San Francisco Estuary Regional Monitoring Program for Trace Substances

Concentrations and Loads of Organic Contaminants and Mercury associated with Suspended Sediment Discharged to San Francisco Bay from the Sacramento-San Joaquin River Delta, California

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EXECUTIVE SUMMARY

Polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and mercury are of current environmental concern in San Francisco Bay due to their persistence in the environment and their potentially adverse effects on wildlife and human health. Concentrations of these contaminants are high enough in Bay sport fish to warrant the issuance of an interim consumption advisory for fish caught in the Bay. Consistent with this advisory, all segments of the Bay are listed as impaired on the Clean Water Act 303(d) list for PCBs, mercury, and the OC pesticides, DDT, chlordanes, and dieldrin. In addition, PAHs are currently on a regulatory watch list of compounds that require further study to determine their impact on beneficial uses of the Bay.

These contaminants have been distributed throughout the Sacramento and San Joaquin River watersheds through long-term human disturbances involving agriculture and expanding urbanization in the Central Valley, as well as historic mercury, gold, and silver mining in the Sierra Nevada and Coast Range Mountains. The large magnitude of sediment and runoff entering the Bay from the Rivers makes their combined input an important transport pathway of contaminants to the Bay. The annual mass loadings of contaminants entering the Bay from the Rivers have important implications in understanding the long-term fate of persistent contaminants and the necessary steps towards managing and improving water quality. However, there are large uncertainties associated with current estimates of contaminant fluxes between the Rivers and the Bay. This study was implemented through the Regional Monitoring Program for Trace Substances (RMP) to assess the influence of water and sediment runoff processes on concentrations and loads of PCBs, OC pesticides, PAHs, and mercury entering the Bay via the Sacramento-San Joaquin River Delta.

Suspended sediment is an important vector of transport for particle-associated contaminants entering San Francisco Bay. Since February 1994, USGS has collected time-continuous turbidity and suspended-sediment concentration (SSC) data at Mallard Island, located approximately 8 km downstream of the confluence of the Sacramento and San Joaquin Rivers. Turbidity data were collected every 15 minutes using an optical backscatterance (OBS) instrument located 1 m below the water surface and calibrated with discrete water samples collected and analyzed for SSC. The continuous SSC data from WY 1995 to WY 2003 were used to develop a methodology for estimating loads of suspended sediment and particle-associated contaminants from the Rivers and improving our understanding of hydrological and sediment transport processes influencing contaminant transport. Daily fluvial advective sediment loads were estimated by combining estimated Delta outflow with daily averaged SSC and correcting for dispersive fluxes due to tidal action. Annual suspended-sediment loads over the nine-year period at Mallard Island averaged 1.2± 0.4 Mt (million metric tonnes) and varied from 0.26±0.08 Mt in WY 2001 to 2.6±0.8 Mt in WY 1995. Given that the average water discharge for the 1995-03 period was greater than the average discharge for the last decade, it seems likely that the average suspended-sediment load may be less than 1.2± 0.4 Mt SSC. Annual loads of SSC for WY 2002 and WY 2003 were 0.31±0.09 and 0.55±0.18 Mt, respectively, which were less than half the long-term annual average SSC load.

From January 10, 2002 to May 6, 2003, 24 discrete water samples were collected for analyses of organic contaminants during and after major storm events. Organic contaminant concentrations ranged from 200 to 6,700 pg/L of ΣPCBs, 240 to 1,600 pg/L of Σ DDT, 40 to 180 pg/L of ΣChlordanes, 60 to 250 pg/L of dieldrin, and 12 to 36 ng/L ΣPAHs. Pesticide concentrations were significantly correlated to SSC and displayed a first flush effect consistent

