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MEMORANDUM

December 23th, 2002

To: Dyan Whyte, San Francisco Bay Regional Board
Khalil Abu-Saba, Applied Marine Sciences

From: Lester McKee, SFEI
Chris Foe, Central Valley Regional Board

Subject: Estimation of Total Mercury Fluxes Entering San Francisco Bay from the Sacramento and San Joaquin River Watersheds

Objectives

The objectives of this technical memo are threefold:

1. To use the Hg data collected by Region 5 at X2 in combination with the USGS Mallard Island sediment data to provide a preliminary estimate of the rate of mercury export from the Central Valley to San Francisco Bay
2. To make recommendations on future steps to improve loads analysis
3. To encourage closer cooperation between researchers and regulators in the Central Valley and Bay Area in conducting mercury research and developing control programs to solve a mutual contamination problem

Background

At the Regional Monitoring Program annual meeting (March 2002), Lester McKee presented a discussion of an analysis of sediment loads entering San Francisco Bay from the Central Valley (a collaborative work between SFEI and USGS, Sacramento). After seeing the oral presentation, Chris Foe of Region 5 approached Lester and suggested that the data that Region 5 had collected at X2 in the Delta could be applied to the sediment data set to better estimate Hg loads. After a quick review of the data Lester agreed and performed the analysis. The following memo is the product of that that interaction.

San Francisco Bay is listed on the Clean Water Act 303(d) list as an impaired water body for mercury (Hg). Several reports prepared by the Sources Pathways and Loading Workgroup (SPLWG) of the San Francisco Bay Regional Monitoring Program for Trace Substances (RMP) have concluded that the major contemporary allochthonous source of mercury (Hg) to San Francisco Bay is the Sacramento and San Joaquin drainages of the Central Valley (Davis et al 1999; 2000). In response to Hg concerns, the San Francisco Regional Water Quality Control Board (Region 2) initiated the preparation of a Hg TMDL (Abu-Saba and Tang, 2000). That report added further support to the relative importance of loads entering the Bay from the Central Valley compared to contributions from: 1. Direct wastewater inputs, 2. Atmospheric deposition, 3. Erosion and resuspension of legacy deposits largely derived from 19th century mining activities, and 4. Stormwater loads from local small urban drainages directly tributary to the Bay. However, it should also be recognized that management actions designed to reduce impairment and the response time of the system to those actions will be sensitive to the accuracy of estimates of loads in the present model. In particular, if loads from the Central Valley were estimated too high, efforts initiated by the Central Valley Regional Water Quality Control Board (Region 5) may not have the expected impact on the San Francisco Bay Hg budget.

In 1971 a human health advisory was issued for the Sacramento-San Joaquin Delta-Estuary advising pregnant women and children to not consume locally caught striped bass. The advisory, which is still in place, had led the State to include the freshwater side of the Estuary on its 303(d) list for mercury. Furthermore, the Central Valley Regional Board (Region 5) committed to the U.S. EPA to develop a Total Maximum Daily Load (TMDL) by June of 2003. A key element of a TMDL is the identification of sources and quantification of their loads. In 1999 CALFED awarded a multi year grant to Stephenson *et al*. to, estimate a methyl and total mercury mass balance budget for the freshwater side of the Estuary, among other things. To accomplish this, raw and filtered water samples were collected monthly (March 2000 to October 2001) from all the major riverine inputs and export sites from the Estuary for mercury and suspended sediment analysis. Samples were taken from X2[1] to estimate the export rate of mercury from the fresh to saltwater side of the Estuary. The details of this work can be found on the CALFED Mercury Project Website (http://loer.tamug.tamu.edu/calfed/) in a progress report (Foe, 2000, 2002).

