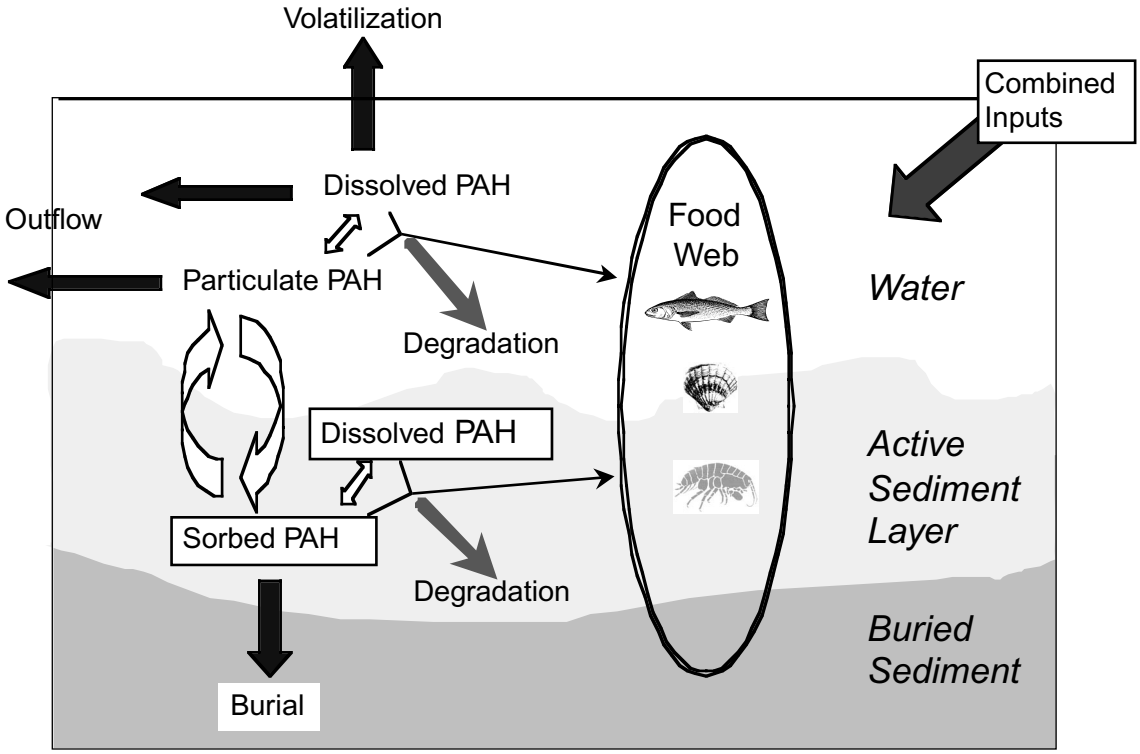

Figure 8. PAH pathways in the Bay.

b. PAHs

Conceptual Model and Mass Budget Considerations

A detailed conceptual model and mass budget have not yet been developed for PAHs in the Bay because no Workgroup focused its attention on PAHs. In general, however, PAHs have physical and chemical properties that are similar to those of the PCBs. PAHs generally are persistent, have low water solubility, are hydrophobic and lipophilic, and have low but consequential volatility. The mass budget model that has been developed for PCBs in water and sediments of the Bay could be readily adapted to PAHs. Lun *et al*. (1998) applied a similar model to PAHs in a Canadian fjord. One major difference between PCBs and PAHs is that PAHs are more susceptible to degradation, due to both abiotic metabolic processes, so losses due to degradation can be a significant component of the mass budget. Another major difference is that PAHs occur naturally, although human activities have caused greatly increased concentrations in the environment. The important features of PAH cycling in the Bay are illustrated in Figure 8.

Like the PCBs, PAHs are actually a class of compounds with widely varying structures and properties. PAHs consist of two or more fused benzene rings in various arrangements (Figure 9). A tremendous variety of PAHs occurs in nature, with different combinations of benzene rings, other ring structures, and attached carbon chains. A subset of 15 to 20 PAHs with 2 to 6 rings is typically measured in aquatic environments because they are the most abundant, mobile, and toxic members of this class of compounds. Lower molecular weight PAHs (LPAHS, 2- and 3-ring compounds) tend to be more water soluble, more volatile, more readily metabolized, and less persistent. Higher molecular weight PAHs (HPAHS, 4- to 6-ring compounds), are less water soluble, less volatile, less readily metabolized, and more persistent.

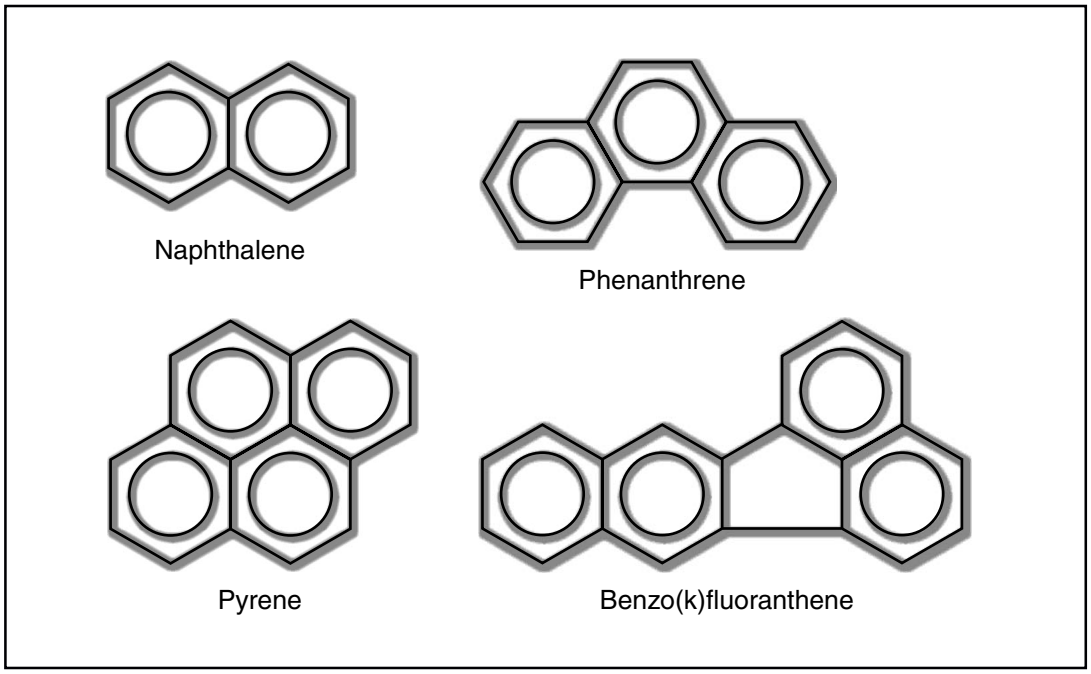

Figure 9. Chemical structures of some PAHs. The smallest PAH molecule is naphthalene. PAHs shown range from 2 to 5 rings.

The variability in properties among the PAHs leads to widely varying behaviors in the environment. For example, the model developed by Lun *et al*. (1998) predicted that of the naphthalene (the lowest molecular weight PAH) entering Saguenay Fjord, 88% is degraded, 9% evaporates, and 3% is advected out of the Fjord. For the high molecular weight PAH benzo(a)pyrene, on the other hand, advection (57%), degradation (34%) and burial (9%) are the major loss pathways.

The PAHs of greatest regulatory concern are the high molecular weight PAHs (HPAHs) like benzo(a)pyrene, many of which are carcinogenic. The HPAHs are persistent and associate with sediments in the Bay, similar to the PCBs, and therefore some of the findings of the PCB mass budget analysis can be expected to apply to the HPAHs as well. Historic sediment deposits will play a central role in the PAH budget for the Bay. The response time of the Bay for HPAHs is likely to be very slow due to the persistence of these chemicals in sediment and the deep active sediment layer in the Bay. In addition, PAH sources continue to exist in the watershed and result in continuing PAH loading to the Bay; the PCB model illustrated the effect such loading could have in further slowing declines in ambient concentrations.

Sources, Pathways, and Loading

Uses and Sources of PAHs

The majority of PAHs in the environment are of pyrolytic origin, formed during the burning of petroleum, wood, and coal under oxygen-deficient conditions (McVeety and Hites 1988). Major pyrolytic sources of PAHs include motor vehicles, forest fires, residential wood combustion, coke manufacturing, aluminum production, power generation, and waste incineration (Environment Canada 1994). These sources result in emission of PAHs to the atmosphere. PAHs in the air subsequently are deposited on land and water surfaces in watersheds. PAHs on the land surface are carried by runoff to aquatic ecosystems. Other sources of PAHs lead directly to contamination of aquatic ecosystems, including discharges or spills of crude oil or other petroleum products and leaching of PAHs from wooden structures treated with creosote. PAHs from all of these pathways accumulate in aquatic sediments.

The proportions of individual PAHs present in environmental samples (the PAH "fingerprint") provide information on PAH sources. The fingerprint of PAHs from combustion sources is quite different from the fingerprint of oil or refined petroleum products. Because of this difference it is possible to tell whether PAHs from environmental samples are predominantly attributable to either crude oil (petrogenic) or combustion (pyrogenic) sources. Studies of environmental PAH contamination frequently employ PAH fingerprints in this manner (Blumer 1976, LaFlamme and Hites 1978, Boehm and Farrington 1984, Pereira *et al*. 1992, Bouloubassi and Saliot 1993, Yunker and Macdonald 1995, Maruya *et al*. 1996, Maruya *et al*. 1997, Simcik *et al*. 1996, Budzinski *et al*. 1997, Baumard *et al*. 1998, Pereira *et al*. 1999). PAHs in aquatic sediments, especially near urban areas, have been found to originate largely from anthropogenic combustion (LaFlamme and Hites 1978). PAH studies in the Bay have similarly found a predominantly pyrogenic profile (Pereira *et al*. 1992, 1999, Maruya *et al*. 1996, 1997). RMP water, sediment, and bivalve samples have almost invariably shown a predominantly pyrogenic PAH profile.

Sources of PAH emission to the atmosphere include forest fires, industrial activities such as aluminum smelting and coke production, vehicle emissions, residential wood burning, and agricultural burning (Bjorseth and Ramdahl 1985, Environment Canada 1994). In the U.S., motor vehicles are thought to be the major source of atmospheric PAHs, accounting for 36% of the annual total. Other sources include aluminum production (17%), forest fires (17%), residential wood burning (12%), coke manufacturing (11%), power generation (7%), and incineration (3%) (Bjorseth and Ramdahl 1985). Much of the emitted mass of PAHs deposits on land or water surfaces near the site of emission. Thus, motor vehicles emissions also have a relatively large impact on aquatic ecosystems in urban areas because a high proportion of these emissions are transported to water bodies in runoff (Sharma *et al*. 1997).

Many studies have concluded that motor vehicles are a source of PAHs in the atmosphere, street dusts, and aquatic sediments near areas with heavy traffic. Tunnel studies are frequently used to assess motor vehicle emissions under realistic conditions. Miguel *et al*. (1998) measured emissions of PAHs in two bores of the Caldecott Tunnel in the Bay Area in 1996. One of the bores was influenced by heavy-duty (diesel powered) truck emissions; a second bore was reserved for light-duty (gasoline powered) vehicles. Diesel vehicles were the major source of lighter PAHs, while gasoline vehicles were the dominant source of high weight PAHs. Benner *et al*. (1989) estimated emission rates of individual PAHs in a study of the Baltimore Harbor Tunnel. The PAHs emitted in largest quantities by cars and trucks in the Tunnel were phenanthrenes, fluoranthene, and pyrene. HPAHs were also emitted, but at lower rates. This study also concluded that diesel exhaust had a relatively high proportion of LPAHs and alkylated PAHs compared to exhaust from light-duty vehicles. In addition to differences in the PAH fingerprints of diesel and gas exhaust, the quantities released by these two classes of vehicle differ. A tunnel study in Switzerland (Staehelin *et al*. 1998) estimated that emission rates of PAHs from diesel vehicles were significantly larger, generally about 10-fold, than emission from gasoline vehicles.