with that found for sediment. In contrast, ΣPCB and ΣPAH concentrations were influenced to a greater extent by tidal variation and potential urban inputs from localized or episodic sources. The relative abundances of individual PCB, DDT, and PAH compounds (or congeners) provided information on potential sources of organic contaminants and sediment sampled at Mallard Island. Total PCBs were comprised predominantly of low-molecular weight congeners and indicated potential PCB sources from either a more localized source of low-molecular weight Aroclors (e.g. 1026 or 1242) or an influence of atmospherically-derived PCBs. Ratios of different ΣDDT compounds showed that proportions of DDT and DDE (o,p' and p,p'-isomers), a major aerobic breakdown product of DDT, increased with increasing SSC and discharge, whereas proportions of DDD, an anaerobic breakdown product, decreased. This pattern presumably results from greater contributions of eroded watershed soils with increasingly fresh inputs of DDT residues in samples collected during higher flows at Mallard Island. Ratios of PAH compounds indicated a potentially large contribution of PAHs from unburned petroleum sources to Mallard Island sources, along with the expected contributions of PAHs from combustion.

Organic contaminant mass loads were estimated over the study period using available flow information for the Sacramento-San Joaquin Delta and time-continuous SSC data collected at Mallard Island. Correlations between SSC and pesticide concentrations were used to estimate daily concentrations and loads of these contaminants. ΣPCB and ΣPAH loads were estimated based on flow-weighted mean concentrations and flow. Daily contaminant loads varied by one to three orders of magnitude ΣPCBs (1.6 to 550 g), ΣPAHs (58 to 5,200 g), ΣDDT (1.4 to 150 g), ΣChlordanes (0.22 to 22 g), and dieldrin (0.37 to 56 g). Annual loads for WY 2002 and WY 2003 respectively were 6.0 ± 2.0 and 23 ± 18 kg ΣPCBs, 230 ± 60 and 350 ± 90 kg ΣPAHs, 6.0 ± 2.3 and 9.7 ± 3.7 kg ΣDDT, 0.93 ± 0.36 and 1.5 ± 0.57 kg ΣChlordanes, and 1.8 ± 0.8 and 3.0 ± 1.3 kg Σdieldrin. Extrapolation of pesticide data from WY 2002 and WY 2003 over a nine year period using SSC data (WY 1995 to WY 2003) resulted in long-term average annual loads of 18±7.0 kg ΣDDT, 2.7±1.0 ΣChlordanes, and 6.2±2.7 kg dieldrin.

In addition to organic contaminants, total Hg (Hg_T) was measured in 30 water samples collected in WYs 2002 and 2003. Hg_T concentrations ranged from 4 to 14 ng/L, whereas dissolved Hg (Hg_{TF}) concentrations in seven samples ranged from 0.8 to 1.6 ng/L. Despite Hg_{TF} concentrations making up between 11-24% of the Hg_T concentrations a linear relationship was observed between instantaneous SSC and Hg_T. As with SSC and pesticide concentrations, Hg_T concentrations displayed a first flush effect from the Delta and a tidal influence from the Bay. The linear relationship between SSC and Hg_T allowed for estimation of daily average Hg_T concentrations and daily contaminant loads that varied from 3 to 1,803 g Hg_T. Annual loads for WY 2002 and WY 2003 respectively were 58±20 and 97±33 kg for Hg_T. Extrapolation of mercury data from WY 2002 and WY 2003 over a nine year period using SSC data (WY 1995 to WY 2003) resulted in long-term average annual loads of 201±68 kg Hg_T.

Contaminant and sediment monitoring in this study occurred during flow years with relatively low annual discharge and relatively small floods (< 2 year return interval). Estimates of mercury and pesticide for WY 2002 and WY 2003 were considered to be reliable; however, long term estimates of those loads based on suspended sediment data (WY 1995-2003) and daily discharge data were confounded by a lack of understanding of flood characteristics at discharge beyond 2,600 m^3/s. Given that the Sacramento River at Mallard Island is capable of a daily discharge in excess of 16,000 m^3/s (e.g., WY 1997), there still are serious gaps in our understanding of the riverine flux of particle-associated contaminants to San Francisco Bay. Filling these data gaps is the topic of further study at Mallard Island.