In order to assist with development of TMDL strategies for Hg and other trace substances that are bound to sediment particles, the SPLWG conducted a literature review and analysis of existing data on loads of suspended sediment entering the Bay from the Central Valley (McKee et al, 2002). This reported concluded that data collected since 1994 by the USGS at Mallard Island (8 km downstream of the confluence of the Sacramento and San Joaquin Rivers) are suitable for estimation of suspended sediment loads. However, the report also concluded that existing data on particle-associated trace elements collected by the RMP <u>are not</u> sufficient for contaminant loads estimation. In

[1] By definition X2 is the location in the estuary with 2 ‰ salinity on the bottom. Its location is determined by the amount of freshwater outflow and strength of the tidal prism. Geographically, X2 ranged between Sherman Island and Martinez and was roughly centered in the CALFED study around Mallard Island.

response to these recommendations, the Technical Review Committee (TRC) of the RMP recommended that a study be conducted with the objective of collecting suitable data during floods at Mallard Island to improve estimates of loads of particle-associated trace substances. That 3-year study began in January 2002; however, preliminary results are not expected until 2003.

Available data and methods

Discharge

Given water circulation at the Mallard Island location is tidally influenced, the net (tidally-averaged) discharge cannot be gauged using standard hydrological techniques for riverine discharge such as the area-velocity method. Instead, the Department of Water Resources (DWR) estimates discharge at Mallard Island using the DAYFLOW model. As the term suggests, the DAYFLOW estimates have a time interval of one day, but do not include variation due to the spring-neap cycle. The data are available from the Interagency Ecological Program (IEP 2002) from 1956 to present. Delta outflow estimated using the DAYFLOW model is the longest running record of water discharge entering San Francisco Bay from the Delta.

USGS suspended sediment data

The suspended sediment concentration (SSC) data used in the development of this technical memo were collected at Mallard Island (Figure 1) from October 1st 1994 to September 30th 2000, a total of 6 water years (Buchanan and Schoellhamer 1996, 1998, 1999; Buchanan and Ruhl 2000, 2001, Buchanan and Ganju 2002). The channel depth at the Mallard Island gauge is approximately 7.6 m, the adjacent shipping channel has a depth of about 17 m and the tidal range averages 1.25 m. About 25 % of the days had no data record because of vandalism or malfunction. The data were collected 1 m below the water surface using an optical back scatter (OBS) instrument calibrated with water samples collected at the same point and analyzed in a laboratory for SSC (e.g., Buchanan and Ruhl 2000). Data were also collected at 2 m above the base of the channel at Mallard Island, however, the surface data are the most continuous and are likely to be the most representative of average water column concentrations (David Schoellhamer, USGS, unpublished observation).

Sediment loads analysis

Analysis of sediment loads for the water years (WYs) 1995, 1996, 1997, and 1998 was conducted previously (McKee et al., 2002). Freshwater advective loads were estimated by combining Delta outflow with daily average suspended sediment concentration. Errors associated with this calculation were determined to be ±17%. Tidally driven advective and dispersive fluxes were estimated using velocity data and SSC data collected by the USGS during 1994 and 1996. Estimate of tidally driven fluxes were used to adjust the freshwater advective loads estimates. If tidal processes had not been taken into account, total loads would have been over estimated by an average of

14% per year during WYs 1995 to 1998. For details of the methods and results, the reader is referred to McKee et al. (2002) or principal authors Lester McKee (lester@sfei.org), Neil Ganju (nganju@usgs.gov), or Dave Schoellhamer (dschoell@usgs.gov). In addition, the suspended sediment loads presented in McKee et al. (2002), this memo also presents suspended sediment loads information for WY 1999 and 2000 that was calculated using the same methods as described by McKee et al. (2002) and presented by McKee at the RMP SPLWG meeting (August 2002).

