Mercury Source Assessment for San Francisco Bay

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1. Executive Summary

Mercury loads to San Francisco Bay are estimated and incorporated in a mass balance to identify remaining uncertainties. The facts that mercury concentrations in sediments have not changed substantially over the past decade and that sediment outputs from the Bay roughly balance sediment inputs help constrain the mass balance, although the resulting range is relatively large. The best direct estimates of mercury loads to the Bay, including wastewater, stormwater, airborne deposition, and Central Valley runoff, total 640 kg/yr, with a likely range of 430-1350 kg/yr. The major portion of this total comes from Central Valley runoff and local stormwater sources. Mass balance considerations suggest that additional loads of 300 kg/yr enter the Bay, but the range on the additional load is between –2600 kg/yr and 3000 kg/yr. Steps to reduce this uncertainty and the expected outcomes are discussed.

2. Background

A mass balance model for mercury loads to San Francisco Bay is an important component of a mass-based watershed management strategy. This paper summarizes existing knowledge of mercury mass loadings to the Bay in a simple mass balance model that identifies remaining uncertainties and key steps to reducing those uncertainties.

3. Approach

The approach is to initially treat the Bay as the simple, one-box model depicted in Figure 1, and write down what is known about each of the first five terms: the Central Valley load, Bay Area urban stormwater, Bay Area non-urban stormwater, Bay Area wastewater, and direct air deposition onto the Bay. Then the mass balance is evaluated, to put an upper limit on the "additional loads." This is a first order estimate which, in the absence of any other information, would be a reasonable basis for establishing a total maximum daily load for a particle-associated pollutant based on a target concentration in sediment.

Watershed loads (i.e., stormwater runoff from urban areas, non-urban areas, and the entire Central Valley) are estimated as the product of the average mercury concentration in watershed sediments times the average sediment load:

Equation 1

$$\text{Hg Load} = [\text{Hg}]_{sed} \times \text{Sediment Load}$$

Where (for each source category):

Hg Load = total mercury load (kilograms per year, kg/yr)
$[Hg]_{sed}$ = concentration of mercury in sediment (parts per million, mg/kg)
Sediment Load = sediment entering the bay (millions of kilograms per year, M kg/yr).

Local air deposition and wastewater loads are estimated from direct measurements (i.e., atmospheric deposition rates and mercury concentrations in wastewater).

"Additional loads" includes identified and unidentified mine sites, remobilization of polluted sediments from deeper layers of the bay floor, existing and potential hot spots along the Bay margins, and natural variations of local mineralogy. "Additional loads" also incorporates any missing loss terms, such as burial, offgassing, or biological uptake and removal.

Simplifying assumptions and resultant uncertainties in the overall approach

Two fundamental assumptions in developing a mass balance model for mercury in the Bay and its watersheds are that:

1) Watershed mercury loads can be estimated as the product of mercury concentrations in watershed sediments and the amount of sediment discharged from a watershed; and
2) The Bay can be modeled as a simple, single box of sediment, with all inputs and outputs treated as advective processes.

The first assumption is reasonable, although the methods used to select representative values for mercury concentrations in sediments and mass of sediment discharge can introduce considerable uncertainty. Also, rather than a simple product, a better approach is to model sediment loads and mercury concentrations dynamically, where the data are sufficient to do so. Dynamic modeling means using the relationships between flow, suspended sediments, and mercury concentrations in sediments to estimate loads. This approach has been implemented to estimate the Central Valley watershed load, and recommended for estimation of Bay Area stormwater loads.

The second assumption fails when attempting to describe dredging, tidal outputs, and exposure of old sediments, which are all mixing, rather than advective processes. However, as subsequent sections reveal, this simplified approach is sufficient to describe the overall picture of mercury loads to the Bay, and suggests next steps necessary to reduce uncertainties (i.e., develop a model that accounts for mixing between different segments of the Bay).

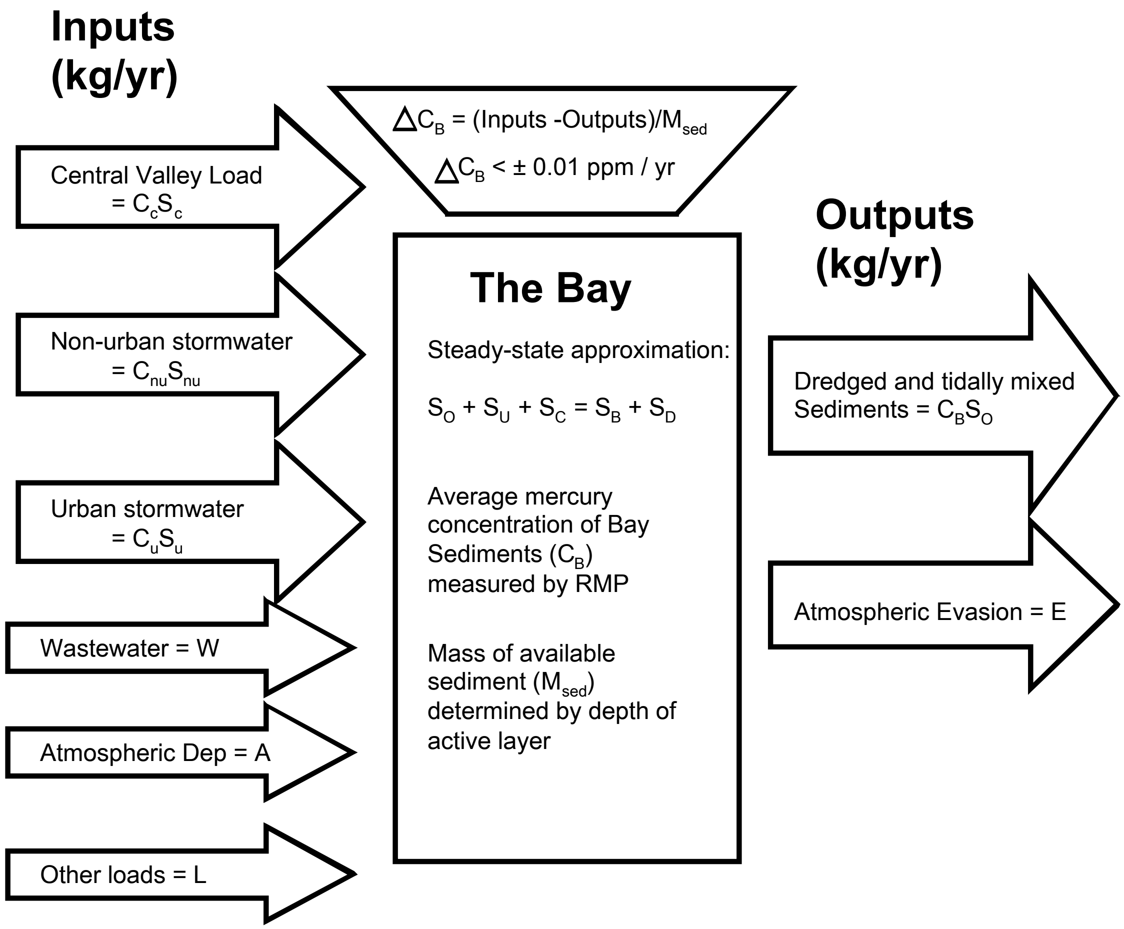

Figure 1: Conceptual illustration of the mercury mass balance for San Francisco Bay. C_x = mercury concentration in sediments (mg/kg), S_x = Sediment loading (M kg/yr), M_{sed} = mass of sediments available for resuspension (M kg), ΔC_B = rate of change in the average concentration of mercury in San Francisco Bay sediments.

4. Initial loads summary

4.1 The Central Valley Load

Hg Loads from the Central Valley = 435 kg/yr (range 240 – 630 kg/yr)

The best estimate for the average mercury concentration in sediments exported from the Central Valley range is 0.3 ppm, based on measurements at the Sacramento River mouth between March 2000 and October 2001 (McKee and Foe, 2002). Measurements by the RMP confirm that a likely range for this value is 0.2 ppm – 0.4 ppm (Appendix-1). Sediment loads from the Central Valley between 1995 and 2001 ranged from 300 to 2600 M kg/yr, based on continuous monitoring of suspended solids concentration (SSC) and flow (Buchanan and Ganju, 2002; Buchanan and Ruhl, 2000; Buchanan and Ruhl, 2001; Buchanan and Schoellhamer, 1996; Buchanan and Schoellhamer, 1998; Buchanan and Schoellhamer, 1999). The six-year average discharge of sediments from that study was 1600 ± 300 M kg/yr. Dynamic modeling of sediment discharges and mercury concentrations result in an estimate of 435 ± 96 kg/yr for the mercury load discharged into San Francisco Bay from the Central Valley. These estimates represents six-year means; the uncertainty represents one standard error about the six-year means. The total range on the Hg load estimate (240 – 630) kg/yr represents ± two standard errors around the mean.

Simplifying assumptions and resultant uncertainties in the Central Valley loads

The dynamic modeling approach employed by McKee et al. makes the following assumptions:

1) The relationship between TSS and particulate mercury concentrations ([Hg]p) measured in 2000 – 2001 represents the typical average mercury concentration in suspended particulate matter exported from the Central Valley.
2) Total Suspended Solids (TSS) and Suspended Solids Concentrations (SSC) are equivalent.
3) The six-year averaging period represents long-term trends.

The first assumption introduces uncertainty because the [Hg]p / TSS ratio may, in fact, vary systematically with flow. This has been observed in other, smaller, mining impacted watersheds. The 2000 – 2001 sampling period represented relatively low-flow conditions. The uncertainty introduced by this assumption can be reduced using long-term monitoring data.