SECTION TWO

1. INTRODUCTION

1.1 INTRODUCTION

San Francisco Bay, a shallow estuarine system on the north coast of California is listed as impaired for mercury (Hg), polychlorinated biphenyls (PCBs), and organochlorine (OC) pesticides on the Clean Water Act 303(d) list. These substances are toxic to fish, wildlife, and humans and bioaccumulate and biomagnify in the foodchain. They are transported into the Bay attached to sediment particles and persist in bed sediments within the Bay for long periods. The Bay receives 96% of its freshwater and >50% of its sediment supply from the Sacramento and San Joaquin Rivers (the Rivers) (McKee *et al.* 2003), which drain approximately 40% of the watershed surface area of California (Conomos *et al.* 1985). The large magnitude of sediment and runoff entering the Bay from the Rivers makes their combined input an important transport pathway of particle-associated contaminants: mercury, PCBs, OC pesticides, such as DDT, chlordanes, and dieldrin, and polycyclic aromatic hydrocarbons (PAHs) (Davis *et al.* 2000, Davis *et al.* 2001, Bergamaschi *et al.* 2001, Domagalski and Kuivila 1993, McKee and Foe 2002). These contaminants have been distributed throughout the Sacramento and San Joaquin River watersheds through long-term human disturbances involving agriculture and expanding urbanization in the Central Valley, as well as historic mining in the Sierra Nevada and Coast Range Mountains (Gilliom and Clifton 1990, Brown 1999, Pereira *et al.* 1996, Kratzer 1999, Domagalski 1998, Alpers and Hunerlach 2000).

The annual mass loading of contaminants entering the Bay from the Rivers have important implications in understanding the long-term fate of persistent contaminants (Davis 2004, Greenfield and Davis 2004, Leatherbarrow *et al.* 2003) and the necessary steps towards managing and improving water quality. In particular, the San Francisco Bay Regional Water Quality Control Board (Regional Board) has identified contaminant inputs from the Rivers as an essential factor in developing Total Maximum Daily Load (TMDL) plans for managing mercury and PCBs (Johnson and Looker 2003, Hetzel 2004). However, there are large uncertainties associated with current estimates of contaminant fluxes between the Rivers and the Bay (Davis *et al.* 2000, McKee and Foe 2002). This is due to limited availability of data appropriate for characterizing the episodic nature of contaminant fluxes from the Rivers.

In 2001, the San Francisco Estuary Regional Monitoring Program (RMP) for Trace Substances initiated this study to address the major data gap in our knowledge of contaminant loads to the Bay from the Sacramento and San Joaquin Rivers. The three-year study had the following objectives:

- Estimate the magnitudes of fluxes between the Sacramento/San Joaquin River Delta and San Francisco Bay.
- Improve our understanding of the influences of hydrology and sediment dynamics on contaminant transport processes.
- Assist in developing and refining mass budget models and TMDLs.

To fulfill these objectives, the study was conducted downstream of the confluence of the Rivers in the northeast region of the Estuary at a location called Mallard Island (Figure 2.1). This progress report summarizes the first two years of data (of a three-year study) collected in WY 2002 and WY 2003. The report is organized to discuss methods and results of data collection for suspended sediment (Section 2), organic contaminants, including PCBs, OC pesticides, and PAHs (Section 3), and mercury (Section 4). A final report summarizing all three years is planned for completion in 2005.

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SECTION TWO

2. SUSPENDED SEDIMENT

L.J. McKee, D.H. Schoellhamer, and N.K. Ganju

2.1 ABSTRACT

This study demonstrates the use of suspended-sediment concentration (SSC) data collected at Mallard Island as a means of determining suspended-sediment load entering San Francisco Bay from the Sacramento and San Joaquin River watersheds. Optical backscatter (OBS) data were collected every 15 minutes during water years (WYs) 1995 to 2003 and converted to SSC. Daily fluvial advective sediment load was estimated by combining estimated Delta outflow with daily averaged SSC. On days when no data were available, SSC was estimated using linear interpolation. A model was developed to estimate the landward dispersive load using velocity and SSC data collected during WYs 1994 and 1996. The advective and dispersive loads were summed to estimate the total load.