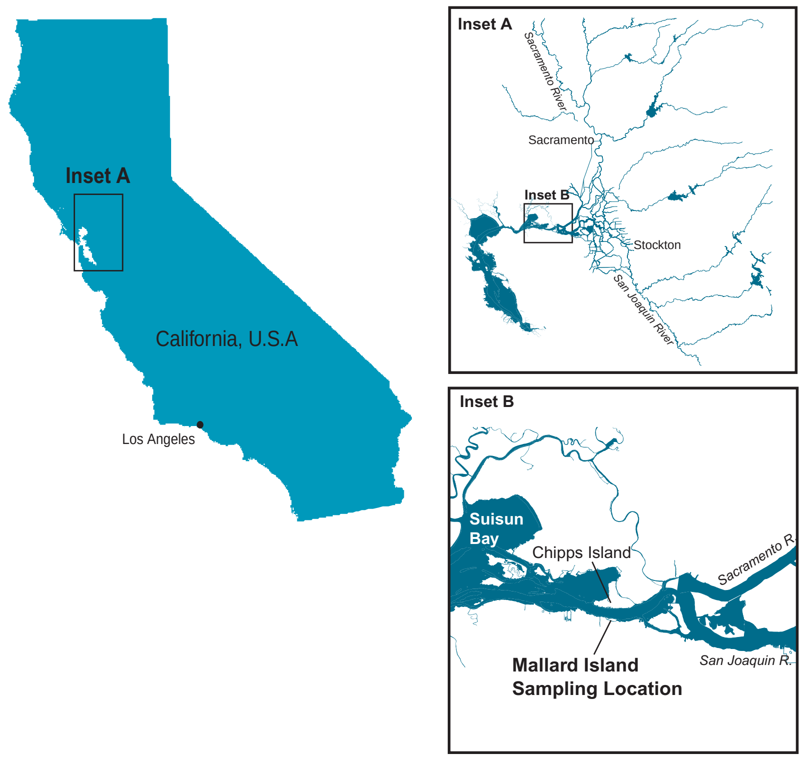

Figure 1. Map of the Delta showing the Mallard Island sampling location.

Region 5 TSS and Hg data

Water samples at X2 were collected by boat from mid channel on a monthly basis from March 2000 to October 2001. The site was located by finding surface salinity of about 0.5‰ and then repeatedly taking bottom samples until the 2‰ salinity zone was located. Briefly, each water sample was collected using clean hands techniques in acid washed double bagged 4-liter amber glass bottles that had previously been rinsed three times in ambient water. The samples were collected by lowering the sampling bailer to within several feet of the bottom and slowly pulling it back to the surface. Samples were placed on ice and aliquots subsequently decanted from the same bottle for total suspended solids, raw and filtered mercury after vigorous shaking. All samples were filtered within 8 hours of collection. Inorganic mercury analysis was done by the California Department of Fish and Game at Moss Landing using EPA method 1631. Laboratory blanks, duplicates and spikes were prepared and analyzed, and field blanks and replicates were collected, with the results reported in Foe (2000).

Particulate Hg load estimates

Given that the Hg and TSS data do not coincide with USGS SSC data, and that Hg data are scarce in comparison to the length of record for SSC, the following steps were followed to interpolate Hg loads from existing data:

Step 1. Determine particulate Hg (Hg_p) concentration (ng/L) by subtracting the dissolved fraction from total Hg.
Step 2. Develop a regression relationship between TSS and Hg_p
Step 3. Assume TSS and SSC are equivalent
Step 4. Use time continuous daily averaged SSC data (or estimates based on interpolation when data is missing) (McKee et al. 2002) to estimate daily Hg_p concentration.
Step 5. Combine estimated daily Hg_p concentration (ng/L) with daily Delta outflow (Mm^3) to estimate daily fluvial advective Hg_p load (kg).
Step 6. Correct daily advective Hg_p load for the effects of tidal advection and dispersion assuming the bias is the same as that estimated for suspended sediment loads (McKee et al. 2002)
Step 7. Errors are estimated using the same method as outlined in McKee et al. (2002) with the addition of an error for laboratory analysis of total Hg and dissolved Hg (±10%) and an error for the regression relationship between TSS and Hg_p (±2.5%) giving a total error of ±22%.

Results

Hg_p varies proportionally to TSS in the water column (Figure 2). The scatter about the regression line is similar throughout the range of TSS suggesting the model is valid as a means of predicting Hg_p when suspended sediment data are available. Using this regression model and daily average estimates of SSC (McKee et al. 2002), Hg_p concentration was estimated for the period October 1st 1994 to September 30th 2000 (6 water years). Daily average Hg_p estimated thus varied from 1.8 ng/l to 99.9 ng/l. The flow weighted mean concentration for that period was estimated to be 13.2 ng/l. Daily loads ranged from <1 kg to 65 kg. Annual loads varied from 162±36 kg to 701±154 kg and averaged 435±96 kg for the 6-year period (Table 1). On average, 46% of the total annual Hg_p load was transported in the highest 30-day period and on average 88% was transported during the period December to May. Note that, 13.5% of the total 6-year Hg_p load was transported during the first 15 days of January 1997 when a large flood passed though the Delta.