PAHs emitted from vehicles deposit on roads and nearby impervious surfaces. The PAH fingerprints of street dusts have been observed to match those of motor vehicle exhaust (Takada *et al*. 1990). Storms transport these street dusts to aquatic ecosystems. Between emission to the atmosphere and deposition to Bay sediments, the more volatile, soluble, and reactive LPAHs are lost along the way, contributing to the pyrogenic profile dominated by fluoranthene, pyrene, and other HPAHs that is commonly seen in Bay samples.

Other potential sources of PAHs to the local atmosphere include industrial activities and residential wood burning. In other regions, industrial facilities have had a large impact on PAH mass budgets, including aluminum smelters (Bjorseth and Kamdahl 1985, Environment Canada 1994, Lun *et al*. 1998) and coke producers (Bjorseth and Kamdahl 1985, Environment Canada 1994, Mayer and Nagy 1992, Li *et al*. 1998, Sharma *et al*. 1997, Simcik *et al*. 1996, Su *et al*. 1998). Residential wood burning has been found to make minor contributions to overall PAH emissions, often observed as a seasonal increase in characteristic PAHs in winter (Bjorseth and

Kamdahl 1985, McVeety and Hites 1988, Environment Canada 1994, Dickhut and Gustafson 1995, Sharma *et al*. 1997, Su *et al*. 1998).

Several other sources lead to direct transport of PAHs to water bodies and could be important in the PAH mass budget for the Bay. Spills of petroleum or petroleum products periodically occur in the Bay. An example of such a spill occurred in 1988 when approximately 400,000 gallons of crude oil was released into Suisun Bay due to an accident at the Shell Oil Company refinery in Martinez. With the presence of several refineries and many other activities that use petroleum products in the Bay Area, and the associated transport and processing of petroleum, the possibility of significant spills and PAH contamination will remain. Creosote is a coal tar derivative, rich in PAHs (Huntley *et al*. 1995), that is used to preserve wood in both aquatic and terrestrial applications and is a significant source of PAHs in the environment (Environment Canada 1994, Gevao and Jones 1998). Desorption of PAHs from treated wood is a potential source to the Bay. Crankcase drippings from motor vehicles deposit on roadways and parking lots, leading to PAH transport to water bodies (Environment Canada 1994). This potential source has not received much attention in the literature.

Pereira *et al*. (1999) have provided a long term perspective on PAH contamination of the Bay through analysis of sediment cores. Prior to 1900, pyrogenic PAH concentrations were very low, more than two orders of magnitude lower than concentrations in recently deposited sediments. The sources of the low concentrations of PAHs present prior to 1900 were probably combustion of wood or coal and natural fires. A sharp increase in concentrations occurred after 1910, with maximum concentrations occurring around 1950. This pattern, with the onset of anthropogenic influence around 1900 and peak concentrations around 1950, is a recurring pattern that has been observed in sediment cores from other ecosystems (McVeety and Hites 1988). PAH concentrations decreased in the most recent layers analyzed.

PAH Pathways

Studies in other aquatic ecosystems have identified urban runoff, atmospheric inputs, riverine inputs, effluent discharges, spills, and sediment-water exchange as the major pathways of PAH input. These are also the primary potential pathways for PAH transport to the Bay. The relative importance of each major pathway in the overall PAH budget for the Bay is summarized in Table 3.

Historic Sediment Deposits

Historic sediment deposits are a significant pathway for exposure of Bay biota to PAHs. As the mass budget model indicated for PCBs, historic sediment deposits will have a strong influence on the response time of the Bay for PAHs. The estimate of Fuller *et al*. (1999) that 82% of a 1-year pulse input of contaminated sediment would remain in the mixed layer 20 years after deposition can be extended to PAHs, since little degradation of PAHs, particularly HPAHs, is observed after deposition (e.g., Lun *et al*. 1998). Sediment deposits have also been observed to play an important role in Chesapeake Bay, another shallow estuary where sediment resuspension is a primary supply of particles to the water column. Ko and Baker (1995) concluded that sediment resuspension may control the concentrations and distributions of PAHs and other persistent organics in the water column of Chesapeake Bay.

Development of a mass budget model for PAHs would be an essential first step in understanding PAHs in the Bay, and specifically in quantifying the role of historic sediment deposits. The same modeling approach employed for PCBs could be employed for PAHs, and since the model has already been developed this would be a relatively easy task.

Better estimates of mixing depths in the Bay will be needed to understand response times of PAHs in the Bay. As discussed for PCBs, a variety of sources of existing information (e.g., data on the depth of the oxidized layer, estimated shear stresses) could be used to better understand this parameter. Additional measurements of sediment cores may also be needed.

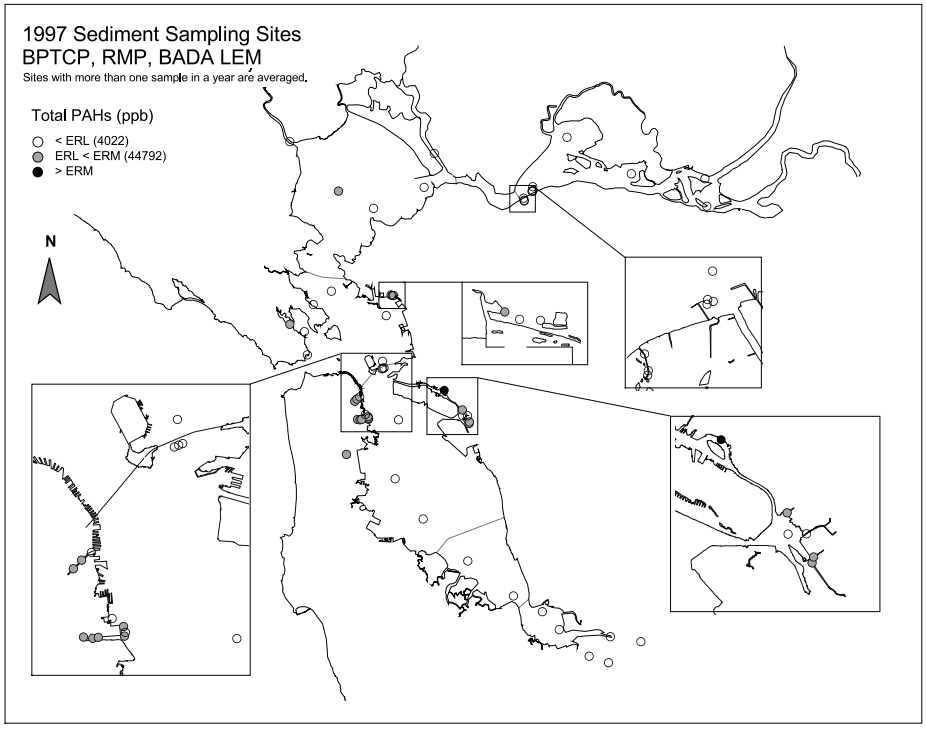

Figure 10. PAH concentrations in Bay sediments measured in the BPTCP and RMP.

Further refinement of the mass budget model would result in better estimates of PAH behavior in the Bay. Extension of the mass budget model to consider resuspension of deeper, more contaminated sediments could be important. Large expanses of the Bay are experiencing net erosion of sediments (Jaffe *et al*. 1998, Cappiella *et al*. 1999), increasing the likelihood of remobilization of buried sediments. These buried sediments, depending on when they were deposited, may contain generally higher PAH concentrations.

Elaboration of the model from a one-box to a multi-box model would also improve its accuracy. A first step would be developing a budget for the South Bay. A further improvement would be modeling remobilization of sediments from specific sites with high PAH concentrations. Many hotspots of PAH contamination exist in the Bay (Figure 10) (Hunt *et al*. 1998, SFBRWQCB 1999). An extreme example is Castro Cove, which received wastewater from the Chevron refinery from around 1900 until 1987. Up to 1972 the wastewater discharged to Castro Cove was treated only by an oil-water separator (SFBRWQCB 1999). This site has yielded some of the highest sediment PAH concentrations measured in California (Gunther *et al*. 1997, Hunt *et al*. 1998). The fingerprint is petrogenic with some unusual features (Newman 1998).

Small Tributaries (Including Storm Drains)

Knowledge of PAH sources, environmental fate, and monitoring data suggest that small tributaries (including storm drains) probably represent a significant pathway for continuing PAH input to the Bay. Urban runoff primarily enters the Estuary through small tributaries, and has been identified as a significant pathway for PAH entry into aquatic ecosystems. Hoffman *et al*. (1984) found that urban runoff accounted for 71% of the total inputs of HPAHs and 36% of LPAHs to Narragansett Bay. Urban runoff inputs of HPAHs were higher due primarily to the stronger association of HPAHs with particles washing out of the Narragansett Bay watershed. Bomboi and Hernandez (1991) found high concentrations of PAHs in urban runoff, especially in areas with the highest motor vehicle traffic. Herrman (1981) also found urban runoff to be a

primary pathway for PAH transport. PAHs in urban runoff originate primarily from motor vehicle exhaust, deposit on impermeable surfaces as street dusts, and are transported to the Bay in creeks and storm drains.

The spatial distribution of PAH concentrations and PAH fingerprints at RMP stations are generally consistent with the hypothesis that street runoff is a primary source of PAHs to the Estuary. PAH concentrations in water and sediment are highest at stations from the South Bay to the San Pablo Bay station, and are markedly lower further upstream in Suisun Bay and the Rivers. This range of elevated concentrations corresponds with the most urbanized portion of the Estuary. Sediment sampling under the Bay Protection Program (Hunt *et al*. 1998) and the RMP has frequently found high PAH concentrations at the points where local tributaries enter the Bay (Figure 10). A recent intensive survey of sediment contamination in San Leandro Bay has also found elevated PAH concentrations in surface sediments of small tributaries to San Leandro Bay (Daum *et al*. 1999). Very limited data on PAH concentrations in sediment of local creeks also indicate contamination gradients and possible PAH transport to the Bay by small tributaries (Woodward-Clyde Consultants 1991). Many studies of sediment contamination in other ecosystems have implicated runoff as a primary source of PAHs.

Overall, it is probable that small tributaries account for a significant portion of the total PAH input to the Bay. Little quantitative information is available, however, to evaluate the magnitude of PAH loads from small tributaries. The sequence of studies proposed to evaluate PCB loading from small tributaries should also be performed to evaluate PAH loading. Further review of existing data for local watersheds will help define the potential for inputs from specific drainage areas. Development of a conceptual model describing PAH transport from local watersheds will be essential. Employing land use-based models to estimate loadings will also be valuable. After existing data are thoroughly reviewed, field studies should be performed to determine whether or not specific small tributaries are a significant pathway. A sequence of field studies has been proposed that would identify small tributaries with the greatest potential loading and then quantify these loadings (see Recommendations).

Direct Atmospheric Deposition

Direct atmospheric deposition of PAHs to the Bay surface probably accounts for a significant fraction of total PAH inputs. Processes that can transport PAHs to the water from the atmosphere include wet deposition (including washout of gaseous and particle-bound PAHs), dry deposition of particles, and absorption of gaseous PAHs by Bay waters. Volatile compounds, including LPAHs, are delivered primarily through gas transfer processes while less volatile compounds such as HPAHs associate with particles and are deposited through washout and dry deposition of particles (Dickhut and Gustafson 1995).

Studies in other ecosystems have concluded that wet deposition, dry deposition, and gas exchange can represent significant pathways of PAH input to aquatic ecosystems. Gaseous exchange is a major transport process for LPAHs and semi-volatile PAHs (Gustafson and Dickhut 1997, Nelson *et al*. 1998). In Chesapeake Bay, gas absorption rates for the volatile PAHs fluorene and phenanthrene are much larger than the loading from wet deposition, dry deposition, and riverine inputs combined (Nelson *et al*. 1998). Dry and wet deposition are the dominant atmospheric input pathways for PAHs with low volatility (McVeety and Hites 1988, Leister and Baker 1994, Dickhut and Gustafson 1995, Gustafson and Dickhut 1997, Nelson *et al*. 1998). Reported dry deposition rates usually exceed wet deposition rates.