The second assumption introduces uncertainty because the two different analytical methods, TSS and SSC, don't always produce comparable values[Gray, 2000 #61]. The difference between the two methods comes down to subsampling. If a bottle of water is collected and its entired contents filtered to determine the dry mass of particles, the resulting measurment is the SSC. If a subsample of the bottle is filtered, then the measurment is the TSS. Subsampling can lose coarse sediments that settle between agitation and pouring the subsample, so TSS can be systematically lower than SSC, especially in waterbodies transporting large amounts of coarse sands (> 63 μm). The data used by [McKee, 2002 #31] to determine mercury concentrations in particles rely upon TSS measurements, whereas the data used to determine particle loads rely upon SC measurements. In this case, the TSS and SSC measurements are thought to be comparable, because the sediments transported by the Sacramento River have been found to be predominantly fine materials (< 12 μm). The uncertainty of this assumption can be reduced in the future by either requiring SSC measurements from monitoring studies (i.e., no subsampling), and / or ultra-clean filtration to directly extract and analysze concentrations of mercury on filtered particles.

The third assumption can be re-evaluated as more sampling years are added. Preliminary results from the 2001 – 2002 water year suggest that the seven-year average mercury load is 383 +/- 84 kg / yr. Evaluation of the true, long-term average requires enough monitoring to reproducibly capture the full range of flow conditions, and then application of the observed

4.2 Stormwater loads

Hg loads from urban stormwater: = 180 kg/yr (range 60-300 kg/yr)

Hg loads from non-urban stormwater = 80 kg/yr (range 20 – 100 kg/yr)

Stormwater loads are divided into urban and non-urban components. These loads are assessed using the best estimate for sediment loads discharged from urban and non-urban watershed, and the best estimate for the concentration of mercury sediments discharged from urban and non-urban watersheds. Since rigorous assessments of discharged sediments are not available, assessments of bedded sediments in storm drain conveyances are used to make inferences about discharged sediments.

The best estimates for mercury concentrations in bedded sediments from storm drains from urban and non-urban catchments come from (Kinnetic Laboratories Inc., 2001).

Land Use	Average Total mercury (ppm)	Average Percent Fines (%)	Fines-normalized average mercury (ppm)
Urban	0.29	30	1.0
Non-Urban	0.06	30	0.2

Table 1: Summary of mercury and percent fines data for urban and non-urban land-use types. Data in first two-columns from page 39 of (Kinnetic Laboratories Inc., 2001). Fines-normalized concentrations in third column calculated by dividing the first column by the second column.

To relate bedded sediments to discharged sediments, this approach assumes that the average concentration of mercury in 100% fine, bedded sediments sets the maximum mercury concentration for mercury in discharged sediments. In other words, the working assumption is that bedded sediments are good predictors of discharged sediments, and the only uncertainty is that we don't know the particle size distribution of discharged sediments. From this, the maximum mercury concentrations in sediments discharged from open spaces is inferred from Table 1 to be 0.2 ppm, and the maximum for urban areas is inferred to be 1.0 ppm.

Following that logic, this approach assumes that the average concentration of mercury in bulk, bedded sediments (i.e., un-normalized concentrations) sets the minimum mercury concentration in discharged sediments. In other words, an additional working assumption is that discharged sediments are at least 30% fine, which is supported by the literature review of [McKee, 2002 #49]. Based on this assumption, the minimum mercury concentration in sediments discharged from open spaces is inferred from Table 1 to be 0.06 ppm, and the minimum for urban areas is inferred to be 0.3 ppm.

The mass of sediments discharged from urban and non-urban watersheds is estimated based on the total amount of sediment produced by local watersheds and estimates of the relative contributions made each type of land use. Using mass-balance calculations, the total local tributary load of sediments is estimated at 440-970 M kg/yr (Krone, 1979). A more recent literature review places the range at 600 – 1000 M kg/ yr (McKee et al., 2002b), which is the range that will be used in this calculation.

A recent assessment of stormwater sediment loads using the "rational method" suggests that 70% of sediments are discharged from non-urban areas, and 30% from urban areas (Davis et al., 2000). The overall tributary sediment loads from (Davis et al., 2000) are 2-3 times lower than those of (McKee et al., 2002b), because of the data and assumptions used. The "rational" method accounts for the different sediment production rates per unit area for different land uses and topographies, so the assessment by (Davis et al., 2000) provides the best estimate for the fractional contribution from urban and non-urban areas. These fractional contributions are applied to the total tributary sediment load to estimate sediment loads discharged from urban and non-urban land use types.

Sediment discharged from non-urban areas = 550 M kg / yr (range = 400 – 700 M kg/ yr)

Minimum = 600 M kg/yr x 70% = 400 M kg / yr (rounding to 1 significant figure).
Maximum = 1000 M kg/ yr x 70% = 700 M kg/yr

Sediment discharged from urban areas = 250 M kg / yr (range = 200 – 300 M kg/yr)

Minimum = 600 M kg/yr x 30% = 200 M kg/yr (rounding to 1 significant figure)
Maximum = 1000 M kg/yr x 30% = 300 M kg/yr

Mercury loads from non-urban areas = 80 kg/yr (range 20 – 100 kg / yr)

Minimum = 0.06 ppm x 400 M kg/yr = 24 kg Hg / yr (= 20 kg / yr rounded to 1 significant figure)
Maximum = 0.2 ppm x 700 M kg/yr = 140 kg Hg / yr (= 100 kg/yr rounded to 1 significant figure)
The best estimate taken at the midpoint of the range (before rounding) = 80 kg/yr.

Mercury loads from urban areas = 180 kg/yr (range 60 – 360 kg/yr)

Minimum = 0.3 ppm x 200 M kg/yr = 60 kg Hg/yr
Maximum = 1 ppm x 300 M kg / yr = 300 kg Hg / yr

The best estimate taken at the midpoint of the range (before rounding) = 180 kg/yr.

Simplifying assumptions and resultant uncertainties in stormwater loads

The estimates of urban and non-urban mercury discharges suggest that while urban areas of the Bay discharge less sediment than open spaces, urban areas may discharge higher mercury loads than open spaces, because the concentrations of mercury in urban sediments are higher than non-urban sediments. That observation is predicated on the following assumptions:

1) The only uncertainty in predicting mercury concentrations in discharged sediments from bedded sediments is the particle size distribution of discharged sediments;

2) The relative amounts of sediment discharged from urban and non-urban areas have been accurately quantified by the rational method; and

3) The average mercury concentration in sediments and the average percent fines are good estimates of the expected values, as opposed to the medians.

The first assumption is not strictly true. Watershed processes introduce additional uncertainties that arise from using bedded sediments to predict the composition of discharged. The topography, land use, pollutant form and distribution, and fluvial geomorphology of a watershed affect the observed concentrations of pollutants in both bedded and discharged sediments. Thus, the observation that bedded sediments from urban storm drains have higher mercury concentrations than non-urban storm drains may be simply an artifact resulting from the type of sediment that deposits in urban storm drains. A monitoring approach to reduce this uncertainty would be to collect composite samples of storm events and directly characterize the mercury concentration and particle size distribution of discharged sediments. This is a labor-intensive approach, so the value of the reduced uncertainty should be carefully weighed against the cost of developing the information. The second assumption can also be tested with targeted watershed monitoring.

The third assumption is best addressed through a more sophisticated modeling approach. Rather than simply multiplying an average concentration times and average sediment load, it is better to develop the information needed to characterize the frequency distribution of mercury concentrations and sediment loads for different watersheds. Both distributions are expected to be log-normal (as with many environmental measurements). If a parameter (e.g., sediment load) varies systematically with flow, than it can be simulated for a long-term flow record to develop load estimates. If a parameter (e.g., concentration) varies randomly according to a log-normal distribution, the distribution can be simulated using a Monte-Carlo approach. The computations to implement such a method are fairly straightforward, but producing the data needed to develop the model is potentially a costly undertaking.

4.3 Wastewater Loads

Wastewater loads = 14 kg/yr (range 11 – 17 kg/yr)

Wastewater loads are measured as flow times annual average concentration, summed up over all dischargers. Best estimates are available in SFRWQCB staff reports that summarize NPDES self-monitoring data (Katen, 2001) (So, 2001)**.** Those estimates have recently been updated [Larry Walker and Associates, 2003 #62]. The total is currently 12.2 kg/yr for municipal pollution control plants, and 2.0 kg/yr for industrial facilities. The overall loading to the Bay from combined municipal and industrial facilities is 14.2 ± 3.3 kg/yr. The range results from uncertainties due to interannual variation and propagated error from summing over thirty terms.

Simplifying assumptions and resultant uncertainties in wastewater loads

The only simplifying assumption in the calculation of wastewater loads of mercury is that analytical variability in measured mercury concentration is significantly smaller than monthly variability. Thus, the variance about monthly means was used to determine the uncertainty of individual facility load estimates. That sampling variance was propagated in the summation of all facility loads to generate the range for the total wastewater load estimate.

4.4 Direct Air Deposition

Direct Air Deposition = 30 kg/yr (range 10 – 50 kg/yr)

This means mercury deposited directly on the Bay surface. Airborne deposition over the watersheds is incorporated in the watershed loads. This has been measured by the RMP atmospheric deposition pilot study (Tsai and Hoenicke, 2001). The best estimate of direct deposition onto Bay totals 27 kg (=30 kg rounded to 1 significant figure), with likely range of 10-50 kg. The best estimate comes directly from report, and the range is inferred from "two-fold to five-fold" uncertainty stated in report (Tsai and Hoenicke, 2001).

Mercury can rapidly cycle in aquatic ecosystems between inorganic mercury, methylmercury, and dissolved gaseous mercury (discussed in subsequent sections). When dissolved gaseous mercury builds up in surface waters to concentrations above its saturation solubility, it can evade into the atmosphere, making surface waters a source to the atmosphere, rather than a sink. In San Francisco Bay, the atmospheric evasion rate for the entire Bay is estimated at 66 – 260 kg/ yr [Conaway, 2003 #63]. Considering the atmospheric deposition rate of 10 – 50 kg / yr, this means that the net exchange of mercury between the atmosphere and the Bay is at least a 10 kg loss to the atmosphere, and could be as much as 250 kg per year.