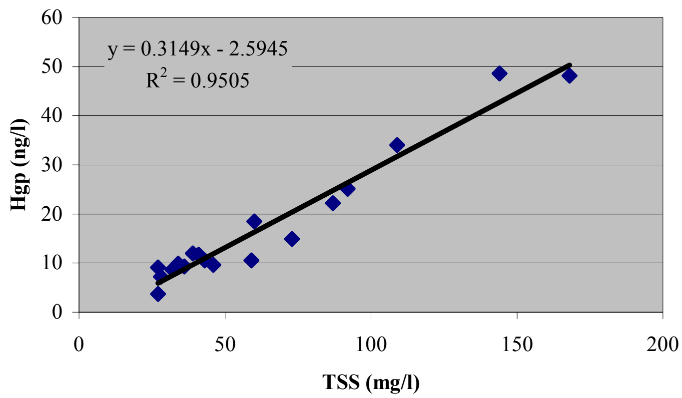

Figure 2. Regression relationship developed between TSS and Hg_p using data collected a X2 by Region 5 on a monthly basis between March 2000 and October 2001.

Table 1. Annual suspended sediment (million metric tonnes) and Hg_p loads (kilograms) estimated for the WYs 1995 to 2000.

Water year	Suspended sediment (Mt)	Particulate Hg (kg)
1995	2.6±0.4	701±154
1996	1.0±0.2	253±55
1997	2.2±0.4	612±134
1998	2.4±0.4	644±141
1999	1.0±0.2	238±52
2000	0.7±0.1	162±36
6-year average	1.6±0.3	435±96

Discussion

TSS and SSC data

There has been discussion on the differences between the TSS laboratory methodology and its reliability and comparability to the SSC methodology (Gray et al., 2000). The SSC methodology demands that an entire sample be analyzed in the laboratory for weight of sediment within a known volume. The TSS methodology differs in that it allows for a sub-sample of measured volume to be analyzed for weight of sediment. Volumes may differ between samples and practices of sub-sampling may differ between laboratories. The greatest difficulty associated with the sub-sampling process is ensuring a representative sample given the difficulty of agitating the whole sample in a way that ensures homogeneity of dispersion of sediment particles and keeping the particles in suspension while pipetting or decanting a sub-sample. Is should also be noted that sub-sampling during field data collection will lead to the same problems as sub-sampling in the lab. Gray et al. (2000) concluded that the TSS methodology when used for analysis of natural waters is unreliable and biased low. The bias tends to increase when particles in the sample are more than 25% sand sized. As such, Gray et al. (2000) recommended the use of the SSC methodology so that reliable and consistent data may be attained between sampling events and between different natural systems.

In practice, however, although laboratories quote TSS, they often actually carry out the analysis without sub-sampling especially if they are given a separate sample attained during field collection that is specifically collected for suspended sediment analysis. In addition, during the winter of 1996, the USGS measured particle sizes in floodwaters at Mallard Island. The D50 particle size (median particle size) by volume in the water column was about 5 to 6 microns diameter with the exception of a very large flow peak (500,000 cfs) in early January when the D50 particle size increased to 8 to 12 microns for about one day (David Schoellhamer, USGS personal communication Jan 2002). Given that these particle sizes are much finer than 63 microns (the sand size fraction cutoff) it seems likely that even if sub-samples were taken in the laboratory, the TSS data may be comparable with the SSC data that the USGS collects at Mallard Island (upon which the analysis of sediment loads are based).