High concentrations of PAHs and high atmospheric deposition rates have been detected in urban plumes when prevailing winds carry air from urban areas over water bodies (Simcik *et al*. 1997, Nelson *et al*. 1998). Nighttime PAH concentrations over Lake Michigan, for example, were an average of 18 times higher when the wind blew from the direction of the Chicago metropolitan area than when the wind blew from other directions (Simcik *et al*. 1997). The atmospheric plumes of urban areas around the Bay would frequently be situated over the surface of the Bay. Local climatic conditions (fog, a turbulent air/water interface) could en-

hance air/water exchange of PAHs. Atmospheric deposition due to the presence of seven heavily trafficked bridges directly over the surface of the Bay probably contributes significant PAH loadings.

It is likely that direct atmospheric deposition accounts for a significant portion of the total loading of PAHs to the Bay. However, little local quantitative information is available to evaluate this possibility. Inclusion of PAHs in the RMP Atmospheric Deposition Pilot Study would provide valuable preliminary information. Ideally, estimation of PAH deposition to the Bay should include sampling of locations that are in the path of the urban plumes that may have a large influence on the PAH budget. Further evaluation of direct deposition from bridges is warranted: a more thorough review of existing information should be conducted, followed by field studies if necessary.

Sacramento and San Joaquin Rivers

PAH loading to the Bay from the Sacramento and San Joaquin Rivers may be a significant component of the overall PAH mass budget. Riverine transport can be a significant component of PAH mass budgets, especially for HPAHs with low volatility, as was found for the Susquehanna River, the largest tributary of Chesapeake Bay (Godfrey *et al*. 1995, Nelson *et al*. 1998). PAH loading from the Sacramento and San Joaquin Rivers can presently be estimated from RMP water column measurements and Delta outflow volumes, as was done for PCBs. For PAHs, however, there is no mass budget to provide context for interpretation of such estimated loads, so there is presently little value to performing these calculations.

PAH sources do exist in the Central Valley, including the urbanized areas around Sacramento and Stockton. Furthermore, future urban growth will likely be greatest in the Central Valley, in areas such as San Joaquin County, rather than the areas surrounding the Bay that are already densely populated. Given the large amounts of flow and sediment transport involved, mass loading of PAHs from the Rivers could potentially be a significant component of the PAH mass budget and should be carefully estimated. Loading from the Sacramento and San Joaquin Rivers are probably smaller than those carried by local tributaries and storm drains in the denser urban regions of the Bay Area or direct atmospheric deposition.

Further analyses are needed to determine whether the rivers are a significant pathway for PAH loading to the Bay. As for the PCBs, additional review of existing data on particle transport to the Bay during high flow periods is needed to produce more realistic estimates of possible PAH loading. If the need is indicated by review of existing data, field studies could be performed to better characterize PAH loading from the rivers.

Effluent Discharges

PAH loading from effluent discharges are probably a minor component of the overall budget. Due to the high detection limits of EPA methods, it is likely that few quantitative data are available on trace organics concentrations in municipal or industrial effluents. This should be confirmed by reviewing recent NPDES monitoring data. If it appears that effluents may contribute significantly to the PAH budget, analysis of effluents using methods with low detection limits may be required.

Municipal wastewater effluents are generally not mentioned in the literature as significant sources of PAHs to aquatic ecosystems. Municipal effluents would be expected to contain a relatively high proportion of LPAHs (e.g., Hoffman *et al*. 1984), since the wastewater treatment process removes most of the particles, along with particle-associated contaminants such as HPAHs, from the effluent. As mentioned previously, PAHs generally have a pyrogenic fingerprint in water and sediment samples from the Bay, with HPAHs predominating over LPAHs. The fingerprint that would be expected if municipal effluents were a major pathway is generally not present in Bay samples.

Prior to establishment of current levels of wastewater treatment, industrial effluents were a significant source of PAHs, as indicated by the extreme PAH contamination around the waste-

water outfall in Castro Cove. Industrial effluents have been identified as PAH sources in other studies (Huntley *et al*. 1995, Li *et al*. 1998). Current data from the refineries and other industrial discharges should be reviewed to determine whether the potential still exists for industrial discharges to contribute significantly to the PAH budget for the Bay.

Vessels

PAHs are present in petroleum and petroleum products, and use of these products by vessels on the Bay leads to contamination of Bay waters. Small spills of petroleum products from small vessels are a regular phenomenon. The contribution of this pathway to the overall PAH mass budget is probably minor, however. Petroleum and refined petroleum products contain relatively high concentrations of LPAHs and alkylated PAHs, and these PAHs are generally minor components in Bay waters and sediments.

Harbor Activities (Including Dredging)

Harbor activities appear to have a minor influence on the overall PAH mass budget for the Bay. Harbor activities and dredging are essentially accounted for under the other pathway categories. Industrial harbors and shipyards often contain sediments with relatively high concentrations of PAHs (e.g., San Leandro Bay [Hunt *et al*. 1998] and Castro Cove [SFBRWQCB 1999]). These PAH residues can generally be attributed to inputs from small tributaries and storm drains, historic effluent discharges, or vessels, three categories already discussed above. Maintenance dredging and dredged material disposal either serves to redistribute sediments within the Bay (for in-Bay disposal), which doesn't affect a Bay-wide mass budget, or to remove sediment from the Bay (ocean or upland disposal), which represents a loss term in the mass budget. New work dredging, which could result in remobilization of older, more contaminated sediment, deserves consideration. In-Bay disposal could be dealt with in a multi-box model, with disposal at Alcatraz, for example, treated as an input to Central Bay.

Desorption of PAHs from pilings treated with creosote (Gevao and Jones 1998) represents a source of PAHs to the Bay that would be prevalent in harbors; this input should be quantified as part of the overall PAH mass budget.

While harbor activities are not a major component of the Bay-wide mass budget for PAHs, they may still lead to significant bioaccumulation of PAHs on a localized basis.

Summary of Information Needs: PAHs

The first step in improving understanding of PAHs in the Bay should be development of a Bay-wide mass budget model. This would allow evaluation of the overall magnitude of continuing inputs and the importance of historic sediment deposits, and would provide essential context for evaluating the overall significance of loading from individual pathways. The most urgent pathway-specific information needs exist for loads from historic sediment deposits, local tributaries, atmospheric deposition, and the Sacramento and San Joaquin rivers, which collectively probably account for the majority of the total annual PAH input to the Bay.

c. Registered Pesticides

"Registered pesticides" (pesticides in current use, including diazinon, chlorpyrifos, and other chemicals) were considered in detail by the Pesticides Work Group. Registered pesticides possess a combination of properties that set them apart from other RMP analytes. These chemicals can be acutely toxic at very low concentrations, are not persistent, and do not accumulate in food webs because they are readily metabolized by vertebrates. Furthermore, these chemicals are applied and carried by stormwater into the Estuary in a very unpredictable way. Very small masses of some registered pesticides can be sufficient to render a section of a tributary or the Estuary toxic to sensitive aquatic organisms. Theoretically, just 67 kg (or 147 lbs) of

chlorpyrifos is needed to bring the entire Bay to 10 parts per trillion, a concentration that could impact sensitive resident aquatic organisms. As little as 30 grams of diazinon can account for observed concentrations in an urban creek (Tom Mumley, SFBRWQCB, pers. comm.).

The combination of the unpredictable loading of registered pesticides to the Estuary, the minute quantities that can cause toxicity, and the transient and localized nature of toxic events in the Estuary make estimation of Bay-wide loading of these chemicals difficult, error-prone, and of little value. The Regional Board has indicated to the Pesticides Work Group that source reduction, rather than load estimation and allocation, will be emphasized in efforts to reduce the inputs and impacts of registered pesticides in the Bay. The focus of the SPLWG with regard to registered pesticides should therefore be on examining use patterns in the Bay watershed, rather than quantitative evaluation of pathways, loading, and mass budgets.

Conceptual Model

A conceptual model of the sources, fates and effects of registered pesticides in the Estuary was developed by the Pesticides Work Group (Figure 11).

Sources, Pathways, and Loading

Uses and Sources of Registered Pesticides

Understanding the uses of registered pesticides is essential to identifying ways of preventing their entry into the Estuary and to developing strategies for monitoring their presence and effects in the Estuary.

One valuable source of information on pesticide use in California is the Pesticide Use Reporting Program run by the California Environmental Protection Agency's Department of Pesticide Regulation. This program is the most comprehensive pesticide use reporting program in the world.

The PURP tracks agricultural applications of pesticides throughout the state. California has a broad legal definition of "agricultural use", so pesticide applications to parks, golf courses, and other areas are included. In addition, commercial pest control operators (such as ground and aerial applicators, structural pest control operators, and professional gardeners) are required to report their pesticide usage. Pesticide applicators report the amount applied, the crop or type of use, the number of applications, and the acreage treated. The primary exceptions to the use reporting requirements are home and garden use and most industrial and institutional uses. The PURP is a source of a great deal of valuable information. However, it should be noted that limited validation is performed on this immense database, and any single data point must be interpreted with caution.

Bay Area data on the use of chlorpyrifos and diazinon illustrate the type of information available from the PURP (Figures 12 and 13). A total usage of 120,101 lbs of chlorpyrifos was reported in Bay Area counties in 1995. Most of this reported amount (59%, or 70,929 lbs) was for structural pest control. In the more urbanized counties, structural pest control was the primary use. In the more agricultural Solano and Sonoma counties other uses, such as on alfalfa or apples, contributed a larger share of the total. The statewide total amount of chlorpyrifos applications reported in 1995 for all uses was 3,524,365 lbs.

A total application of 95,857 pounds of diazinon was reported in Bay Area counties in 1995. Structural pest control was again the primary use (51% of the total, or 49,118 lbs). The statewide total amount of diazinon applications reported in 1995 for all uses was 2,376,883 lbs. Structural pest control accounted for 1,419,055 lbs, or 60%, of this statewide total. In the more urbanized counties, structural pest control was the primary use of diazinon. In the more agricultural Solano and Sonoma counties other uses contributed a larger share of the total.

The PURP database is a valuable tool that can be used to identify the locations and types of applications accounting for significant proportions of registered pesticide use in the watershed of the Estuary. The PURP database, however, does not provide data on all uses of registered

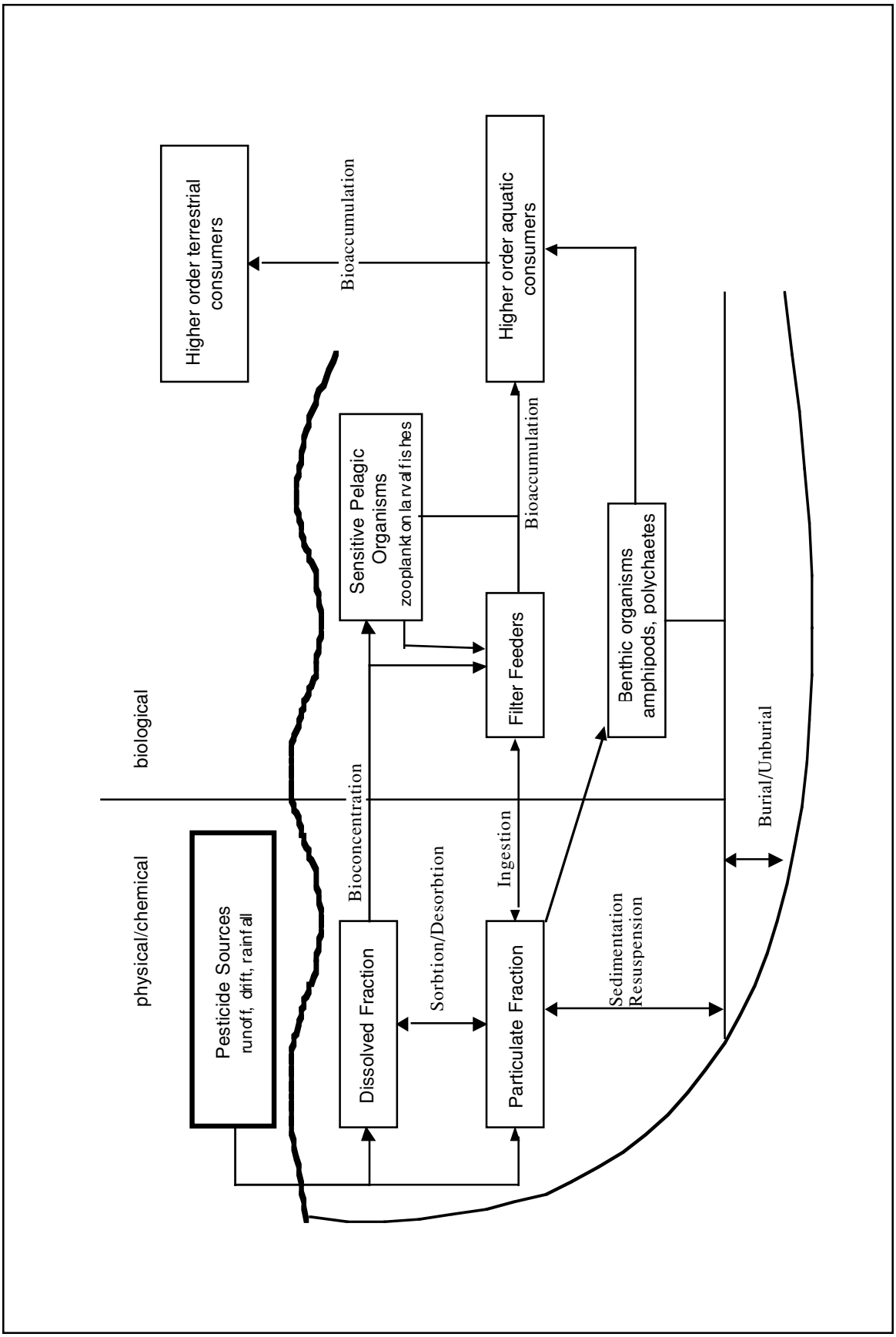

Figure 11. Conceptual model of the sources, fates, and effects of registered pesticides in the Estuary.