Annual suspended-sediment load at Mallard Island varied from 0.26±0.08 Mt (million metric tonnes) in WY 2001 to 2.6±0.8 Mt in WY 1995 and averaged 1.2± 0.4 Mt over the nine-year period from WY 1995 to WY 2003. Given that the average water discharge for the 1995-03 period was greater than the average discharge for the last decade, it seems likely that the average suspended-sediment load may be less than 1.2± 0.4 Mt. Average landward dispersive load was 0.24 Mt/yr, 20 percent of the total. On average during the wet season, 88 percent of the annual suspended-sediment load was discharged through the Delta and 43 percent occurred during the wettest 30-day period. The January 1997 flood transported 1.2 Mt of suspended sediment or about 11 percent of the total 9-year load (10.9 Mt).

The average load calculated for Mallard Island was less than previous estimates by a factor of three, supporting previous studies that indicated a decreasing trend of sediment load on the Sacramento River. Decreasing suspended-sediment loads may increase erosion in the Bay, help to cause remobilization of buried contaminants, and reduce the supply of sediment for restoration projects.

2.2 INTRODUCTION

An understanding of suspended sediment supply to the San Francisco Bay system is of paramount importance for the maintenance of a plethora of human and environmental needs and for predicting geomorphic evolution under varying future climatic and human perturbations. San Francisco Bay is listed by the State of California as contaminated for mercury (Hg), polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides in compliance with Section 303(d) of the Clean Water Act. The California Office of Environmental Health Hazard Assessment has issued an interim heath advisory directed at those who consume fish caught in the Bay (OEHHA, 1994, 1997, 1999). Mercury, PCBs and OC pesticides are transported into the Bay attached to suspended sediment particles (e.g. Davis, in press; Leatherbarrow and McKee, 2004) and are harmful to aquatic life and humans because of the way they bio-accumulate and bio-magnify in the food chain (Davis et al. 2003). Similar to other coastal areas used for portage (e.g. Eyre et al. 1998), sediment itself constitutes a barrier to local shipping in San Francisco Bay and from 1995-2002 an average of 3.1 Mm^3/yr of bottom material was dredged. However, sediment dispersal and deposition during winter storms and reuse of dredged sediment also provide a useful resource for restoring wetland habitats in the Bay-Delta area and there is concern that future climatic and human perturbations may restrict restoration opportunities (eg. Williams 2001; Williams and Orr 2002).

In order to address questions on sediment transport in the Bay and its tributaries, a number of studies have focused on 19th and 20th century sediment loads (Gilbert 1917; Porterfield 1980; Goodwin and Denton 1991; Kondolf 2000; Wright and Schoellhamer 2004), tidal and wind-wave driven resuspension (Krone 1979; Schoellhamer 1997; Jennings *et al.* 1997; Ruhl and Schoellhamer 2004), erosion in various Bay compartments (Jaffe et al. 1998; Capiella et al. 1999; Foxgrover et al. 2004), and sediment budgets for the Bay (Ogden Beeman & Associates Inc. 1992; Krone 1996). Several studies have suggested that sediment loads may be decreasing over time (Krone 1979; Wright and Schoellhamer 2004) but there has been no recent quantification of the magnitude of current sediment loads entering the Bay, yet many issues important to the Bay Area community such as shipping, recreational and commercial fishing, habitat restoration, human health and environmental water quality are reliant on an understanding of sediment supply. San Francisco Bay is bounded on its upstream end by a large river delta that spans an area of about 3,000 km^2 and incorporates thousands of kilometers of waterways and levees. Thus the upstream boundary of the Bay is tidal and slightly saline. The difficultly in measuring sediment load in a tidal cross-section in which both advective and dispersive forces operate (Schoellhamer and Burau 1998) and where cycles of deposition and resuspension can occur (Jennings *et al.* 1997) are some of the reasons for the gap in critical knowledge about recent sediment loads.

In this study we demonstrate an innovative method for quantification of advective and dispersive loads in a tidal cross-section and make estimates of daily and annual sediment loads entering San Francisco Bay. This information will radically change previous perceptions of the sediment budget for the Bay, provide a valuable tool for estimating trace contaminant loads, and make a further contribution to the state of knowledge of sediment transport from large river basins to active continental margins.