Simplifying assumptions and resultant uncertainties in airborne deposition loads

The rate of evasion from surface waters of the Bay is the major uncertainty in determining the net flux of mercury to or from Bay waters and the atmosphere. The estimates of mercury evasion rates are not very sensitive to atmospheric mercury concentrations, but are extremely sensitive to concentrations of dissolved gasous mercury and wind speeds. Therefore, the best way to reduce the uncertainty about atmospheric loads cycling is to obtain more data on dissolved gaseous mercury in Bay waters and to use more detailed models of daily and average wind speeds.

Another major uncertainty is the fate of evaded mercury. How much of the 66 – 260 kg/yr of mercury evaded from the Bay deposits locally, to be cycled back into surface waters via stormwater runoff, how much is transported into the Central Valley, and how much escapes eastward of the Sierra Nevadas?

5. Mass Balance

Referring back to Figure 1, the size of the first five input terms has been estimated. Readily identified mercury inputs to the Bay total 700 kg/yr, with a possible range of 300-1100 kg/yr. To determine what else is missing, we can consider what is known about inputs-outputs and outputs to establish the boundaries of L, the "all other loads."

5.1 Inputs – Outputs

If mercury inputs to the Bay exceed the outputs, then over time, the concentration of mercury in Bay sediments will be gradually increasing. If inputs are less than outputs, then mercury concentrations will decrease over time (one of the desired outcomes of a watershed management plan for mercury). If inputs are equal to outputs, then concentrations in sediments will remain the same. So we can make some preliminary judgments about the difference between inputs and outputs by asking, "how slowly is the concentration of mercury in Bay sediments changing?"

Year	[Hg] (mg/kg)
1993	0.34
1994	0.33
1995	0.23
1996	0.24
1997	0.31
1998	0.19
1999	0.31
2000	0.29

Table 2: Mercury concentrations in suspended particles of the northern reach of San Francisco Bay. Concentrations determined by simple linear regression of total recoverable mercury concentrations against TSS, with the intercept forced through zero.

The concentrations of mercury in suspended sediments of the northern reach over the past eight years are summarized in Table 2. Inspection of Table 2 suggests that the rate of change of mercury concentrations in sediments, ΔC_B, is no more than 0.01 mg/kg/yr and no less than -0.01 mg/kg per year. If the concentration of mercury in Bay sediments were changing faster than ± 0.01 mg/kg/yr, then we would expect a change of ± 0.1 mg/kg over the past decade; that does not appear to be the case. This qualitative statement can be better quantified through a more rigorous statistical approach, but it is still a useful starting point for constraining the mercury mass balance in San Francisco Bay.

Referring back to Figure 1, knowing that $-0.01 < \Delta C_B < 0.01$ helps constrain inputs-outputs, according to Equation 2

Equation 2:

$$(\text{Inputs} - \text{Outputs}) = \Delta C_B \times M_{sed}$$

Where M_{sed} is the mass of actively resuspended sediments (millions of kg)

The best estimate for the depth of the actively resuspended sediment layer is 0.15 m (Davis, 2002). The area of the Bay is 930×10^6 m^2 (Conomos, 1979). Assuming that bedded sediments have a density of 1325 kg / m^3, this means the mass of active sediments is 184,838 M kg:

$$M_{sed} = 0.15 \text{ m} \times 930 \text{ M m}^2 \times 1325 \text{ kg / m}^2 = 185{,}000 \text{ Mkg.}$$

If the average concentration of mercury in Bay sediments is 0.3 ppm, than the mercury mass inventory in the actively resuspended sediment layer is approximately 60,000 kg Hg. If the concentration of mercury in the actively resuspended sediment layer is changing by less than 0.01 ppm, then according to Equation 2 (and rounding to 1 significant figure):

$$- 2000 \text{ kg/yr} < (\text{Inputs} - \text{Outputs}) < 2000 \text{ kg/yr}$$

In other words, from the fact that the concentrations of mercury in Bay sediments are changing by less than 0.01 ppm per year, we infer that the 60,000 kg mercury mass inventory in the Bay is changing by less than 2000 kg/yr, or by less than 3% per year.

With a longer sampling period, the rate of change can be better constrained. For example, data from a 1970 assessment of mercury in the surface of San Francisco Bay sediments suggest that concentrations in surface sediments of the open Bay in 1970 were similar to contemporary concentrations [McCulloch, 1971 #64]. If the average concentration of mercury in Bay sediments has changed by less than 0.1 ppm over the past 33 years, then $- 0.003 < \Delta C_B < 0.003$, and therefore the 60,000 kg mercury mass inventory of the Bay would be changing by less than 600 kg/year (i.e., less than 1% per year).

5.2 Outputs

The outputs rates are determined by the rate of sediment removal from the Bay, primarily by tidal flushing out the Golden Gate and by disposal of dredged sediments to ocean or upland sites. Removal by burial is considered negligible, because the Bay does not appear to be accreting at a significant rate, and may in fact be eroding slightly (Jaffe et al., 2002) (Note that the erosion rate is still small, <1% compared to the total sediment flux through the Bay, so the steady-state approximation that sediment inputs balance sediment outputs is still valid). The total sediment load to the Bay, including the Cnetral Valley and local tributaries, is between 1600 and 3200 M kg/yr. If the total amount of sediment leaving the Bay is roughly equal to the total amount of sediment entering the Bay, then at least 1600 and as much as 3200 M kg/yr of sediment also exits the Bay. If the average mercury concentration of sediments exiting the Bay is between 0.2 and 0.4 ppm, then the mass of mercury leaving the Bay via sediments is between 320 and 1280 kg/yr, with the best estimate taken at the midpoint (800 kg/yr).

Another possible removal pathway is evasion is evasion of dissolved gaseous mercury. As discussed above, this is estimated to be 66 – 260 kg/ yr [Conaway, 2003 #63]. Therefore, the total output rate for mercury in the mass balance model for the Bay is calculated to be between 390 and 1540 kg/yr, with a best estimate of 965 (=1000 kg/yr rounded to 1 significant figure)

5.3 Mass Balance

The total inputs inferred from the steady-state conditions of the Bay is calculated from Equation 3:

Equation 3:

Total inputs = (inputs – outputs) + outputs

Using the values for (inputs-outputs) and outputs calculated above, the best estimate for total mercury inputs to the Bay is 1000 kg/yr, with a likely range of –1600 kg/yr to 3500 kg/yr. This means that the net effect of all processes besides dredging, tidal flushing, and evasion to the atmosphere must be somewhere between an output of 1600 kg per year and an input of 3500 kg/yr , and that the best estimate is a net input of 1000 kg mercury per year to the Bay. Assuming that all other outputs (burial, offgassing, upstream tidal mixing) are negligible, the implication is that total mercury loads to the Bay amount to 922 kg per year.

In comparison, loads to the Bay calculated from readily available data amount to 700 kg/yr. Therefore, the best estimate for all other loads (L, in Figure 1) is 300 kg/yr, with a likely range of –2700 – 3200 kg/yr. The results of the mass balance calculations (rounded to two significant figures) are summarized in Table 3.

6. Discussion of the Mass Balance

6.1 Summary of mass balance calculations

The results of this mass balance analysis can be summarized in a few intuitive statements that help determine the most important next steps to reducing uncertainties about mercury mass loads to the Bay. The initial approach treats the Bay as a single reservoir consisting of 185,000 M kg of sediment. The concentration of mercury in this sediment reservoir doesn't increase or decrease by more than 0.01 mg/kg per year, and the annual flow of sediment into the reservoir balances the annual flow of sediment out of the reservoir. For this simple system, annual mercury inputs of 940 kg/yr are required to balance the estimated mercury outputs. The sum of all direct estimates of mercury inputs is 640 kg/yr, suggesting that there are an additional 300 kg/yr yet to be accounted for.

However, there is a great deal of uncertainty associated with this estimate. The additional loads could be as much as 3000 kg/yr or as little as –2600 kg/yr (i.e., a net loss), based on a strict assessment of uncertainties associated with the mass balance calculation. The uncertainty comes from the approach – the sediment reservoir is massive (1.85×10^{11} kg), so limiting the rate of change in mercury concentration to 0.01 mg/kg/yr allows a difference of up to 1850 kg/yr between mercury inputs and mercury outputs.

	Hg Load, Best Estimate (kg/yr)	Hg Load, Possible Range (kg/yr)
Inputs		
Central Valley	400	240 - 630
Urban stormwater	200	60 - 300
Non-urban stormwater	80	20 - 100
Air Deposition	30	10 - 50
Wastewater	14	11 - 17
Total of Calculated Inputs	700	300 - 1100
Outputs		
Sediment loss	800	300 - 1300
Atmospheric Evasion	200	70 – 260
Total Outputs	1000	400 – 1600
Inputs-Outputs	0	(-2000) – 2000
Mass Balance		
Mass Balance Inputs = (Inputs - Outputs) + Outputs	1000	(-1600) - 3500
Additional loads = Mass Balance Inputs - Calculated Inputs	300	(-2600) - 3000

Table 3: Preliminary Mass Balance Summary for Mercury in San Francisco Bay. Data rounded to two significant figures.

6.2 Approach to reducing uncertainty in the mass balance

Much of this uncertainty can be reduced by just thinking about the system a little more carefully. It is extremely unlikely that total outputs have been underestimated by thousands of kilograms. For that to be true, it would require sediment burial rates, mercury offgassing rates,, or biological uptake and removal rates that conflict with our present understanding of the biogeochemical cycle of mercury in the Bay. While this hypothesis should be more carefully reviewed by a science review team, it is worth considering what the more likely range for all other loads is if all other output processes total nomore than 300 kg per year.