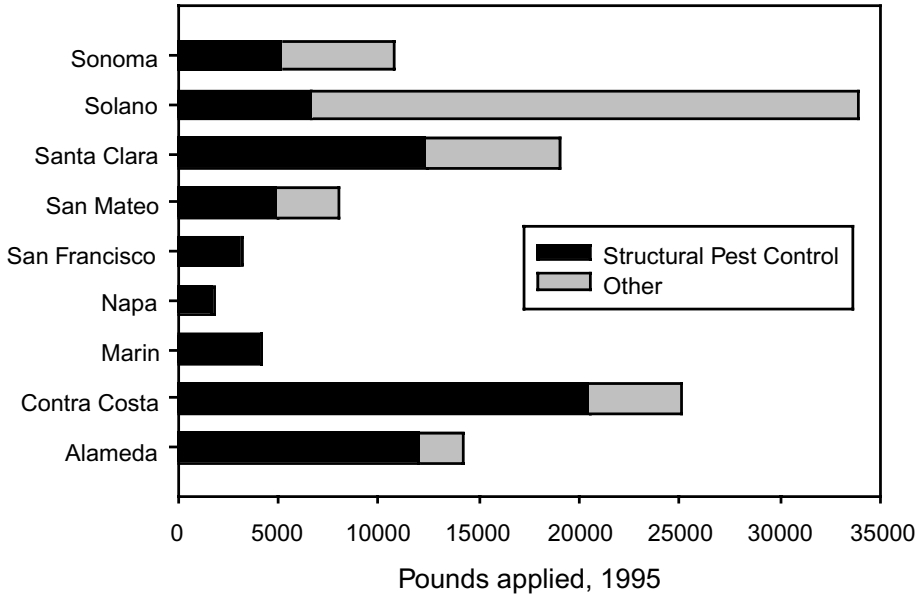

Figure 12. Application of chlorpyrifos in Bay Area counties in 1995, as reported in the Pesticide Use Reporting Program.

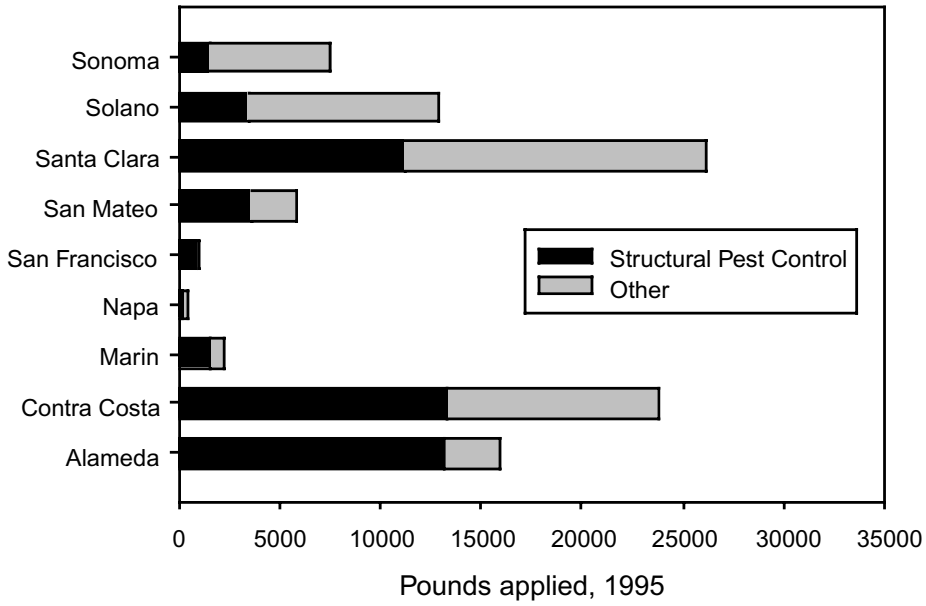

Figure 13. Application of diazinon in Bay Area counties in 1995, as reported in the Pesticide Use Reporting Program.

pesticides. Household use is a major category that is not covered by the PURP. Estimated application rates of household use and other categories not covered by the PURP would be valuable.

Registered Pesticide Pathways

The relative importance of each major pathway in the overall registered pesticide budget for the Bay is summarized in Table 3. The Sacramento River has been demonstrated to export significant concentrations of registered pesticides to the Estuary during specific high flow periods (Kuivila and Foe 1995). High concentrations of registered pesticides and toxicity have

been detected in small tributaries around the Bay, indicating the significance of that pathway (RMP Pesticide Workgroup 1999). Recent data on diazinon and chlorpyrifos in Bay Area POTWs indicate that POTW inputs may account for a large fraction of the mass of these chemicals observed in Bay waters, particularly in the South Bay (Chew et al. 1998). Chew et al. reached the opposite conclusion, but failed to consider the residence time of water in the Bay.

Summary of Information Needs: Pesticides

Increasing understanding of pesticide use and discharge in both agricultural and urban settings might identify relatively easy ways to minimize impacts. The alteration of rice farming practices is an example of how joint strategies can be effective in reducing beneficial use impacts. In the mid 1980s, evidence of toxicity in the Sacramento River was linked to discharge of carbofuran, methyl parathion and malathion from flooded rice fields (Foe and Connor 1991). It was determined that holding water on the rice fields longer greatly reduced the concentration of these pesticides, and the RWQCB prohibited discharge in 1990 unless a 28-day holding period was adopted. The result has been significant reductions in toxicity and contaminant concentrations (Fox and Archibald 1997). Some farmers have adopted water conservation and pesticide use reduction measures (Cohen and Curtis, 1998) that could have a positive influence on restoration and protection of beneficial uses if they were applied more broadly.

d. Mercury

Preface

This report documents the activities of the RMP Sources, Pathways, and Loadings Workgroup in 1999. More comprehensive and detailed assessments of some of the topics presented, especially the mercury discussion and aspects of the PCB discussion, were completed in 2000. While this report is still a good introduction to these topics, the reader is also referred to the following publications for more recent and detailed information:

San Francisco Bay Regional Water Quality Control Board. 2000. Watershed Management of Mercury in the San Francisco Bay Estuary: Draft Total Maximum Daily Load Report to U.S. EPA. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

Davis, J.A. 2001; Draft Report: A PCB Mass Budget for San Francisco Bay. San Francisco Estuary Institute, Richmond, CA.

Conceptual Model and Mass Budget Considerations

A conceptual model and mass budget for mercury have been developed as part of the mercury watershed strategy and are reported in the draft mercury staff report (SFBRWCQB 1998). That report outlines two basic strategies for managing mercury in San Francisco Bay: i) controlling loading so that inputs are less than outputs and ii) protecting areas sensitive to methylation. The key pieces of information needed to make regulatory decisions about mercury are: i) what are the controllable sources, and ii) where does methylation occur most rapidly?

Mercury enters the bay from a variety of sources and pathways (Figure 14). Over 230 million pounds of mercury were mined from the Coast Range between 1846 and 1980; much of this was used to amalgamate gold in Sierra Nevada gold mines (Ron Churchill, Division of Mines and Geology, pers. comm.). Mercury and gold mining resulted in substantial historic deposits in San Francisco Bay and upland watersheds. Inputs from resuspension of historically contaminated sediments and from Central Valley runoff amount to hundreds of kilograms per year, compared to ten to thirty kilograms per year for municipal and industrial discharges. Inputs from urban runoff may also contribute additional annual loading on the order of hundreds of kilograms, but better data are needed to quantify this loading term.

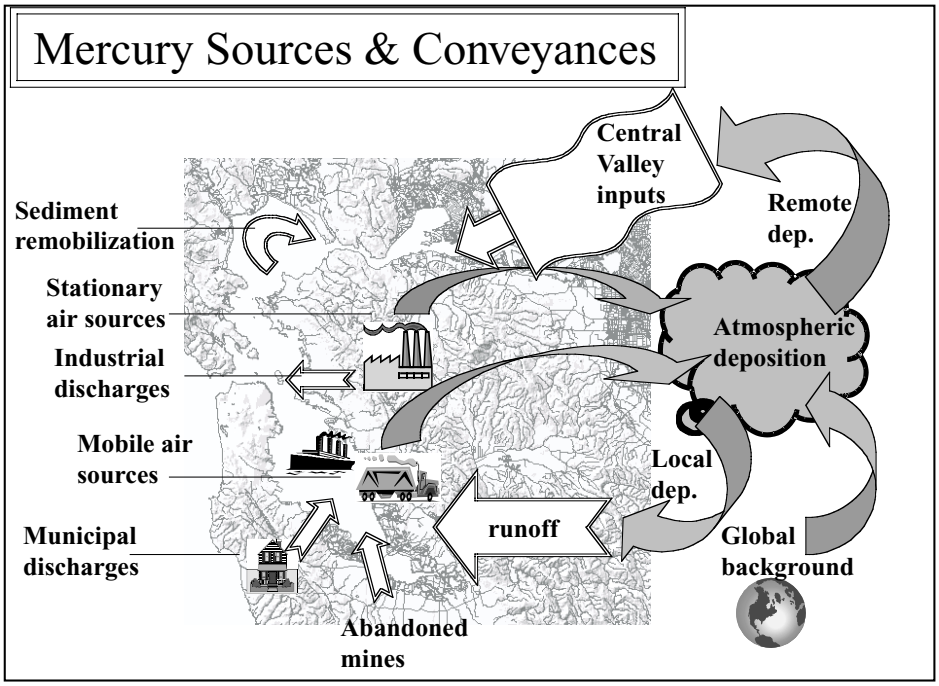

Figure 14. Sources and pathways of mercury in the San Francisco Bay watershed

Controlling mass loading alone is not enough to manage the risks posed by mercury. The Regional Board's target is to reduce mercury concentrations in fish tissue. Tissue concentrations of mercury are driven by mercury methylation rates and food web complexity. As food chain length increases, bioaccumulation of mercury also increases, leading to bioaccumulation factors of a million or more at the highest trophic levels.

The net impact of any mercury load on fish tissue concentration is determined by the form of the load, its residence time in the system, environmental conditions, and the trophic structure of the affected ecosystem. Mercury's chemical form, or speciation, determines its gross susceptibility to methylation (bioavailability). The relative bioavailabilities of mercury species to methylating bacteria are:

- dissolved inorganic Hg^{2+} (most bioavailable)
- colloidal Hg^{2+} (particles < 0.45 µm)
- organic complexes of Hg^{2+} (nonmethylated)
- elemental mercury (quicksilver, Hg^{0})
- particulate mercury (Hg^{2+} bound to particle surfaces)
- mercury minerals HgS (cinnabar, least bioavailable)

Residence time also affects net methylation, because less bioavailable mercury species can be transformed to more bioavailable species given enough time and the right conditions. Cinnabar released in the upper watershed can be transformed to dissolved inorganic mercury (Hg^{2+}) by weathering and dissolution. Methylmercury is produced from Hg^{2+} as a by-product of normal metabolism by sulfate-reducing bacteria. Methylation rates are affected by the amount of mercury available as Hg^{2+} and activity of sulfate reducing bacteria.