2.3 MATERIALS AND METHODS

2.3.1 Physical Description

Mallard Island (Figure 2.1) was chosen as the location for study because it represents the upper end member of San Francisco Bay and because it is the location of long term monitoring by the California Department of Water Resources (DWR). The channel adjacent to Mallard Island conveys runoff from 154,000 km^2 [>37 percent of the land area of California (411,000 km^2)]. The channel depth at the Mallard Island gage is approximately 7.6 m, while the adjacent shipping channel has a depth of about 17 m, the total channel width is approximately 940 m and the location has an average tidal range (DWR unpublished data) of 1.25 m (mean lower low water to mean higher high water). Tides at Mallard Island are mixed semi-diurnal (Figure 2.2). Mallard Island is approximately 8 km downstream of the confluence of the Sacramento and San Joaquin Rivers. Upstream from the sampling location, the channel broadens into a complex system of sloughs, modified channels, and reclaimed islands many of which are productive farming lands that together make up the Sacramento-San Joaquin River Delta. There are two deepwater channels that connect the city of Stockton on the San Joaquin River and state capital of Sacramento on the Sacramento River to the Bay for shipping purposes. In addition, during high flows, floodwaters are diverted north of Sacramento through the Yolo Bypass. Discharge at Mallard Island is influenced by numerous reservoirs further upstream that are managed for flood control, water supply, and environmental flows. This manipulated plumbing system is the conduit for water and sediment between the Sierra Nevada, Central Valley, and San Francisco Bay.

2.3.2 Suspended-sediment Data

SSC data were collected at Mallard Island from February 9, 1994, to September 30, 2003 (3,521 days) (Buchanan and Schoellhamer, 1996, 1998, 1999; Buchanan and Ruhl, 2000, 2001; Buchanan and Ganju, 2002, 2003; USGS unpublished data [WY 2002 and WY 2003]). Data were collected every 15 minutes, giving as many as 96 data points per day. The data were collected 1 m below the water surface using an OBS instrument calibrated with discrete water samples collected and analyzed for SSC (e.g., Buchanan and Ruhl, 2000). Data also were collected at 2 m above the base of the channel but these were not analyzed in detail here because the surface data are more complete. As a result of equipment malfunction, biological fouling, and vandalism, 900 days, or 26 percent of the potential days on record, retained no data even at the upper sensor. There has been critical discussion on the differences between "suspended-sediment concentrations (SSC)" and "total suspended solid concentrations (TSS)" (Gray *et al.*, 2000). The collection of water samples, the analysis of sediment in suspension, and use of the term "SSC" in this report conforms to the methods outlined in Buchanan and Ruhl (2000).