If the minimum values for all the estimated inputs shown in Table 3 are the true values, and additional output processes (i.e., gaseous evasion, biological uptake and removal, burial, disposal of dredged sediments) amounts to -300 kg, than the “additional loads” term would be no less than -514 kg/yr. On the other extreme, if there are no other significant outputs, the maximum values for all the estimated inputs shown in Table 3 are the true values, and the maximum values for all other possible loads (discussed in section 7 below) are added in, then the “additional loads” term would be no more than 1900 kg/yr.
So a more likely range for the “additional loads” term is (–514) – 1900 kg/yr.

Four general approaches are needed to reduce uncertainty in the mass balance:

1) *Improve direct estimates of mercury inputs in Table 3*
   a. The true, long-term annual average concentration of mercury in sediments flushed into the Bay from the Central Valley, including variability during high-flow periods, is a key uncertainty that can be resolved through focused monitoring.
   b. The amount of sediment discharged from urban and non-urban watersheds and the true, long-term annual average concentraion of mercury in those sediments are additional uncertainties.
2) *Improve direct estimates of additional mercury loads discussed in section 7 below.*
   a. Loads from the Guadalupe River are complicated by tidal mixing in the lower reaches of Alviso slough and Lower south Bay. This is a key uncertainty that can be resolved through monitoring and modeleing.
   b. Anomalous storm drain conveyances may contribute additional loads above those calculated using the "urban/non-urban" paradigm. This can be resolved through monitoring.
   c. Benthic remobilization of polluted sediments deposited in deeper layers of the northern reach may be a substantial source. This can be resolved by collection of more cores throughout the Bay, and by modeling the sediment mixing and erosion dynamics.
3) *Refine the estimate for the rate of change in mercury concentrations of Bay sediments.*
   a. The estimate for the rate of change in mercury concentrations can be improved reasonably soon by simply applying a more rigorous statistical approach to existing monitoring data. Such an approach should account for the heteroskedaticity of the regression analysis discussed in Appendix A.
   b. Since the rate of change has time in the denominator, the estimate will improve as the time period of the monitoring data set gets longer.
4) *Refine the simple, one-box model to a multi-segment box model*
   a. One key improvement to the mass balance model would be to improve the estimate for concentrations of mercury in sediments of different segments of the Bay. This can be done using data from a random, stratified sampling program, such as the EMAPS data set, or the redesigned approach of the RMP.
   b. Another improvement is to break the mass balance calculations down into a multiple segment model, to more accurately reflect the segmented nature of San Francisco Bay. Such a model should account for both mixing and advenction in the sediment transport dynamics of the Bay. A simple, two-segment conceptual model for the Bay is discussed in Appendix B.

Some preliminary work has been done on a five-segment mass transport box model for the Bay. This work should be peer reviewed and more rigorously tested. Initial results suggest that additional loads to the northern reach of the Bay, after accounting for stormwater, wastewater, airborne deposition, and loads from the Central Valley, amount to 100-500 kg per year, with a best estimate of 300 kg. For now, this range should be considered a working hypothesis, known as "The Adaptive Management Hypothesis." This working hypothesis is based on Best Professional Judgment resulting from twelve years experience studying trace metal geochemistry on San Francisco Bay, and two years of discussion with experts from the United

State's Geological Survey, the San Francisco Estuary Institute, and the University of California. If greater precision is needed in the mass balance for mercury in San Francisco Bay in order to make key policy decisions, the hypothesis can be tested by addressing the four key uncertainties outlined above.

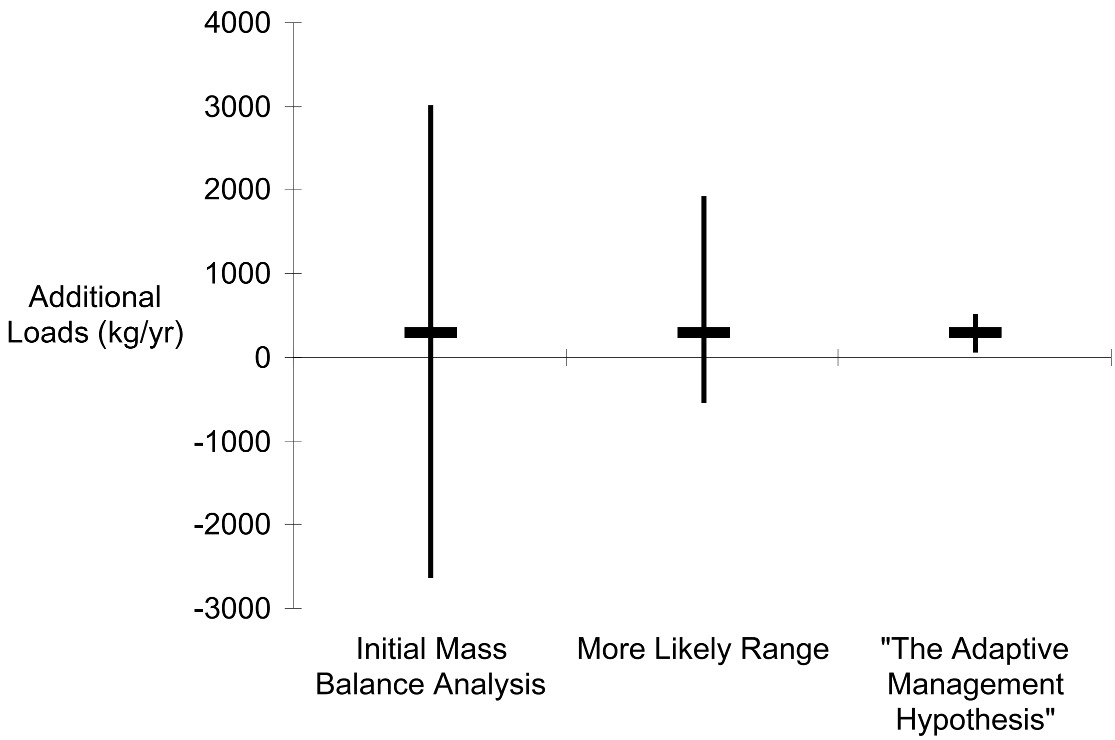

Figure 2: Closure on the mass balance (indicated by additional mercury loads) based on this initial mass balance analysis. The more likely range and the Adaptive Management Hypothesis indicate likely outcomes of improved monitoring and modeling efforts. Vertical lines indicate the range, horizontal lines indicate the best estimates.

7. Estimates of additional loads

7.1 Loads from the Guadalupe River

The mercury mines of the New Almaden mining district left the Guadalupe River watershed with a legacy of mercury-polluted sediments in piles of waste rock, surface soils, and stream sediments. The load resulting from this is calculated based on average mercury concentrations in sediments exported from the Guadalupe River watershed, and average annual sediment loads.

Hg Load from Guadalupe River = 100 kg/yr (Range 7-700 kg/yr)

= 5 mg/kg Hg in Guadalupe River Watershed sediments x 20 M kg sediment/yr

Average Hg concentration in sediments exported from Guadalupe River: We currently observe 1 mg/kg Hg in sediments at Alviso Slough during high flow (Abu-Saba and Tang, 2000), (Leatherbarrow et al., 2002), from data readily available through RMP annual reports and on SFEI website. However, Alviso slough is a bad place to estimate concentration of mercury in sediments leaving Guadalupe R. watershed because of tidal mixing – watershed sediments are diluted with Bay muds, hence 1 mg/kg is a lower limit. Sediments in the lower Guadalupe River near downtown San Jose have 2-10 mg/kg mercury. A reasonable estimate is 5 mg/kg, midway between 1 and 10. This estimate can be refined and substantiated from the wealth of sediment samples analyzed as part of the lower Guadalupe River flood control project. Kleinfelder Consultants also have an extensive data set from corings taken in conjunction with the Rivermark development project.

Sediment load from Guadalupe River : The "rational method" yields an estimate of 7 M kg/yr sediment (URS Greiner Woodward Clyde and Tetra Tech Inc., 1998). The rational method underestimates sediment load by 2-3 fold (Lester Mckee, personal communication). USGS used gauged flow and measured TSS and bed-load estimates to propose 36 – 74 M kg/yr (Porterfield, 1980). The best estimate is 20 M kg/yr, with a likely range of 7-70 M kg/yr.

7.2 Additional stormwater loads

Not all drainages within the Bay Area watersheds fit the "urban / non-urban" paradigm used to estimate stormwater loads. Sediments from some storm drain conveyances in the Bay Area have elevated mercury concentrations in the fine sediments compared to more typical urban and non-urban sediments [Gunther, 2001 #23] **(JASP report)**. Of the over 200 samples collected for determination of mercury concentrations, 20 showed elevated mercury concentrations which did not fit the "urban / non-urban" paradigm. The average concentration of mercury (normalized to fine sediments) was 9 mg/kg, with a standard error of +/- 2 mg/kg. By making the very rough approximation that these anomalous watersheds represent about 1% of the watershed sediment load to the Bay, and assuming a likely range of 5-13 mg/kg (two times the standard error) for the concentration of mercury in these anomalous stormwater conveyances, the best estimate form mercury loads from other stormwater sources is 78 kg/yr, with a likely range of 22 – 126 kg/yr.