Consequently, there is only a weak connection between the magnitude of mercury loading and extent of fish contamination. On a global scale, the most contaminated areas also have the highest bioaccumulation. But on a regional scale, tissue concentrations of mercury cannot be predicted or managed based on mass loading alone. To effectively reduce mercury in fish tissue, regulatory controls on loading must be coupled with information about methylation rates and ecosystem structure (Figure 15).

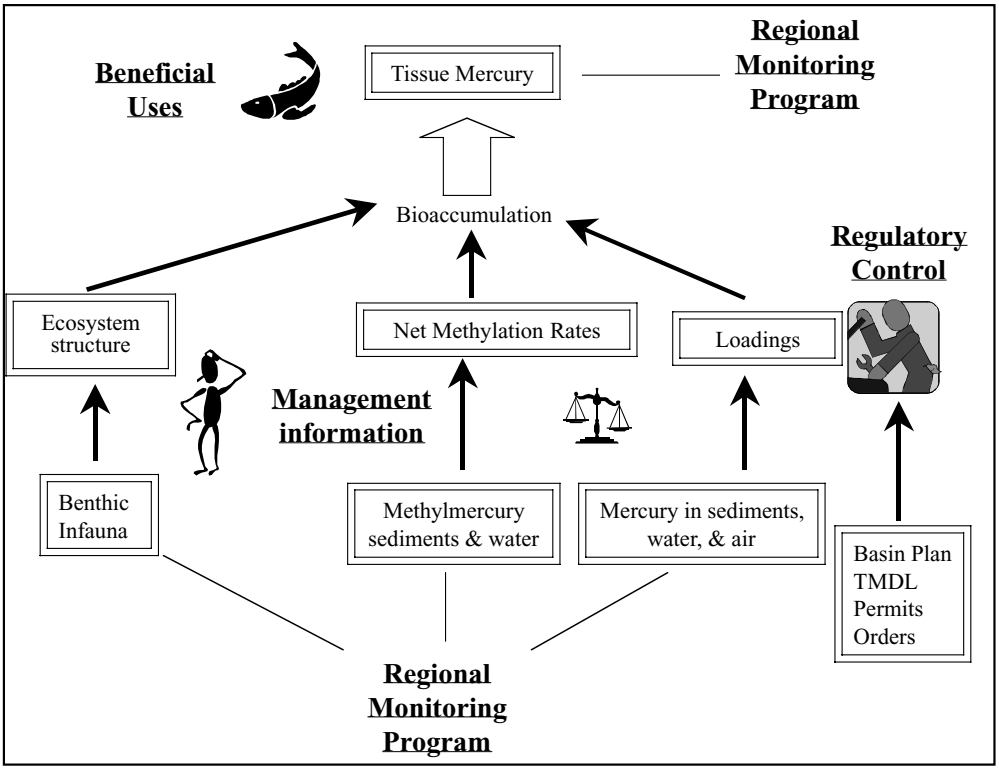

Figure 15. Relationship between the Regional Monitoring Program and the mercury TMDL. The TMDL target, mercury concentration in fish, is assessed by the RMP every three years. Mercury levels in fish are driven by bioaccumulation, which is a function of loadings, methylation rates, and ecosystem structure. The Regional Board has regulatory control over some loadings. However, priorities for loadings reductions must be set by determining the most sensitive aquatic environments. That determination will be informed by the proposed design elements of the RMP, which will assess net methylation rates by measuring methylmercury total mercury ratios.

Sources, Pathways, and Loading

Uses and Sources of Mercury

Mercury has many commercial and industrial uses, including gold mining, caustic soda manufacturing, household thermometers, dental fillings, contact lens solutions and fluorescent lights. The first two uses represent historic inputs to the Bay, while the rest represent contemporary anthropogenic sources. Mercury is also present in other commercial and industrial products, such as older formulations of latex paint and detergent products made with caustic soda produced by the mercury cell process.

Mercury Pathways

Historic Sediment Deposits

Historic activities have deposited mercury-enriched sediment deposits in San Francisco Bay. Over a billion cubic yards of sediment was swept into the northern reach of San Francisco Bay during the hydraulic mining era of the late 1800's. Mercury concentrations up to 1 ppm have been measured in Suisun Bay sediment cores, and much of this material may be continuously exposed for decades to come because of the net erosion occurring in that region (Jaffe and Smith, 1998).

New Almaden Mine, once the largest producer of mercury in North America, drains into the Guadalupe River, which flows into the South Bay. This has resulted in marked mercury

concentration gradients in South Bay sediments. Although New Almaden is currently managed as a Superfund site, and much of the site has been covered, contaminated sediments pervade the Guadalupe River system. This is readily confirmed by panning sediments from the bed and banks of the Guadalupe River and Alamitos Creek. Drops of quicksilver and chunks of cinnabar are readily found in samples taken anywhere from New Almaden down to San Jose.

Sediment deposits may also be substantial sources of methylmercury, because methylation occurs in suboxic and anoxic environments. The relative importance of benthic fluxes and tidal marsh exchange needs to be assessed to determine the impact of historically contaminated sediments.

Small Tributaries (Including Storm Drains)

The magnitude of stormwater and small tributary mercury contributions is probably significant, but can only be crudely estimated at present due to insufficient data. Current estimates for stormwater loading are 200-400 kg per year, based on land use patterns and a limited number of mercury measurements (SFBRWQCB 1998). Better measurements are needed to quantify stormwater loading. This is a major technical challenge because of the difficulty in obtaining representative stormwater samples. Traditional approaches to obtaining flow-weighted composites are confounded by the episodic nature of stormwater inflow and the variability of suspended load. Overcoming these technical challenges is vital to the completion of not only the mercury TMDL but other TMDLs such as PCBs, copper, and dioxins.

Stormwater is a pathway, not a source, of mercury. Runoff pathways reflect the integrated atmospheric deposition in the watershed. Other potential mercury sources to stormwater include improperly disposed paints and cinnabar deposits in upland watersheds. Regional monitoring should be directed at quantifying how mercury concentrations in storm drains and small tributaries respond to reductions in air emissions, mine remediation, and implementation of stormwater best management practices (BMPs).

Since mercury is primarily transported on suspended particles, one key piece of information needed is the mercury concentration of suspended particles entering the Bay. Continuous monitoring of turbidity as a proxy for suspended load is relatively straightforward, but those kinds of monitoring data alone are not sufficient. The mercury concentration of suspended particles must be quantified to derive loading from integrated suspended load measurements, and to relate responses in the watershed to reductions in airborne sources.

More data are also needed on the chemical form and fate of mercury in stormwater. Since the TMDL target, mercury in fish tissue, is linked to both loading and methylation rates, the Regional Board needs to understand how much of mercury loading in stormwater will be eventually converted to methylmercury. This is especially important for wetland and marsh areas impacted by stormwater, because microbial activity in those environments can produce methylmercury.

Direct Atmospheric Deposition

Recent estimates suggest that direct atmospheric deposition to the Bay accounts for 5-15 kg yr-1 (SFBRWQCB 1998). The Regional Monitoring Program is currently undertaking a pilot atmospheric deposition study to better quantify this pathway. Three sites are currently in operation at Martinez, Treasure Island, and near San Jose to collect wet and dry deposition samples. In addition, the South Bay site has recently become part of the National Mercury Deposition Network.

Sacramento and San Joaquin Rivers

The Sacramento River Basin has been shown to export significant quantities of mercury to the Estuary. Although the extraction of gold by mercury amalgamation has been banned in the United States, San Francisco Bay continues to receive mercury from upland watersheds as a result of historic mining uses. There are hundreds of abandoned mercury mines in the Coast

Range, resulting in aboveground sources of solid phase cinnabar (mercury sulfide ore). Although cinnabar is extremely insoluble, the process of mining and roasting tends to increase the availability of mercury in waste-rock (Rytuba and Kim, 1999). The presence of dissolved organic matter has also been shown to enhance cinnabar dissolution (Ravichandran *et al*. 1998). The multitude of abandoned gold mines dotting the Sierra Nevada foothills are substantial sources of quicksilver, or elemental mercury.

A recent study estimated mercury loads between 200 and 450 kg yr-1 from the Sacramento River (Larry Walker Associates 1997). These loads are consistent with estimates using RMP data and flow measurements, but they do not account for inputs from the Yolo Bypass. Another study demonstrated that between May 1994 and April 1995 approximately 800 kg of mercury entered the Estuary from the Sacramento Basin (CVRWQCB, 1998). Approximately 98% of those inputs occurred during the four-month high flow period, and half of the loading entered via the Yolo Bypass. Subsequent studies showed that the major source within the Bypass was the Cache Creek basin, which had storm-flow exports of 5 - 100 kg/day.

Mercury from these upland sources is converted to methylmercury by microbial activity in suboxic sediments. Mercury methylation depends, in part, on its bioavailability. The bioavailability of mercury in Sierra Nevada streams is likely very different from that of Coast Range watersheds, because the two regions have different aquatic environments and different forms of historic mercury. Sierra Nevada streams contain elemental mercury (Hg^0), which must be oxidized to mercuric ion (Hg^{2+}) before methylation can occur. Sierra Nevada streams are also impounded by reservoirs, which appear to block the export of methylmercury and sediment-bound mercury (Slotton, 1997). In contrast, the Coast Range watersheds are mostly impacted by cinnabar. There, the rate-limiting step prior to methylation is cinnabar dissolution rather than reduction. Coast range watersheds are also more heavily influenced by wetlands, which are known areas of methylation.

A CalFed study is currently underway to characterize methylation processes in the Cache Creek watershed and the Estuary and to quantify exports of methylmercury and bioavailable mercury to the Estuary. The latter form, bioavailable mercury, may ultimately have a more significant impact on bioaccumulation in the Bay than methylmercury itself, because the half-life for degradation of unbound methylmercury is days at best. *In situ* methylmercury production from bioavailable mercury may be the dominant process controlling the trophic transfer of mercury.

Effluent Discharges

Mercury mass loading from effluent discharges is probably a minor component of the Bay-wide mass budget. The most obvious controllable anthropogenic mercury source to POTWs is from dental offices. Dental fillings may contribute as much as 10% of the mercury loading to POTWs. The Regional Board has recommended best management practices (BMPs) to minimize loading from dental chairs, and is considering more stringent measures as part of the mercury watershed strategy.

Vessels

Mercury inputs from vessel activity have not been quantified, but are probably a minor part of the mass budget. Mercury associated with fuel combustion may contribute to atmospheric and runoff pathways, but this should be approached within the broader scope of combustion-related sources in the mercury TMDL. Efforts are currently underway to better quantify fuel-associated mercury sources.

Harbor Activities (Including Dredging)

Harbor maintenance and new dredging can mobilize historic sediment deposits of mercury. This would have no effect on the overall mercury mass budget if contaminated sediments are disposed in-bay, and result in a minor export if they are disposed of in the deep ocean. How-

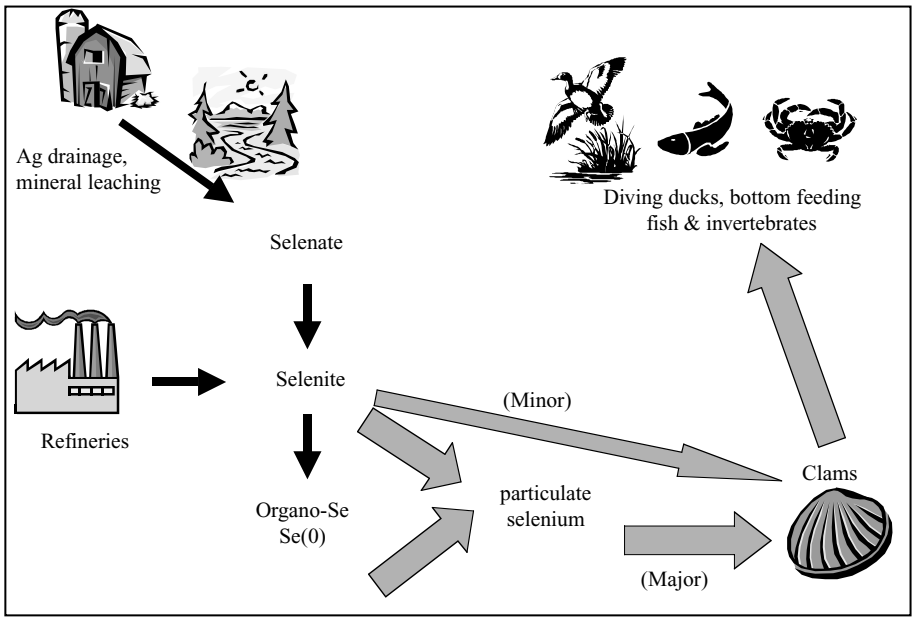

Figure 16. Conceptual model for selenium cycling in San Francisco Bay. Selenium concentrations in the tissue of diving ducks and other predators are forced by bivalve bioaccumulation. Bivalves accumulate selenium primarily from particulates, although some direct selenite assimilation also occurs. Enforcement actions and citizen suits have substantially reduced direct selenite inputs from refineries. Selenate inputs may be eventually converted to selenite. If bivalve selenium concentrations do not respond to reduction of selenite loadings, additional loadings reductions may be required from agricultural sources.

ever, upland disposal of sediments presents an unusual problem with respect to mercury, because wetlands are known to enhance mercury methylation.