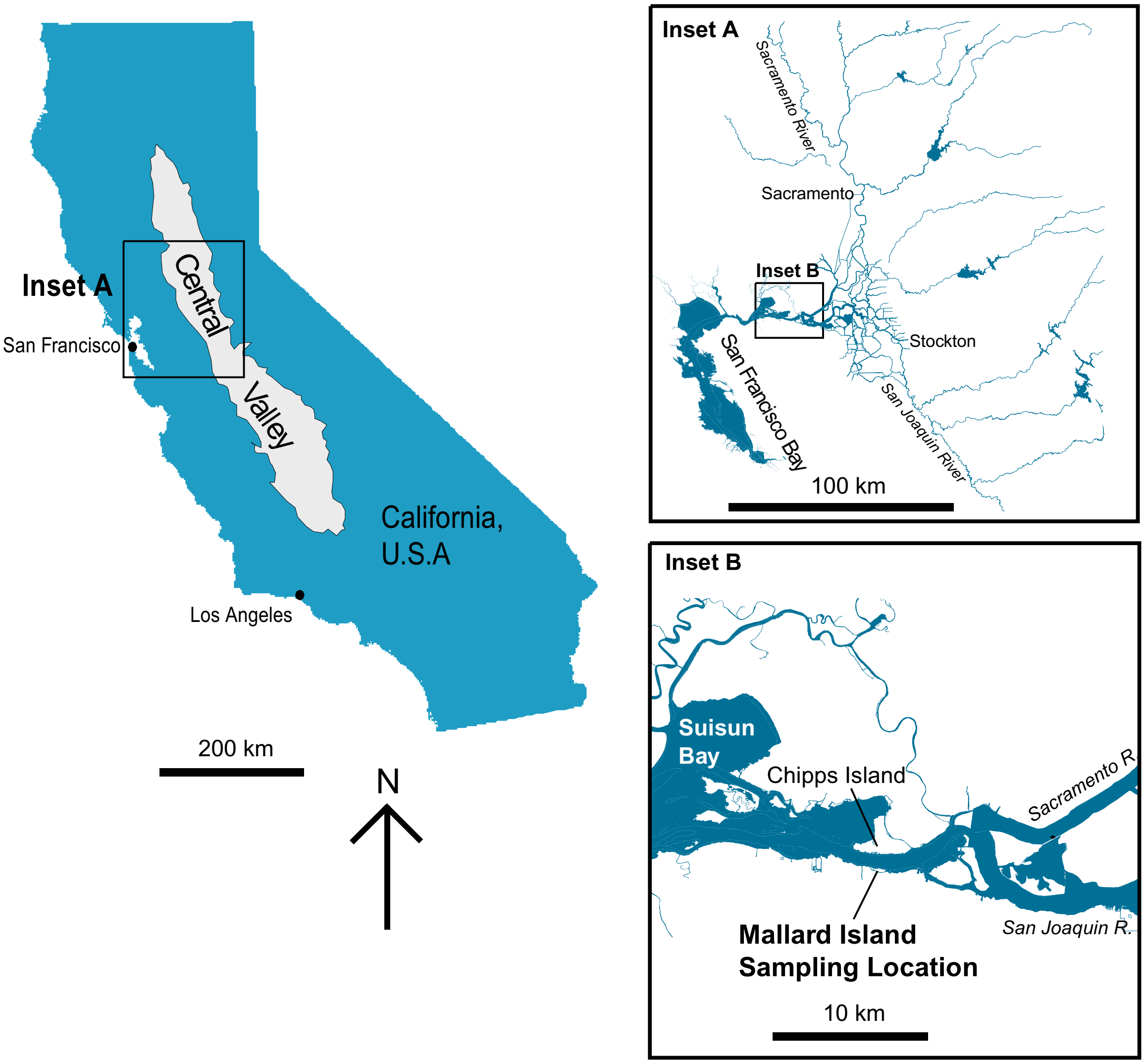

Figure 2.1 The Mallard Island sampling location.

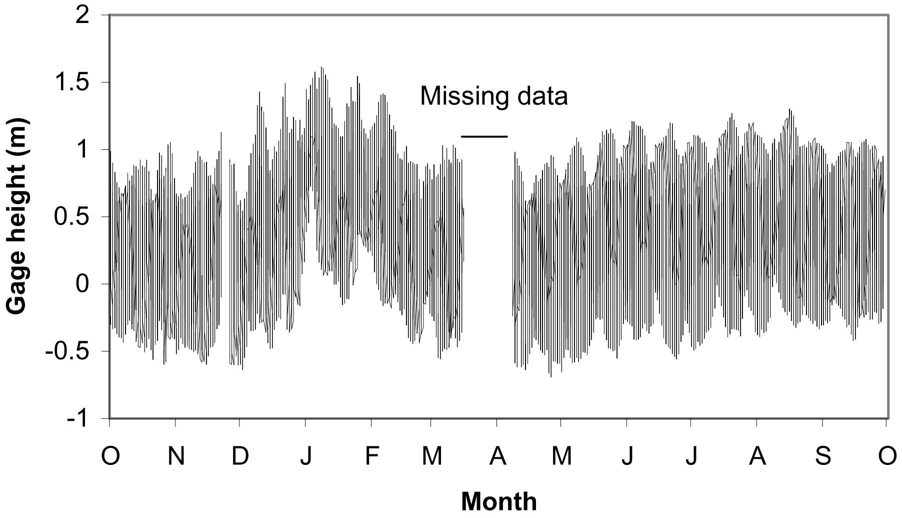

Figure 2.2 Tide at Mallard Island during the 1997 water year. Data from the California Department of Water Resources (Station ID: MAL).