Sediment load from anomalous stormwater conveyances:

Best estimate = 7.1 M kg/yr = 0.01 x 707 M kg/yr (1% of watershed sediment load)
Minimum = 4.4 M kg/yr = 0.01 x 440 M kg/yr
Maximum = 9.7 M kg/yr = 0.01 x 970 M kg/yr

Mercury load from anomalous stormwater conveyances:

Best estimate = 9 mg/kg x 7.1 M kg/yr = 64 kg/yr
Minimum = 5 mg/kg x 4.4 M kg/yr = 22 kg/yr

Maximum = 13 mg/kg x 9.7 M kg/yr = 126 kg/yr

7.3 Loads from undetected local mines in the Northern Reach

There may be additional inoperative mercury mines in the Napa River watershed contributing to the loads for the northern reach. This is suggested by the map of inoperative mines in the 1995 Basin Plan. A reasonable first-order watershed assessment is possible simply by asking "are there possible places where 1-10 M kg/yr of sediment averaging 1-20 mg/kg mercury are discharged downstream?" If so, that could result in 1-200 kg/yr of sediment. Discharge of 5 M kg/yr sediment averaging 5 mg/kg would be 25 kg/yr. So the best estimate is taken as 25 kg/yr, with a likely range of 1-200 kg/yr.
The Gambonini mine in Marin County would be a good "calibration mine" to help think about this in greater detail, as well as site inspections and aerial photographs to identify potential sources of mercury due to erosion and mass wasting of tailings piles.

Mercury load from other mines in the Northern Reach:

Best estimate = 5 mg/kg x 5 M kg/yr = 25 kg/yr
Minimum = 1 mg/kg x 1 M kg/yr = 1 kg/yr
Maximum = 20 mg/kg x 10 M kg/yr = 200 kg/yr

7.4 Loads from sediment pulses from the Central Valley

Pulses of mercury-polluted sediments are transported downstream from mining-impacted watersheds during high-flow periods (Foe and Croyle, 1998; Ganguli et al., 2000; Leatherbarrow et al., 2002; Whyte and Kisrchner, 2000). The concentration of mercury in sediments transported from the Central Valley may peak episodically during high-flow events, as a result of flushing from mining-impacted areas, as well as erosive scour of historically deposited sediments from within the Delta. Therefore, treating the observed 0.21 mg/kg concentration of mercury in sediments at Sacramento River mouth as a year-round average may be an underestimate. Even small departures from this average correspond to relatively large mercury loads, because the sediment load is so high during high-flow events.

For example, if 10% of the sediment load from the Central Valley had an average concenration of 0.31 mg/kg instead of 0.21 mg/kg, that would correspond to an excess of 21 kg over loads predicted from an annual average concentration of 0.21 mg/kg:

(0.31 – 0.21) mg/kg x (0.1)x(2100 M kg.yr) = 0.1 mg/kg x 210 M kg/yr = 21 kg.

Most of the sediment load from the Central Valley enters during high-flow periods (Foe and Croyle, 1998), so it is reasonable that up to 80% of the sediment load could have higher mercury concentrations than the typically observed 0.21 mg/kg. This would suggest a maximum load of 168 kg from seasonal pulses out of the Central Valley:

(0.31 – 0.21) mg/kg x (0.8)x(2100 M kg.yr) = 0.1 mg/kg x 1680 M kg/yr = 168 kg.

The best estimate is taken at the mid-point, 95 kg/yr.

7.5 Loads from benthic remobilization

This is one of the hardest loads to estimate. Benthic remobilization refers to the gradual exposure of mercury – polluted sediments that were deposited over the past 100 years. Deep cores in San Francisco Bay show mercury concentrations up to 1 mg/kg in sediments beneath about 30 cm. The northern reach of San Francisco Bay was filled in up to 2 meters with sediment and debris from hydraulic mining in the late 1800's and early 1900's. Today, dams from the Central Valley Project have cut off considerable amounts of sediment supplied to San Francisco Bay, so the northern reach of the Bay has shifted from a depositional environment to an erosional one (Jaffe et al., 2002; Krone, 1979). As the Bay seeks to restore its natural bathymetry, polluted sediments from deeper layers are gradually mixed upward. This is probably the reason why we observe a concentration gradient between suspended particles and bottom sediments in the northern reach (Appendix 1), and may also explain in part why there is a mercury concentrations in sediments increase by about 0.1 mg/kg between the Sacramento River and San Pablo Bay.

Knowing that the other loads to the Bay add up to at most 284 kg, and that the total loads needed to close the mass balance are less than 1160 kg, it can be said that loads from exposure of polluted sediments are no more than 876 kg/yr.

8. Breakdown of the Central Valley Load

The Central Valley load can be subdivided into the watershed background load, the contribution from atmospheric deposition, mining legacies, and emissions from the urban environment.

8.1 Watershed background load

The concentration of mercury in sediments deposited in the Bay was 0.04 - 0.08 mg/kg in pre-settlement times (Hornberger et al., 1999). This pre-industrial watershed background was caused by mineral weathering and deposition of natural, pre-industrial atmospheric sources. The modern watershed background load has likely increased because the source of sediments has shifted. With the construction of dams and reservoirs, much of the sediment supply from the Sierra Nevadas was cut off from San Francisco Bay, resulting in a shift towards Coast Range sediments as the chief source. Coast range sediments likely have naturally higher average mercury concentrations, so we make the assumption that the modern background load due to mineral weathering is somewhat higher, about 0.06 – 0.10 mg/kg, with a best estimate of 0.08 mg/kg. Applied to the annual sediment load (1800-2400 M kg/yr), this implies a best estimate of 168 kg/yr, with a likely range of 108-240 kg/yr:

Best estimate = 0.08 mg/kg x 2100 M kg/yr = 168 kg/yr
Minimum = 0.06 mg/kg x 1800 M kg/yr = 108 kg/yr
Maximum = 0.10 mg/kg x 2400 M kg/yr = 240 kg/yr

8.2 Atmospheric Deposition over the Central Valley

Atmospheric deposition over the Central Valley probably accounts for between 0.05 and 0.15 mg/kg of the present day concentration of mercury in sediments discharged from the Delta. The upper limit, 0.15 mg/kg, comes from the average of two independent lines of evidence:

i) Mercury concentrations in the upper layer of sediments collected from Lake Tahoe average around 0.2 mg/kg. Lake Tahoe is an alpine Lake in the Sierra Nevadas (Slotton, 2000). Mercury loads to the lake are essentially all atmospheric in origin – there are no known mercury or gold mines in the Lake Tahoe Basin. In deeper, dated cores, collected from the lake, background concentrations were approximately 0.04 mg/kg. Therefore, the inferred effect from modern atmospheric deposition is 0.16 mg/kg. Deposition rates appear to be much higher in the high Sierras than on the California Coast, and dams downstream trap sediments, so the effect of air deposition on mercury concentrations in Central Valley sediments is probably lower than what we see in the Sierras.

ii) The median mercury concentration is also around 0.2 mg/kg for surface background sediments collected throughout the Central Valley (Bradford et al., 1996). Since the natural background of this sediment is 0.06 mg/kg, we infer an effect of 0.14 (=0.2 – 0.06) mg/kg from atmospheric deposition onto the Central Valley.

The best estimate of the lower limit is 0.05 mg/kg. This estimate assumes that since contemporary global atmospheric mercury emissions are 2-3 fold greater than in pre-industrial times, atmospheric deposition must have some effect on the concentration of mercury in surface sediments. Therefore, the lower limit is set by the observation that even in remote areas of the world atmospheric deposition increases mercury concentrations in soils by 0.05 mg/kg (Fitzgerald et al., 1998).

Given these upper and lower limits, atmospheric deposition probably elevates mercury concentrations in Central Valley Sediments by 0.10 +/- 0.05 mg/kg compared to pre-industrial times. Applied to the estimated sediment load from the Central Valley, this suggests a best estimate of 210 kg/yr, with a likely range of 90 – 360 kg/yr.

Best estimate = 0.10 mg/kg x 2100 M kg/yr = 210 kg/yr
Minimum = 0.05 mg/kg x 1800 M kg/yr = 90 kg/yr
Maximum = 0.15 mg/kg x 2400 M kg/yr = 360 kg/yr

8.3 All other Central Valley Sources, including inoperative mines

With an estimate of the total mercury load discharged from the Central Valley, and estimates of the amount of that load cause by mineral weathering and atmospheric deposition, the load from all other sources, including inoperative mercury mines, can be estimated by difference. Mineral weathering plus atmospheric deposition account for at least 0.11 mg/kg, and may account for almost all of the 0.21 mg/kg mercury concentration observed in Central Valley sediments. Thus, the impact of discharges from all other Central Valley sources, including inoperative mercury mines, urban runoff, and wastewater, is between 0.01 and 0.10 mg/kg.

This yields a possible range of 18 – 240 kg for all other Central Valley sources:

Minimum: 0.01 mg/kg x 1800 M kg/yr = 18 kg/yr
Maximum: 0.1 mg/kg x 2400 M kg/yr = 240 kg/yr
Best estimate: 441 kg/yr (Central Valley Total) – 210 kg/yr (Best estimate for air deposition) – 168 kg/yr (best estimate for mineral weathering) = 68 kg/yr

	Hg Load, Best Estimate	Hg Load, Possible Range	[Hg]sed	Sediment Flux
Mineral Weathering	168	108 - 240	.06 - .10	1800 - 2400
Air Deposition	210	90 - 360	.1 - .2	1800 - 2400
All other Central Valley Sources, including mines	63	1 - 243		
Total	441			

Table 4: Breakdown of estimated loads contributing to total Central Valley load.

Appendix A: How we know what we know about mercury concentrations in Bay sediments

The basis for calculating a Total Maximum Daily Load for mercury in San Francisco Bay is the concentration of mercury in sediments. Like many pollutants, mercury preferentially partitions onto sediments. In the Bay, for every atom of mercury in the dissolved phase, there are about a million mercury atoms stuck to particles[1]. So, even though the Bay is a complex, tidally mixed estuary with multiple mercury sources, we can simplify the mass balance problem by just considering mass transport of mercury in the particulate phase:

Hg load (kg Hg / yr)	=	Concentration in sediments (ppm, mg Hg / kg sed)	x	Sediment load (M kg sed / yr)

Equation 4: Relationship between mercury loads, mercury concentrations in sediments, and sediment load.