The Regional Board needs to develop sediment mercury guidelines for wetlands creation. Those guidelines should be directed towards preventing additional bioaccumulation of historically deposited mercury, and reducing it where possible.

Summary of Information Needs: Mercury

The most urgent priority for the Regional Monitoring Program is to characterize areas of enhanced methylation within the Bay. Stormwater loading, benthic fluxes, and marsh/wetland inputs must be accurately measured. This information has been identified as essential to completion of the mercury TMDL.

e. Selenium

Conceptual Model and Mass Budget Considerations

A conceptual model (Figure 16) for selenium cycling in the Estuary has been developed (SFBRWQCB, 1997). The model divides the selenium problem into managing short-term and long-term risks. Inputs of selenite (Se^{4+}) represent immediate threats, because selenite is approximately tenfold more bioavailable than selenate (Se^{6+}). Inputs of selenate represent long term risks, because selenate can eventually be converted to selenite.

Refineries have been identified as a major source of selenite, as a result of the high selenium content of shale oils. Selenium measurements across the salinity gradient in northern San Francisco Bay revealed an internal selenite source located near the Carquinez Straits (Cutter, 1989). Mass balance calculations showed that refinery effluent was the most likely source of that selenite, with selenium loading from the five Bay Area refineries totaling roughly 2500 kg

per year. As a result of a series of enforcement actions and citizen suits, the refineries have reduced their selenium loading to below 1200 kg per year, mostly as selenate. Preliminary results indicate that the selenite peak has disappeared, but several more years of monitoring are needed to confirm this.

The Sacramento – San Joaquin River system is the other major source of selenium to the Estuary, contributing another 2500 kg of selenium as selenate. Loading from the San Joaquin River will likely increase as discharge from agricultural drainage increases. Loading may substantially increase if the proposed San Luis Drain project is completed. This poses a potential environmental threat, as selenate can be reduced to the more bioavailable selenite through microbial dissimilatory selenate reduction in anoxic sediments (Oremland *et al*., 1989).

Transfer to higher trophic levels is mediated by filter feeders, primarily the introduced Asian clam, *Potamocorbula amurensis*. Particulate selenium is the most efficient pathway for uptake by bivalves, although some direct uptake of dissolved selenite also occurs (Luoma *et al*., 1992). Concern for selenium impacts is greatest for organisms that feed on bivalves, including diving ducks (scoter and scaup), bottom feeding fish (sturgeon) and higher invertebrates (Dungeness crab).

The Regional Board's TMDL work plan for selenium calls for continued bivalve monitoring. If bivalve concentrations do not decrease sufficiently, additional loading reductions may be required from agricultural sources.

Sources, Pathways, and Loading

Uses and Sources of Selenium

Selenium is used industrially to manufacture photovoltaic cells, and commercially as a nutritional supplement. It is also released as a by-product of copper sulfide ore processing. However, none of these uses and sources are particularly relevant to the selenium TMDL in San Francisco Bay. Selenium in the Bay originates primarily from weathering of geologic deposits in the watershed and from refinery processing of shale oils with high selenium content.

Selenium Pathways

Historic sediment deposits do not appear to be substantial sources of selenium compared to refinery inputs and agricultural drainage. However, sediments are a critical link in the trophic transfer of selenium. As discussed above, selenate is converted to selenite and organo-selenium in anoxic sediments, and transferred to filter feeders by particles.

Other sources, including small tributaries, direct atmospheric deposition, effluent discharges, vessels, and harbor activities play relatively minor roles in the selenium budget. According to the Regional Board's TMDL work plan for selenium, no significant anthropogenic inputs of selenium to the southern embayments have been identified. Stormwater and treatment plant monitoring has only turned up loading contributions from small domestic water supply companies in the Santa Clara Valley drawing water from local groundwater sources.

Summary of Information Needs: Selenium

The Regional Board's TMDL workplan for selenium clearly defines the additional information needs. Continued monitoring of selenium in water is needed to quantify the effect of loading reductions by refineries. A follow-up study of the selenium speciation in refinery effluent is needed now that selenite removal technologies have been implemented. Bivalve monitoring is required to measure ecosystem responses to loading reductions. However, no special studies are required of the RMP, because selenium monitoring has already been funded as a result of a settlement with the refineries. Continued monitoring of upland watersheds, such as the monitoring being performed under the Grasslands Bypass Project Compliance Monitoring Program (USBR *et al*. 1999), will help in evaluation of the potential need for future reductions from agricultural drainages.

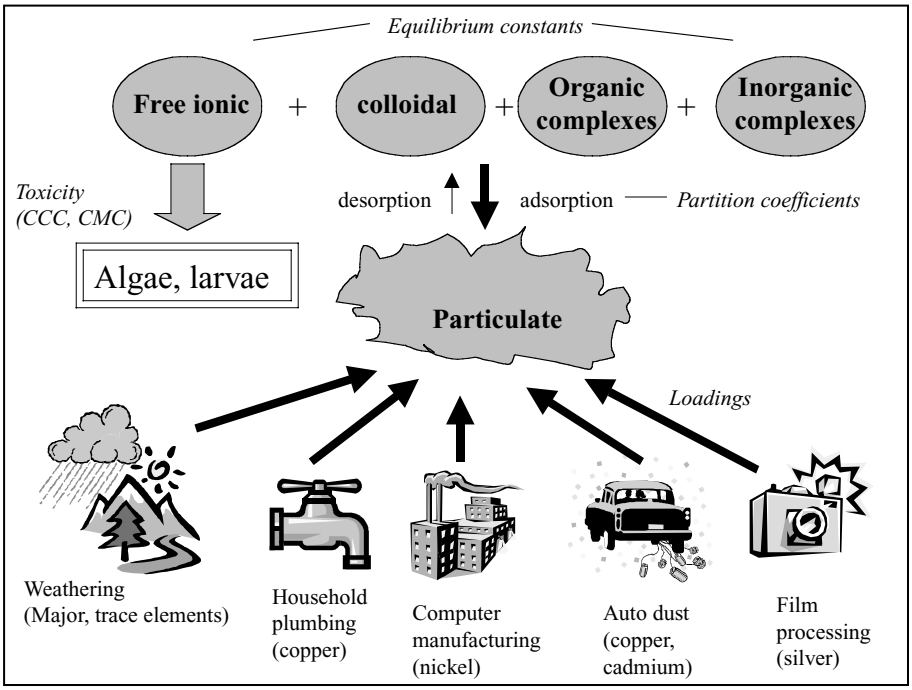

Figure 17. Generalized regulatory model for cadmium, copper, nickel, and silver. Natural sources of dissolved and particulate metals are enriched by anthropogenic inputs. Particles can act as sources or sinks of dissolved metals through adsorption and desorption; partition coefficients (K_ds) quantify the ratio between dissolved and particulate forms. Dissolved, uncomplexed (free ionic) metals are much more biologically available than particulate of complexed metals. Toxicity data for sensitive species are used to develop dissolved metal criteria. Loadings reductions are the regulatory too used to ensure maintain concentrations below ambient criteria. Effluent limits are derived from water quality criteria are using management information, such as the partition coefficient and equilibrium constants for complex formation.

f. Copper, Nickel, Silver, and Cadmium

Conceptual Model and Mass Budget Considerations

Conceptual Model for Copper, Nickel, Silver, and Cadmium

A common general conceptual model for fate and effects applies to copper, nickel, silver, and cadmium (Figure 17). All of these metals have both natural and anthropogenic sources, although silver and cadmium are low in their natural abundance. All of the metals partition preferentially onto sediments to varying degrees.

The ratio of adsorption to desorption is referred to as the partition coefficient, or K_d. The K_d depends on both intrinsic metal chemistry and site-specific factors, such as salinity, suspended load, and dissolved organic carbon. The K_ds of these four metals in San Francisco Bay can be calculated using RMP measurements (Table 4). Cadmium is more soluble than copper or nickel, which are more soluble than silver. However, K_d can vary in both space and time, which has implications for source and loading analysis.

Dissolved trace metals exist as inorganic complexes (e.g., $CdCl_2^-$), organic complexes (e.g., copper-EDTA), colloids (particles < 0.45 µm), and free cationic species. It is the latter form which is most biologically available. Cadmium, copper, nickel and silver do not strongly bioaccumulate. Small organisms such as phytoplankton and larvae are most susceptible to metal toxicity, because metals must diffuse or be taken up across cell membranes to have an effect.

Table 4. Trace metal K_ds calculated from RMP measurements.

Metal	K_d
Cadmium	100
Nickel	30,000-50,000
Copper	30,000-50,000
Silver	> 100,000

There are two tools that help us understand sources, sinks, and geochemical cycling of trace metals in the San Francisco Estuary. Plots of the spatial and temporal distribution of metal K_ds highlight where remobilization and removal of dissolved metals occurs. Salinity plots of dissolved metal concentrations facilitate calculation of inputs and removals.

Figure18 illustrates three types of dissolved metal-salinity distributions. A conservative distribution implies that no contaminant inputs or removals are observed in the Estuary, so contaminant concentrations in the freshwater inflows to the Estuary are diluted by saline water from the ocean and fall on a straight line when plotted against salinity (Figure 18A). Metal and nutrient concentrations are usually higher in river (low salinity) waters compared to marine (high salinity waters), because of erosion, weathering, and runoff.

A non-conservative excess (Figure 18B) occurs when the actual concentrations (boldface line) are above an imaginary line connecting river concentration and ocean endpoints (dashed line). This suggests an internal contaminant source, i.e., more contaminant is added to the waterbody as it mixes between the river and the ocean. Examples of internal sources could include direct effluent discharges, stormwater runoff, or release from sediments within the Estuary. The height above the theoretical dilution line at mid-Estuary gives the excess concentration; that excess concentration multiplied by the volume of the water mass yields the excess metal mass. Dividing the excess mass by the water mass replacement time gives an estimate of the net (input minus removals) loading rate of dissolved metal.

Similarly, a non-conservative depletion is inferred if the actual concentrations (boldface line) are below the theoretical dilution line (Figure 18C). This means that there is a net internal contaminant sink, i.e., contaminant is removed from the waterbody as it mixes between the river and the ocean. Internal sinks could include adsorption onto particles, particle sinking, and biological uptake. Net removal rates for dissolved metals can be estimated using the volume and replacement time of the water mass.