Hg_p model space and predictions for larger events

Data collection at X2 by the Region 5 Regional Water Quality Control Board was conducted during a period of relatively low flow (Figure 3). Flow during the 2001 WY (8,605 Mm^3) was much less than the average for the past 10 years (27,474 $Mm^3\ y^{-1}$). Total suspended solids concentrations collected at X2 were between 27 mg l^{-1} and 168 mg l^{-1}. During WYs 1995 to 2000, SSC estimated using OBS sensors by the USGS at Mallard Island ranged between 5 mg l^{-1} and 420 mg l^{-1}. Therefore the calibration space of the regression model developed using the Region 5 data (Figure 2) was less than the range of sediment concentration and flow variability occurring at Mallard Island. The current model makes the assumption that Hg concentrations on particles (slope of equation in Figure 2) will remain constant under all conditions. If this is not true and sediment mercury concentrations change, then the load estimates will also change accordingly.

Results for the present CALFED study (Region 5) suggest that the mercury content of sediment entering the freshwater side of the Estuary is lower than that exported at X2 (0.2 versus 0.3 ppm Hg/TSS). The primary cause of this appears to be that the freshwater side of the Estuary is exporting more inorganic mercury than it is importing. Whether or not this phenomenon is caused by the low freshwater outflow conditions that occurred during the CALFED study is not known. Regardless, the phenomenon cannot continue indefinitely and when it changes the slope of the regression is likely to also change.

The CALFED mercury mass load study was funded for an additional two years. Staff from Region 5 recommend that mercury researchers from the Central Valley and Bay area coordinate their studies in the future to insure we agree on the load estimates and develop a more holistic understanding of mercury transport and cycling in the Estuary.

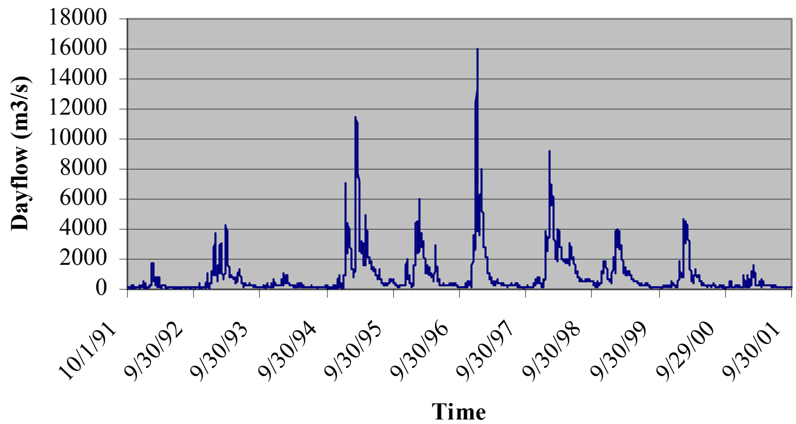

Figure 3. Delta outflow for water year 1992 to water year 2001.

The SPLWG just began a study that has the objective of improving estimates of particle related contaminants entering San Francisco Bay from the Central Valley. The methodology builds upon the work of McKee et al. (2002) and is funded for three years. Water samples will be collected at the DWR sampling location at Mallard Island during floods to determine the concentration of Hg, trace metals, legacy pesticides, PAHs and PCBs in the water column. These will then be combined with continuous SSC estimates and Delta outflow to determine loads. Preliminary results are not expected until the late summer of 2003.

Conclusion and recommendations

The majority of loads of sediment and related pollutants are transported from the Central Valley to San Francisco Bay during large floods that occur relatively infrequently. Given the lack of data during flood flow and therefore the lack of understanding of how the relationships between sediment, Hg, and discharge might change at high flow, the estimates provided here should be seen as a hypothesis. We expect the SPLWG will present revised estimates over the next three years and we hope this memo is the beginning of an improved collaborative relationship between partners upstream and downstream of Mallard Island.

We make the following recommendations:

1. That groups in the Bay Area encourage laboratories to follow USGS recommendations and carry out analysis of suspended sediment in water without sub-sampling either in the field or in the laboratory

2. That mercury researchers in the Central Valley and Bay area coordinate their work in the future to insure agreement on load estimates and develop a more holistic understanding of mercury transport in the Estuary

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