The power of the "view from downstream" is its simplicity. By asking "what causes the contemporary observed concentrations of mercury in receiving water sediments," we are led to some rather straightforward measurements of mercury concentrations in sediments in different parts of the Bay and its watersheds. The purpose of this memo is to explain how we analyze the thousands of data points from the RMP to quantify the concentration of mercury in Bay sediments.

[1] This is quantitatively expressed as the partition coefficient:

$$Kd = \frac{10^6 \text{ x } ([Hg]tot - [Hg]diss)}{[Hg]diss \text{ x } TSS} \quad (L/kg)$$

Values for total mercury in water ([Hg]tot), dissolved mercury ([Hg]diss) and total suspended solids (TSS) are available from the Regional Monitoring Program, at www.sfei.org. The Kd for Mercury in the Bay ranges from 100,000 – 10,000,000 L/kg, and is most commonly on the order of 1,000,000 L/kg.

A.1 Available Data

The data set for making these determinations comes from the RMP, which archives the data for public access at www.sfei.org. Data are available for sampling cruises conducted between 1993 and 2000. Subsequent data have been collected, but have not been reviewed and approved for release yet. Much of the Hg data from later years (1999 and 2000) has been "blank flagged," indicating they should be considered with caution, because the contracting laboratories reported high blanks (<30% of sample signal)[2] in their analyses that year. The analyses for this study were conducted both by using the full 1993-2000 data set and by deleting "blank-flagged" data. The conclusions are not affected by removing the blank flagged data, so all discussions are based on the full data set.

The United States Environmental Protection Agency has also collected a survey of pollutant concentrations in Bay sediments (their EMAPS program). The EMAPS survey used a random stratified sampling design to choose station locations. When this data becomes available, it will be a useful check as to whether sample design affects the conclusions. Until then, what we know "now" is established by the RMP data set.

There are two types of measurements available in the RMP data set: water column and bottom sediments. This analysis uses both. Water column measurements are collected by pumping water from approximately one meter below the water surface into sample bottles. Samples are analyzed for total recoverable mercury (i.e., the concentration of mercury in an unfiltered water sample after it has been acidified to pH <2). Water column measurements also quantify the total suspended solids (TSS) in a sample. Total recoverable mercury and TSS measurements are combined to make inferences about the concentration of mercury in suspended sediments. Bottom sediment samples are collected by dropping an Eckman dredge overboard to collect a large (about 1 m^3) chunk of the Bay floor. The top five centimeters of sediments in the dredge are homogenized and analyzed for total mercury and grain size (i.e. the percent fine material, less than 63 microns). Total mercury and percent fines measurements are combined to make inferences about the concentration of mercury in fine bottom sediments.

[2] The fact that the blank flags went up is a sign that the QC program is working.

A.2 Data analysis: Basic calculations

Analysis of both the water column and the bottom sediment data relies upon simple linear regression to make scientific inferences about mercury concentrations in Bay sediments. This approach yields not only estimates of mercury concentrations, but also reasonable descriptions of the uncertainty of those estimates. We have to use regression analysis because for both water column data and bottom sediment data, there are gross physical processes that affect observed mercury concentrations. Total mercury in the water column tends to increase with increasing suspended load. Total mercury in bottom sediments tends to increase when sediments have more fine material. We "normalize" water column data to suspended load and bottom sediment data to percent fines in order to detect differences in mercury concentrations that are due to mercury loads.

For the water column data, we plot total recoverable mercury against TSS. The slope of the best fit line gives the average concentration of mercury in the suspended particulate matter, according to .

$$[Hg]_{sediment}\ (\mu g/g,\ mg/kg) = [Hg]_{water}\ (\mu g/L)\ /\ [TSS]\ mg/L \times 1000\ (mg/g)$$

Equation 5: Water column mercury concentrations ($[Hg]_{water}$) as a function of mercury concentrations in sediments ($[Hg]_{sediment}$) and suspended load ([TSS]).

Equation 5 simply expresses the slope of the regression line as the rise over the run, and performs the unit conversion to get the answer in µg Hg per g of suspended sediment. This is the basic calculation to determine mercury concentrations in suspended particles. The complete analysis also considers segmentation of the Bay and uncertainty of the basic calculation, as discussed below. For now, the important point is that for the water column data, we use regression analysis to determine a slope, and that slope has physical meaning. We are looking at a data set and asking, "given the observed relationship between total mercury in the water column and suspended sediment concentration, what does that tell us about the average concentration of mercury in the suspended sediments?"

When using simple linear regression, we can choose to calculate the intercept (Figure 3—A), or to force the intercept through zero (Figure 3-B). Our basic assumption is that essentially all the mercury is in the particulate phase, so the water column mercury should be zero at zero suspended load. This suggests that the best approach for the regression analysis is to force the intercept to zero. This makes use of known information and reduces the effect of high relative uncertainty at low suspended loads. The forced intercept approach (Figure 3-B) is used consistently for all regressions in this analysis, but the results are always compared to the calculated intercept approach (Figure 3-A) to see if the conclusions change with the statistical model selected.

For the bottom sediment data, we plot total recoverable mercury against percent fines, and then calculate mercury concentration where the best fit line crosses the Y axis at 100%. This is slightly different than the approach to the water column data, because we are working in different media. In the case of sediments, we are looking at a data set and asking, "given the observed relationship between mercury in sediments and the percentage of fine material present, what is the inferred concentration of mercury in just the fine sediments?"

The underlying assumption is that all of the mercury in bottom sediments is stored in the fines, and none in the sandy material. This turns out to be a reasonable assumption for Bay sediments, but not necessarily in the watersheds. The reason the two cases are different is that the watersheds are truly dynamic, where as Bay sediments are at dynamic equilibrium. Large chunks of cinnabar rolling down the Guadalupe River watershed can substantially elevate mercury concentrations in coarse sediments. But large chunks tend to drop out in the depositional reaches of the lower watershed, where they are ground and weathered into smaller particles that are tidally mixed into the Bay. Within the Bay, mercury is constantly adsorbing to and desorbing from particles – the observed partition coefficient is a dynamic equilibrium. There is statistically a much greater chance that an adsorbing mercury atom will hit the surface of a fine particle that a coarse one, because of surface area to volume ratios. This could be demonstrated using a complex statistical mechanical approach, but it is far simpler to plot mercury concentrations vs. grain size and note that in the Bay, the concentration approaches zero as the percent fines approach zero.

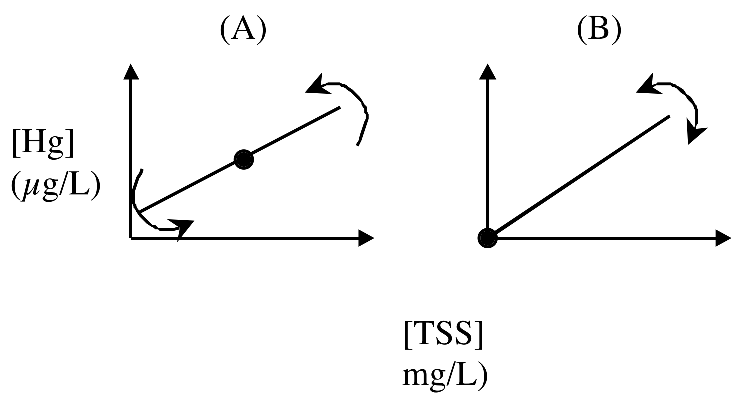

Figure 3: Regression analysis can either calculate the intercept, in which case the best fit line pivots around the centroid of the data (Case A) or force the intercept, in which case the best fit line pivots around the intercept (Case B).

As with the water column data, the regression analyses of bottom sediments consistently force the intercepts through zero, but compare the results to the unforced calculations to see if the conclusions change with the statistical model used. The basic calculations used to determine mercury concentrations in suspended and bottom sediments are compared in Figure 4.

Concentrations can be compared between media (suspended and bottom sediments) by making the assumption that suspended sediments are 100% fine (< 63 microns). This is a reasonable assumption, given that coarse sediments tend to rapidly drop out of suspension. Concentrations determined by this method can also be compared to historic concentrations measured in deep cores by the USGS. Sediments from those cores were sieved to less than 63 microns prior to analysis, so the measurements published by Hornberger et al (1999) reflect mercury concentrations in 100% fine sediments.

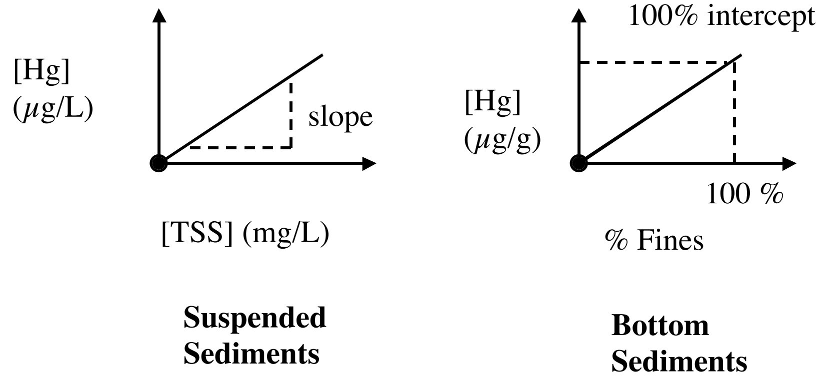

Figure 4: Comparison of regression approaches to determine mercury concentrations in suspended sediments and bottom sediments.

A.3 Data analysis: Segmentation of the Bay

The next step is to divide the Bay into segments in order to identify whether there are spatial gradients in the concentration of mercury in Bay sediments. The conceptual basis for segmenting the Bay is discussed in Appendix 2). For this discussion, the Bay is divided into four segments: Suisun Bay, San Pablo Bay, Central Bay, and South Bay. South Bay refers to the portion of the Bay between the Dumbarton Bridge and the Bay Bridge. Lower South Bay (south of the Dumbarton Bridge) is a unique environment. Because of the large concentration gradients observed in some contaminants, it is more appropriate for this anlaysis to regard Lower South Bay as an interfacial region between the South bay watersheds and the Bay, rather than a segment of the Bay. Data from Suisun Bay, San Pablo Bay are also combined to describe a segment called “the northern reach.” The nomenclature for RMP stations makes it possible to quickly sort a data set by station code and divide the data into segments (Table 5).