Dissolved copper and nickel both have non-conservative excesses in the northern reach of the Estuary (Figures 19 and 20). However, copper excesses in the northern reach are relatively consistent during both wet and dry seasons, whereas dissolved nickel excesses are as much as ten-fold greater during the wet season. This difference is due to several coupled processes,

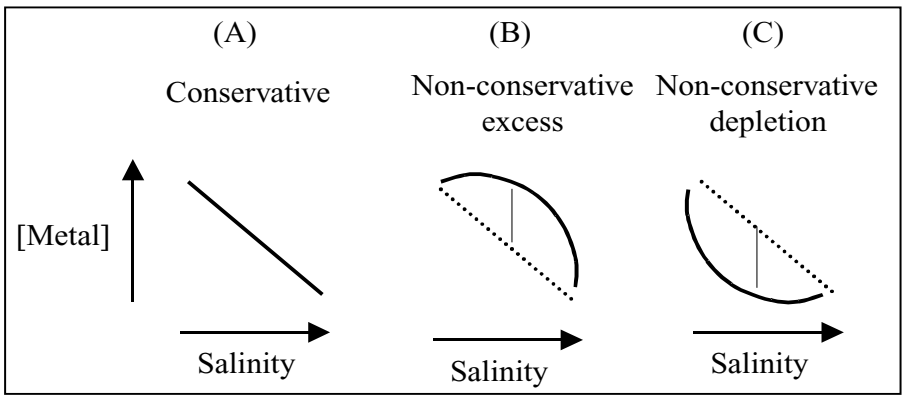

Figure 18a-c. Idealized trace metal - salinity distributions.

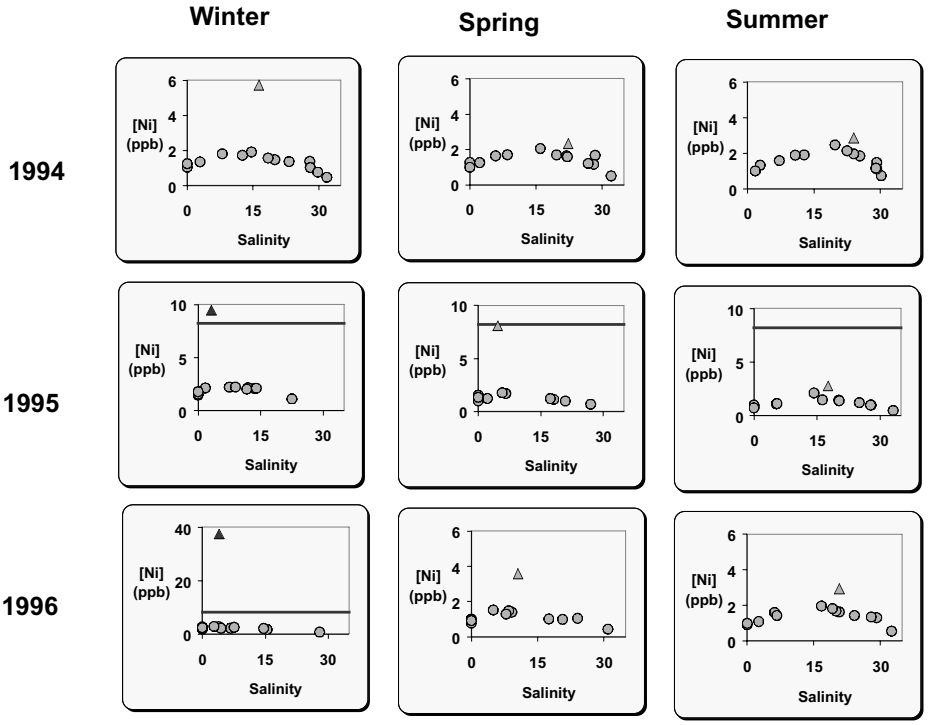

Figure 19. Dissolved nickel – salinity distributions in the northern reach of San Francisco Bay. The triangle indicates station BD15, at the mouth of the Petaluma River. The heavy horizontal line indicates the dissolved criteria proposed by EPA in the California Toxics Rule.

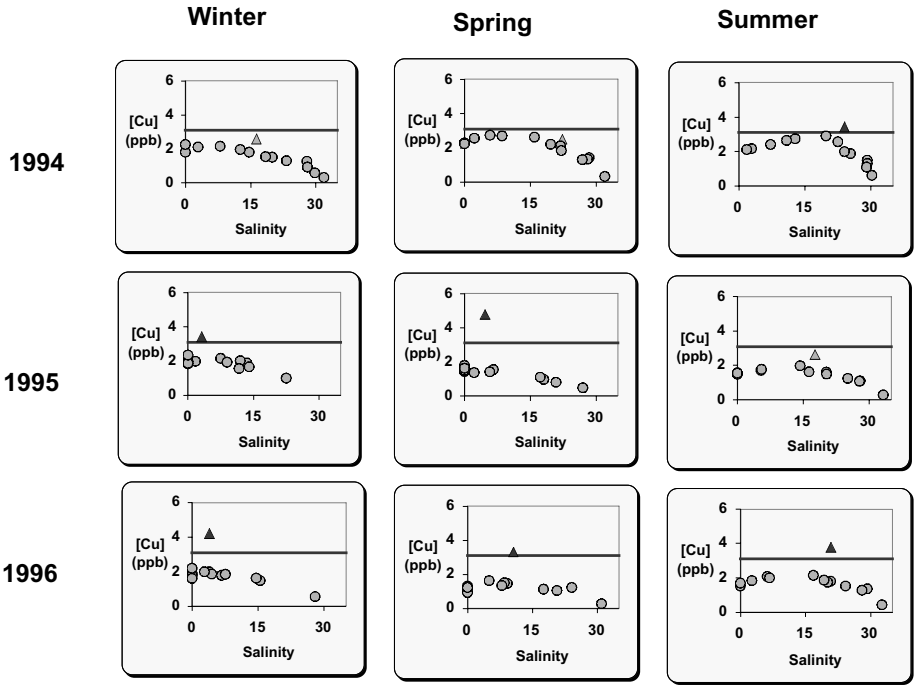

Figure 20. Dissolved copper – salinity distributions in the northern reach of San Francisco Bay. The triangle indicates station BD15, at the mouth of the Petaluma River. The heavy horizontal line indicates the dissolved criteria proposed by EPA in the California Toxics Rule.

including weathering of nickel-enriched serpentine soils, formation of soluble nickel-sulfide complexes, and episodic flushing of adjacent wetlands (Abu-Saba 1998).

In the southern reach, dissolved nickel from municipal treatment plants is conservatively mixed with seawater, whereas dissolved copper has internal inputs in addition to direct discharges (Figures 21 and 22). Excess dissolved copper in the southern reach is likely due to a combination of benthic flux, particle dissolution, and regeneration after the spring phytoplankton bloom. The summertime increase is driven by the markedly slower flushing rate of the southern extremities of the Bay.

The K_d for nickel is relatively constant throughout most of the Estuary, and shows little seasonal variability. However, at the mouth of the Petaluma River, wintertime inputs of dissolved nickel substantially lower the observed K_d compared to the summer (Figure 23). In contrast, the copper K_d at the mouth of the Petaluma River is depressed both winter and summer (Figure 24).This suggests that copper inputs are from benthic fluxes within the Estuary, whereas nickel inputs are forced by water inflow. In the southern reach, the copper K_d shows a continuous increase from south to north (Figure 24), suggesting that internal inputs of dissolved copper are re-adsorbed onto particles or taken up by plankton.

Mass Budget Considerations for Copper, Nickel, Silver, and Cadmium

A mass balance model for San Pablo Bay and South Bay has been developed by Rivera-Duarte and Flegal (1997a, 1997b) using RMP data. The loading data, summarized in Tables 5 and 6, show that benthic remobilization of trace metals is a dominant source of trace metals to the

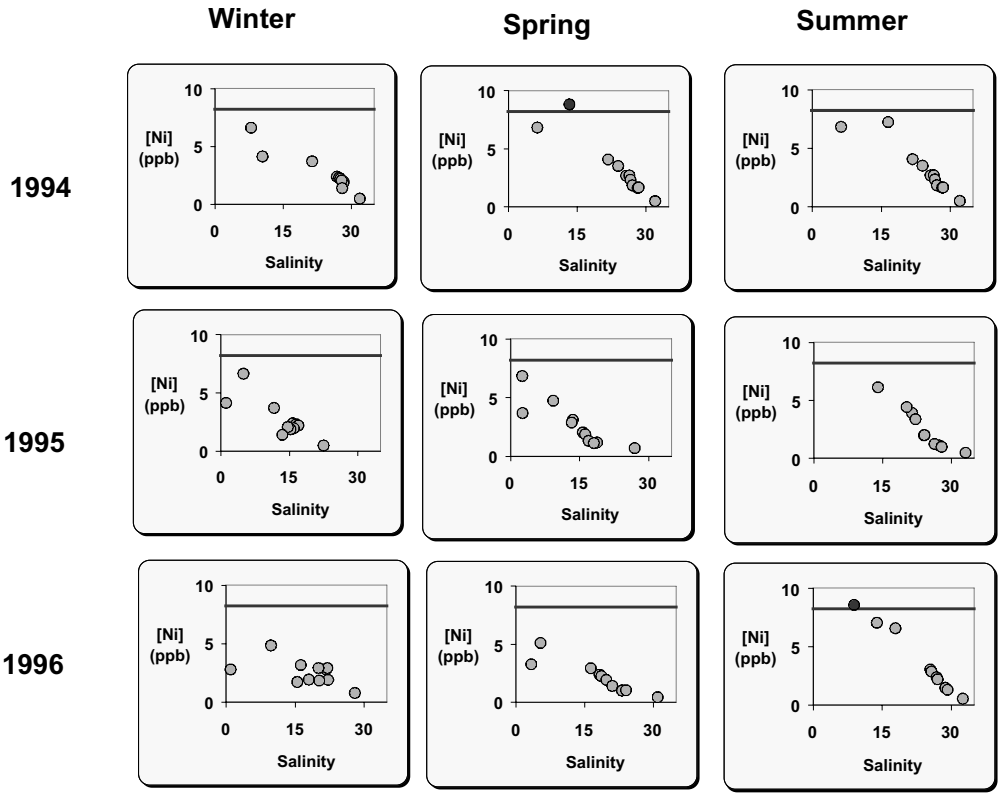

Figure 21. Dissolved nickel – salinity distributions in the southern reach of San Francisco Bay. The heavy horizontal line indicates the dissolved criteria proposed by EPA in the California Toxics Rule.

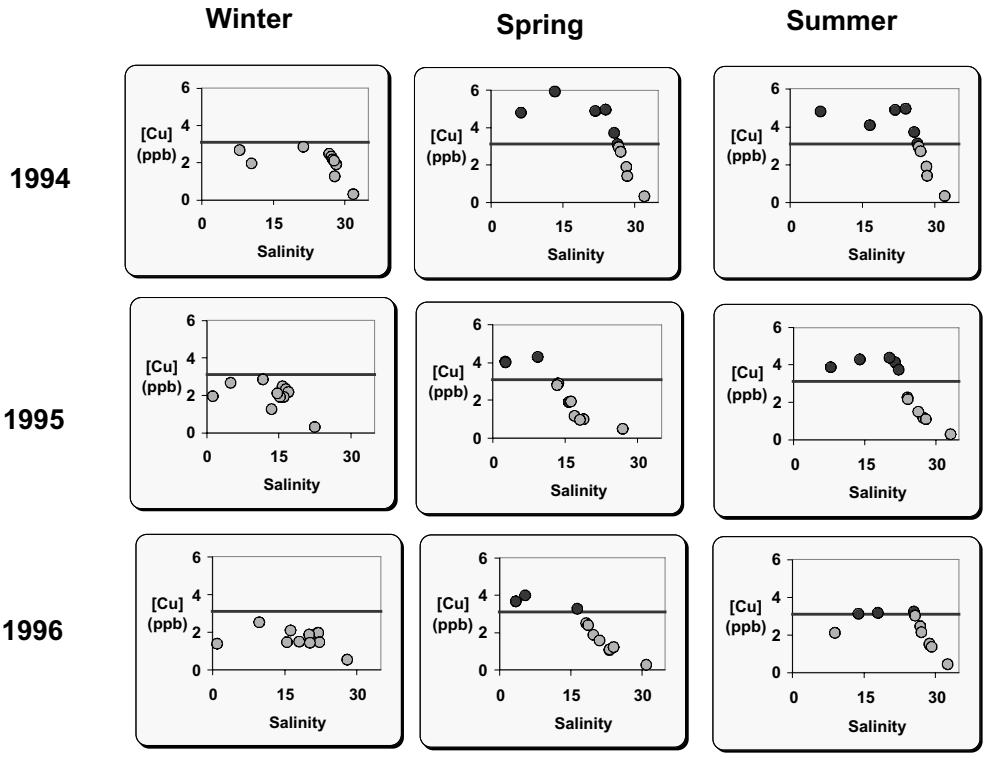

Figure 22. Dissolved copper – salinity distributions in the southern reach of San Francisco Bay. The heavy horizontal line indicates the dissolved criteria proposed by EPA in the California Toxics.