Segment	RMP Stations
South Bay	BA10, BA20, BA30, BA40, BB15, BB30
Central Bay	BB70, BC10, BC20, BC30, BC41, BC60
San Pablo Bay	BD15, BD20, BD30, BD40, BD50, BD60
Suisun Bay	BF10, BF20, BF30, BF40
Sacramento River	BG20
San Joaquin River	BG30

Table 5: Segmentation of the San Francisco Bay estuary by RMP station code.

The Sacramento River station (BG20) is used to make assessments about the concentrations of mercury entering the estuary from the Sacramento – San Joaquin River delta. Because this is a tidally mixed interface region, this assumption needs to be considered with some caution – some of the observed concentrations at BG20 are due to tidal mixing of fluvial sediments with sediments already in the estuary. This is an acknowledged uncertainty that is discussed in greater detail elsewhere (Memo-2). For this analysis, it is sufficient to state that BG20 gives us our best approximation for the concentration of mercury in sediments flushed into the Bay from the Delta.

The San Joaquin River station (BG30), while nominally in the San Joaquin River, doesn't necessarily reflect the nature of sediments entering the Bay from the San Joaquin river basin, because flows through the Delta are extremely complex in this region. BG30 appears to be a depositional region, because the sediments in this region typically have more fine material compared to BG20. This station has some unusual properties that raise some interesting questions about the concentration of mercury in sediments originating from the Delta, but those details are beyond the scope of this discussion.

Results

	South Bay	Central Bay	Northern Reach	San Pablo Bay	Suisun Bay	Sac River
(Forced intercept)						
Surface	0.48 +/- 0.02	0.34 +/- 0.01	0.26 +/- 0.01	0.26 +/- 0.01	0.26 +/- 0.01	0.21 +/- 0.01
Bottom	0.37 +/- 0.11	0.32 +/- 0.07	0.36 +/- 0.08	0.37 +/- 0.09	0.31 +/- 0.06	0.34 +/- 0.03
(Calculated Intercept)						
Surface	0.45 +/- 0.02	0.26 +/- 0.01	0.24 +/- 0.01	0.23 +/- 0.01	0.23 +/- 0.02	0.20 +/- 0.02
Bottom	0.34 +/- 0.10	0.30 +/- 0.07	0.35 +/- 0.08	0.36 +/- 0.09	0.31 +/- 0.06	0.30 +/- 0.03

Table 6: Summary of regression analyses of RMP from San Francisco Bay segments. Surface concentrations refer to the slope of the best fit line for a plot of total water column mercury vs. TSS. Bottom concentrations refer to the 100% intercept of the best fit line. Uncertainties show one standard error. All calculations were done using the LINEST function of Microsoft EXCEL.

Two general trends emerge from the data analysis (**Table 6**). First, mercury concentrations in surface sediments tend to increase as we move from the Sacramento River mouth, through the northern reach, and into Central and South Bay. This is true regardless of whether or not we do the regression calculations with a forced intercept. Second, mercury concentrations are higher in bottom sediments than in surface sediments in the northern reach, are roughly comparable in the Central Bay, and higher in the surface than at the bottom in the South Bay. This is also true regardless of whether or not the regression calculations force the intercept. *The observed north-south and surface-bottom gradients provide important clues about sediment transport and mercury loads to San Francisco Bay.*

The data from **Table 6** are combined and summarized in a conceptual model (**Figure 5**). One important clue that emerges from the conceptual model is that the concentration of mercury in sediments increases by about 0.1 mg/kg between the Delta and San Pablo Bay. This increased concentration can be used to put an upper limit on the internal loads of mercury to San Francisco Bay.

The top-bottom gradient probably reflects the different depositional environments of the northern and southern reaches. In the northern reach, a massive plug of mercury-laden sediment was deposited during and after the gold rush. That plug is being gradually exposed as the Bay seeks to attain its natural bathymetry. The South Bay isn't really erosional or depositional – sediments washed in from surrounding watersheds just slosh back and forth until they are tidally mixed out the Golden Gate. So the insult from the New Almaden mine isn't buried deep in the sediments of South Bay. Past and present mercury loads to South Bay are stored in the active layer, where they are continuously deposited, mixed with deeper, cleaner sediments, and then resuspended. This is most likely the reason that the top-bottom gradient is reversed in South Bay.

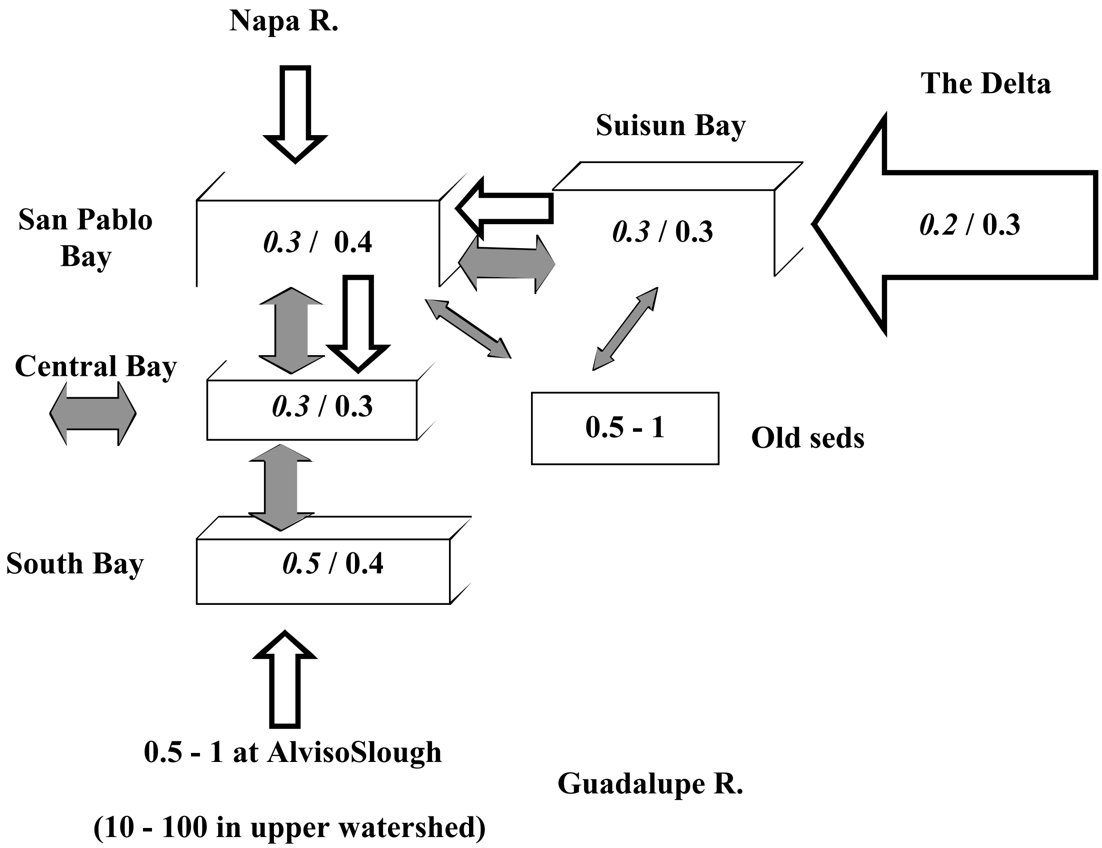

Figure 5: Conceptual model for sediment transport processes affecting the concentration of mercury in San Francisco Bay sediments. Single white arrows indicate advection, double dark arrows indicate mixing. Italicized numbers indicate suspended sediment concentrations, bold-faced numbers indicate bottom sediment concentrations.

Appendix B: Conceptual model for segmenting the Bay

Detailed analysis of Bay loads required breaking the Bay into segments. A good starting point is to consider the Bay as two distinct segments, the northern reach and South Bay, which are joined at Central Bay (Figure 6). This is conceptual model is warranted because the hydraulic and sediment transport processes are different in the northern reach compared to South Bay. In the northern reach, the dominant transport mechanism for sediments is river flow. Although tidal action is significant in the Delta, there is still a strong net tidal residual transport in the downstream direction up to the Carquinez straits. From San Pablo Bay to the Golden Gate, the dominant transport mechanism shifts to wind and tidal mixing. Sediment transport out of the South Bay is predominantly by wind and tidal mixing.

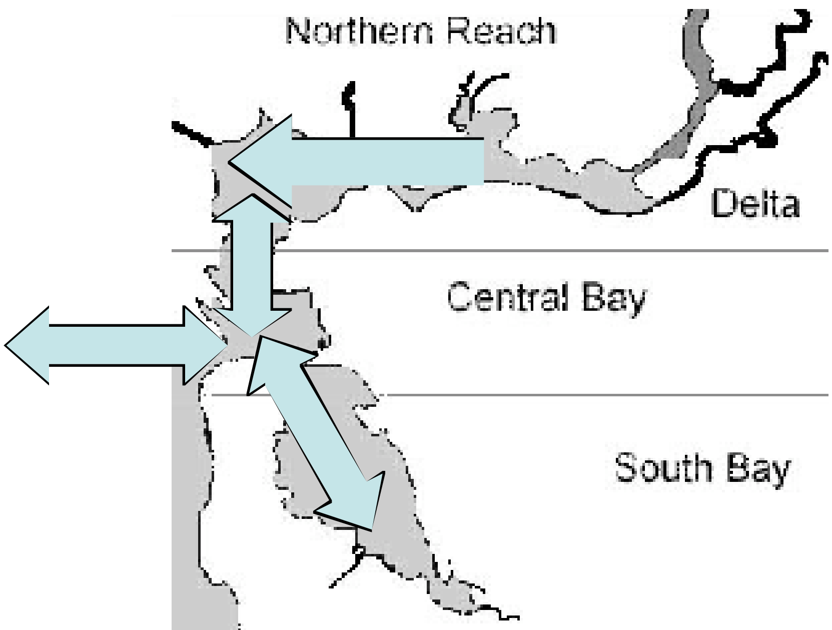

Figure 6: Conceptual model for sediment transport dynamics in the Bay, treated as a three-segment system. Single arrows indicate sediment transport that is predominantly advective, double arrows indicate sediment transport that is predominantly wind and tidal mixing.