Estuary. Stormwater loading was not included in Rivera-Duarte and Flegal's anthropogenic load estimates because of insufficient data.

A recent summary of lower South Bay copper and nickel loading (Tables 7 and 8) indicated that average daily tributary loading, including stormwater, amounted to 3 kg copper and 4 kg nickel (South Bay Watershed Management Initiative, 1998). The POTW loadings in Tables 5 and 6 may be somewhat overestimated. A more recent summary using NPDES self-monitoring data from San Jose/Santa Clara, Sunnyvale, and Palo Alto POTWs indicates that average daily loading for the three sources combined amount to 3 kg copper and 4 kg nickel.

The benthic remobilization estimates of Rivera-Duarte and Flegal (Tables 4 and 5) are two orders of magnitude higher than the diffusive flux estimates appearing in the Source Characterization Report (Tables 7 and 8). That is because the former is an estimate of total fluxes including sediment resuspension, whereas the latter is a diffusive flux, representing only the amount of dissolved metal diffusing across the sediment water interface. Considering only the diffusive flux may underestimate true dissolved fluxes, as bioturbation can greatly enhance porewater exchange rates (Caffey *et al.* 1996, Kuwabara *et al.* 1999a,b). Benthic remobilization of sediment may also contribute to dissolved fluxes if coupled with desorption. Quantifying

Table 5. Mass balance summary for San Pablo Bay. All values are in kg/day. Silver fluxes represent dissolved inputs, all others represent inputs of total (unfiltered) trace metals. Data from Rivera Duarte and Flegal (1997a, 1997b).

Metal	Anthropogenic Load (POTWs)	Benthic Remobilization	Atmospheric Inputs	River Inputs
Cadmium	1	0.8	0.2	197
Copper	7	353	6	127
Nickel	10	509	1	137
Silver	NA	NA	NA	12

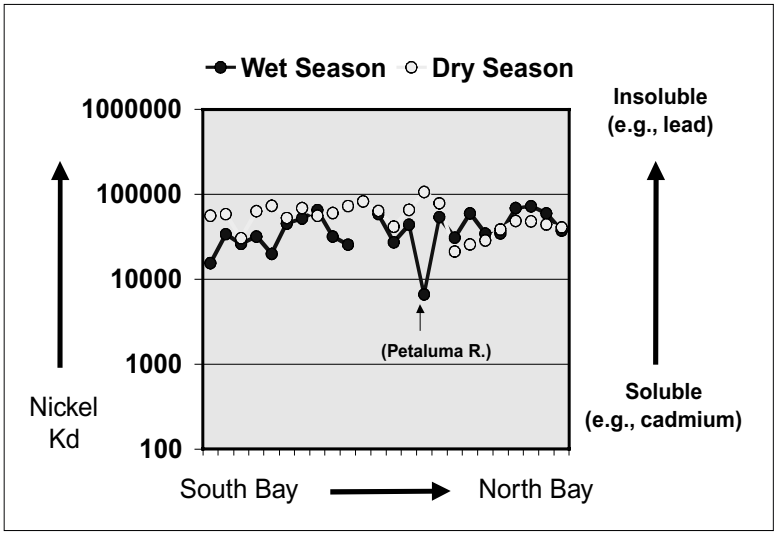

Figure 23. Spatial and temporal variability of the partition coefficients for nickel in San Francisco Bay.

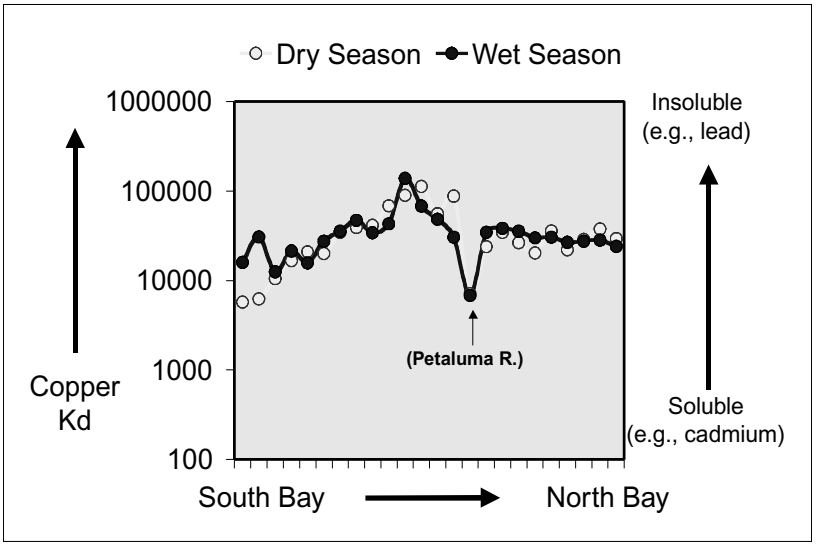

Figure 24. Spatial and temporal variability of the partition coefficients for copper in San Francisco Bay.

these processes is critical in order to understand the internal inputs of dissolved copper which lead to frequent exceedances of proposed water quality criteria in South Bay.

Summary of Information Needs: Copper, Nickel, Silver, and Cadmium

A better understanding of the role of benthic fluxes in the trace metal mass budget is needed. Measurements of benthic fluxes using whole core incubations along gradients leading toward the Bay margins can help elucidate the role of suboxic sediments as trace metal sources and sinks. The design of monitoring efforts should also account for the spring diatom bloom in the South Bay, which may play a role in the release and uptake of dissolved copper leading to gradients in the observed partition coefficient (Figure 24). Finally, better characterization of the composition of suspended particles is needed to assess the role of desorption as an internal source.

Table 6. Mass balance summary for South Bay. All values are in kg/day. Silver fluxes represent dissolved inputs, all others represent inputs total of total (unfiltered) trace metals. Data from Rivera Duarte and Flegal (1997a, 1997b).

Metal	Anthropogenic Load (POTWs)	Benthic Remobilization	Atmospheric Inputs
Cadmium	6	9.7	0.3
Copper	46	840	10
Nickel	40	1296	2
Silver	NA	3-30	NA

Table 7. Mass balance summary for copper and nickel in the lower South Bay during the wet season. All values are in kg/day. Data from the South Bay Watershed Management Initiative (1998): Task 2.1, Source Characterization Report. Diffusive fluxes from Rivera Duarte and Flegal (1997a).

Metal	Anthropogenic Load (POTWs)	Diffusive fluxes from sediments	Atmospheric Inputs	Tributary Inputs
Copper	1.8	0.3	0.2	9.8
Nickel	2.2	1	0.05	16.5

Table 8 Mass balance summary for copper and nickel in the lower South Bay during the dry season. All values are in kg/day. Data from the South Bay Watershed Management Initiative (1998): Task 2.1, Source Characterization Report. Diffusive fluxes from Rivera Duarte and Flegal (1997a).

Metal	Anthropogenic Load (POTWs)	Diffusive fluxes from sediments	Atmospheric Inputs	Tributary Inputs
Copper	1.1	.3	0.1	0.4
Nickel	1.8	1	0.03	0.1

III. Recommendations

The Findings presented above (Section II) provided the basis for recommendations of the SPLWG on how to design the RMP to satisfy the objectives and management questions established for the Program. SPLWG recommendations were explicitly tied to the RMP objectives and management questions. The recommendations were developed in the form of tasks to be completed.

In addition to the recommended tasks described below, several other possible tasks were discussed by the Workgroup but were deferred until completion of Task 1 (Information Review and Analysis). These tasks included:

- Tributary Mouth Sediment and Bivalve Survey (Special Study);
- Small Tributary Load Measurements (Pilot Study);
- Active Sediment Depth Survey (Special Study); and
- Benthic Flux Study (Special Study).

Completing the Information Review will allow more informed decisions on the priority and scope of these possible tasks.

1) Information Review and Analysis (RMP Special Study)

Priority: ***High***

Timing: ***1999/2000***

Many information needs relating to SP&L have been identified by the SPLWG. Collectively, they suggest the need for a report or series of reports on SP&L that address these specific questions. This work is a necessary precursor to field studies relating to SP&L, and therefore should be performed as soon as possible. This work will likely identify other areas where further analyses are needed either in the field or on paper. For each contaminant, information on SP&L should be placed in the context of a quantitative conceptual or mass budget model of the fate of that contaminant in the Estuary. The information needs are summarized below for each major pathway.

Small tributaries (including storm drains)

- Develop a conceptual model of contaminant inputs via storm drains and small tributaries
- Compile information on drainage areas and contamination potential for priority contaminants for storm drains and small tributaries
- Review information on PCB uses in watersheds
- Review information on primary sources of PAHs
- Review existing data on contamination at the mouths of storm drains and local tributaries, especially BPTCP data
- Review information on metal contamination associated with land use (i.e., roadways vs. greenways), including information already gathered by the Watershed Management Initiative
- Estimate stormwater loading using a McCreary-type land use based model and runoff coefficients. This should be coordinated with a SFEI/Moss Landing/SCCWRP project (funded by the State Board) estimating stormwater loads for coastal California
- Review information on selenium geology in the South Bay watershed and possible transport from geological deposits and groundwater
- Review information on land use in the South Bay watershed with regard to selenium
- Review information on urban and agricultural uses of OPs and resulting transport to the Bay

Sacramento and San Joaquin Rivers

- Obtain information on sediment transport during large resuspension events and estimate contaminant loading, identify information gaps that could be addressed by field sampling
- Review information on agricultural practices for use and discharge of OPs

Historic sediment deposits

- Perform further analysis of data pertaining to the active sediment layer, including information from sediment budgets, BPTCP data on the depth of the oxidized layer, shear stresses due to wind waves and tidal currents, sediment density, resistance to erosion, and other data.
- Expand PCB mass budget model to include the possible influence of resuspension from deeper sediments at hotspots and erosional areas in the Bay
- Further analysis of possible magnitude of benthic fluxes of trace elements

- Refine/develop mass budget models for all priority contaminants. The role of historic sediment deposits must be placed in the context of overall mass budgets. Budgets for PCBs and Hg need refinement. Budgets for other contaminants are also needed

Effluent discharges

- PCBs and PAHs Use small amount of existing data to estimate overall inputs

Harbor activities including dredging

- Estimate mass of PCBs and other contaminants released at in-Bay sites for comparison to estimates of overall loading to the Bay. Also estimate mass of PCBs removed from the Bay via upland or ocean disposal

Direct atmospheric deposition

- Attempt to estimate possible loads based on latest literature, especially for contaminants not included in Phase 1 of the Atmospheric Deposition Pilot Study

2) Direct Atmospheric Deposition Measurements (RMP Pilot Study)

Priority: ***High***

Timing: ***ASAP***

Direct atmospheric deposition is a potentially significant pathway for loading of PCBs, PAHs, dioxins, and trace elements to the Bay. A RMP Atmospheric Deposition Pilot Study has already been initiated this year. Due to the lack of funds for a more extensive study, the only analytes included in this first phase of sampling are mercury, copper, and nickel. Although atmospheric loading of PCBs, PAHs, and dioxins may be significant, these analytes are not currently included in the study.

3) Gradient Studies (RMP Special Study)

Priority: ***High***

Timing: ***2000 or 2001***

Sediments in the shoals and mudflat areas of the Bay are potentially large reservoirs of bioavailable contaminants. Small tributaries are also potentially significant pathways of many contaminants to the Bay. Gradient studies should be designed to evaluate contributions from shoals and mudflats and small tributaries. Water samples and sediment cores should be taken along transects leading up to shoal areas and tributary mouths. Core incubations would also help quantify the significance of benthic fluxes. Analysis of contaminant covariances will also help to distinguish tributary inputs from benthic fluxes. This Special Study should also include measurements of the depth of the active sediment layer. The depth of the active sediment layer is a variable with a prevailing influence on how long it will take for the Bay to respond to reduced loading of persistent contaminants, and measurements of this variable are only available for a few locations in the Bay. Collecting this information would complement the other measurements in the Gradient Study and serve as a pilot for measuring the active sediment depth more widely throughout the Bay. Details of the Gradient Study should be worked out under the guidance of the SPLWG.

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