In summary, the way the Bay works is that sediments are flushed in from the Central Valley, through the Delta, and into San Francisco Bay by predominantly advective forces. In the northern reach, sediments are deposited on the bottom, mixed with deeper sediments, and resuspended. Transport of sediments out of the northern reach is by tidal mixing. In the South Bay, transport is exclusively by wind and tidal mixing. This is an extremely simplified description of a complex superposition of processes, including seasonally variable freshwater outflow, spring-neap variability in suspended load inventories, mixed tidal and fluvial transport, and wind-driven mixing and circulation. These processes are the focus of ongoing research, all of which has been considered or relied upon to develop this simplified conceptual model (Schoellhamer, 1996 May 15), (Cappiella et al., ; Conomos, 1979; Conomos et al., 1985; Schoellhamer, 2001; Smith, 1987) [U.S. Environmental Protection Agency, April, 1996 #24; Walters, 1985 #25] (Cheng et al., 1993). Although it is a complicated subject, the essential points of the science needed to understand the generalized conceptual model for sediment transport, mixing and dynamics in the Bay illustrated in Figure 6 are captured by Figure 7 and Figure 8.

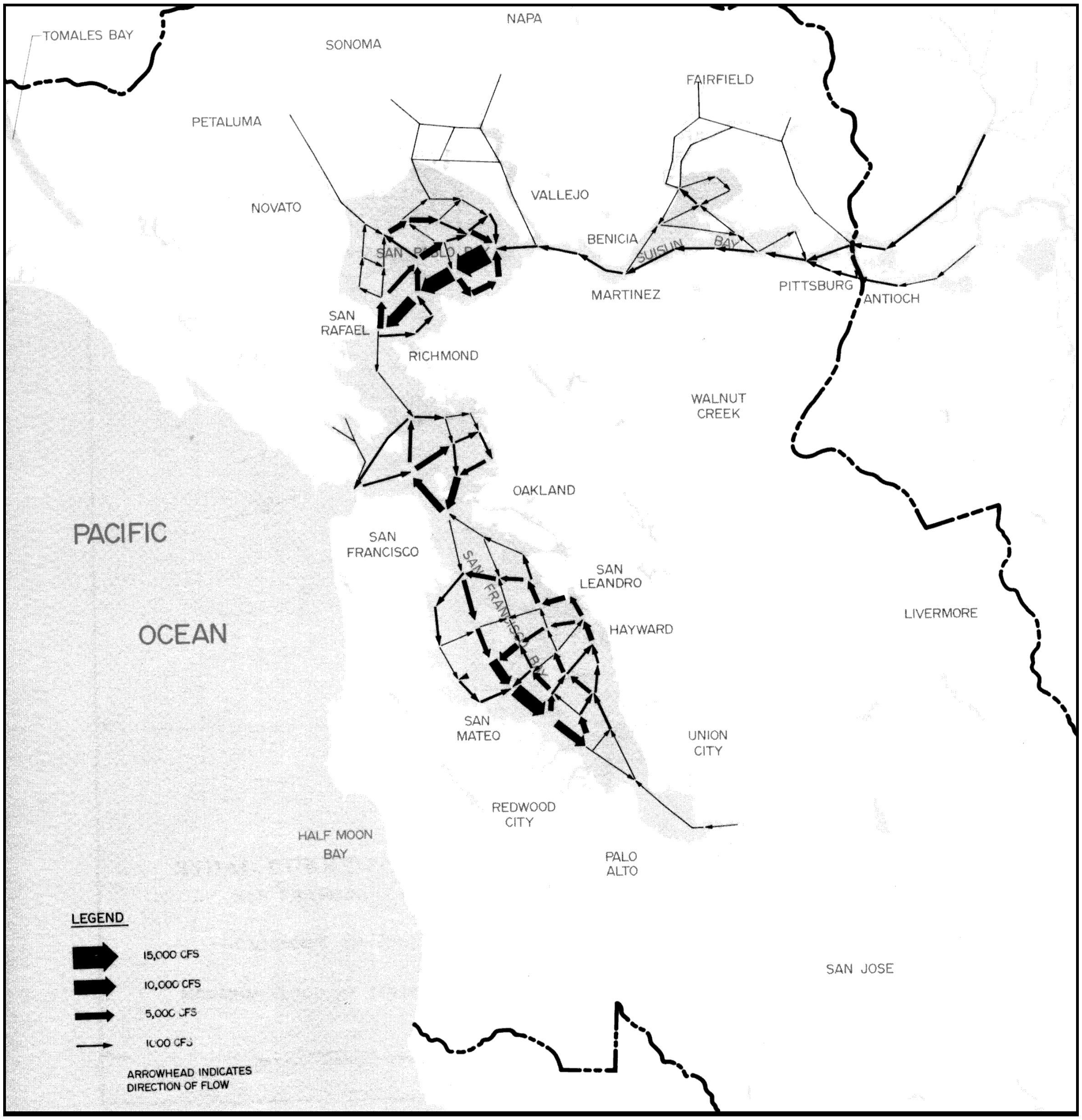

Figure 7: Flow and circulation of San Francisco Bay. Figure taken from (San Francisco Bay Regional Water Quality Control Board, 1975).

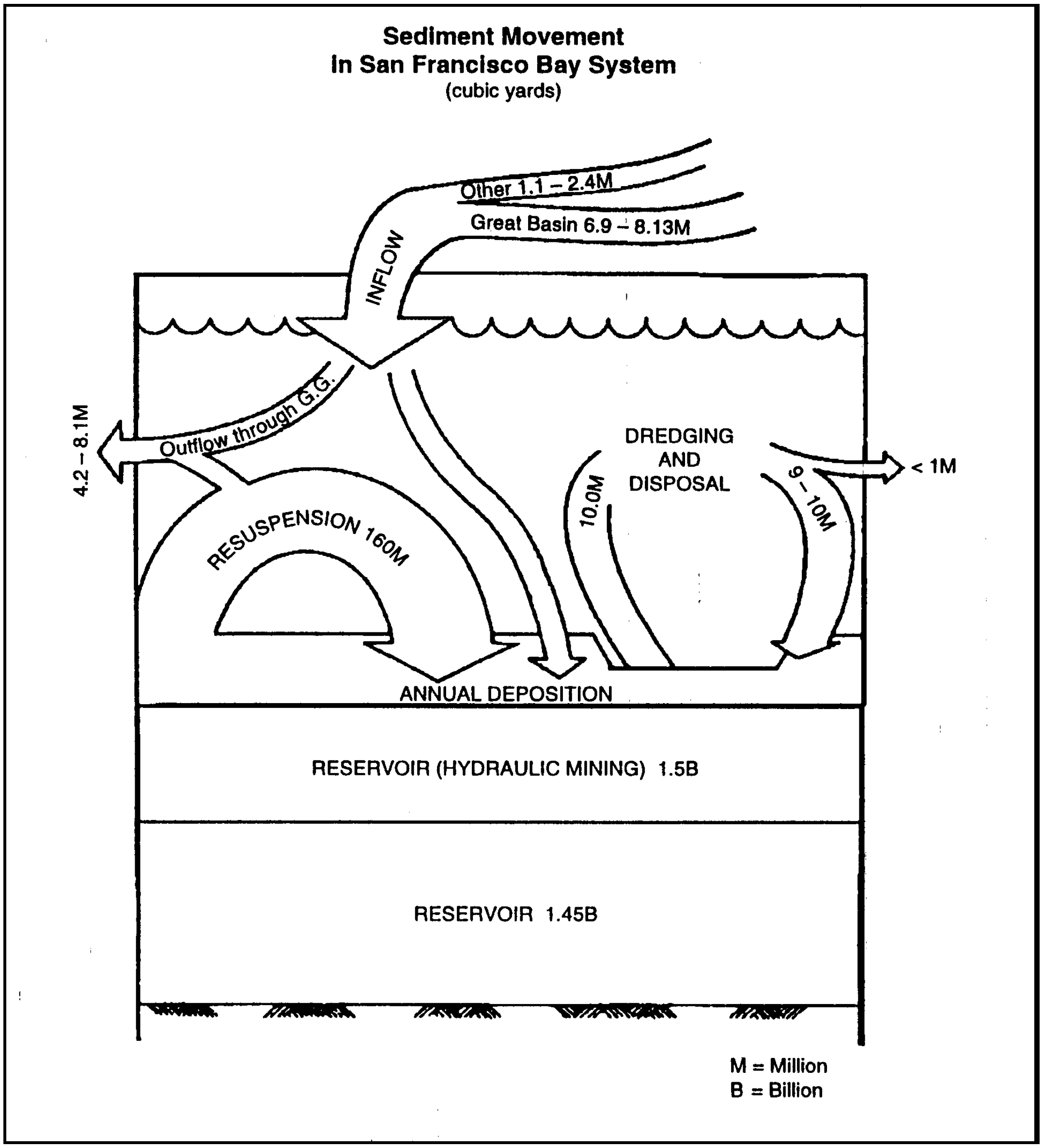

Figure 8: Annual sediment budget for San Francisco Bay. Figure taken from [U.S. Environmental Protection Agency, April, 1996 #24].

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