2.3.3 Hydrology

Given that water circulation at the Mallard Island site is tidally influenced, the net (tidally averaged) discharge cannot be gaged using standard hydrological techniques for riverine discharge, such as the area-velocity method. Instead, discharge is estimated at Mallard Island by the DWR (Interagency Ecological Program, 2004a) using a mass-balance approach and the DAYFLOW model. As the term "DAYFLOW" suggests, the Delta outflow estimates have a time interval of 1 day but do not include variation due to the spring-neap cycle. DAYFLOW data are available for 1956 to the present from the Interagency Ecological Program (IEP) (Interagency Ecological Program, 2004b). Delta outflow estimated using the DAYFLOW Model is the longest-running record of water discharge entering San Francisco Bay from the Delta. This data is periodically updated when model parameters are refined by new information. Data used in this report are from the last data update that was published on January 7th 2004. Tidal gage height data have been measured at Mallard Island since 1900 and are available from the DWR.

2.3.4 Load Calculation

The total residual load [L] (in this case the flux in the downstream direction) of a given constituent can be decomposed into eleven terms (Dyer, 1974) as follows:

$$[L] = [[A]]\,[U_a]\,[C_a] + [[A]]\,[U_a'C_a'] + [A'U_a']\,[C_a] + [A'C_a']\,[U_a] \qquad (1)$$

$$+ [A'U_a'C_a'] + [[A]]\,([U_{dt}][C_{dt}])_a + [[A]]\,([U_{dv}][C_{dv}])_a$$
$$+ [[A]]\,([U_t'C_t'])_a + [[A]]\,([U_v'C_v'])_a + [A'(U_t'C_t')_a] + [A'(U_v'C_v')_a],$$

where A = area
U = velocity
C = concentration
[ ] = a tidally averaged value
′ = denotes the deviation of the instantaneous value from the tidally averaged value
$_a$ = a cross-sectionally averaged value
$_v$ = a vertical average
$_t$ = a transverse average
$_{dv}$ = the deviation of the depth average at any position from the cross-sectional average
$_{dt}$ = the deviation of the average value at any depth from the depth-averaged value.

The terms describe the contribution of various types of forcing on the total load. In their respective order they are (1) the load contribution of river discharge (advective load), (2) correlation between fluctuations of velocity and concentration (dispersive load), (3) inward transport of the progressive tidal wave, (4) correlation between tidal height and concentration, (5) third-order correlation of tidal height, velocity and concentration, (6) net transverse circulation, (7) net vertical circulation, (8) transverse oscillatory shear, (9) vertical oscillatory shear, (10) covariance of cross-sectional area fluctuations with the transverse oscillatory shear, and (11) covariance of cross-sectional area fluctuations with the vertical oscillatory shear (Dyer, 1974).

Simplifications and assumptions

Limitations of the data collected at Mallard Island preclude solving all terms in the load equation. The variable that accounts for the fluctuation in area is unknown, which prohibits calculation of an exact solution. The cross-sectional variability in the velocity and concentration fields also is unknown. Term 1 (advective load) is the only term that can be estimated over the desired timescale in this study, though simplification of that term also is required.

Advective load

Given the constraint of a daily time interval for estimated discharge, daily advective load was estimated using the following equation:

Daily advective load = $C_{av}Q_{DO}$ (2)

where C_{av} is the average SSC for a 24-hour period (the average of 96 data points taken every 15-minutes) and Q_{DO} is the Delta outflow estimated using the DWR DAYFLOW model for the same period. SSC data [milligrams per liter is equivalent to tonnes per million cubic meters ($mg/L = t/Mm^3$)] were combined with daily discharge [million cubic meters (Mm^3)] to give the advective load of suspended sediment in metric tonnes (t). On days with no SSC data, load was estimated by linear interpolation. SSC was estimated by interpolating across the data gaps, and the load was estimated by multiplying the estimated SSC by daily discharge. Interpolation of the SSC data was preferred to interpolating between load measurements because the latter estimate retained the variation associated with discharge.

The advective load method assumes that the point SSC data at Mallard Island is representative of the entire cross-section. While lateral and vertical structure of the concentration profile is unknown, it is reasonable to assume that during high-flow (when most of the sediment is delivered), the cross-section at Mallard Island is well mixed due to high velocities. During low-flow, this may not be the case, due to stratification effects, flood/ebb asymmetries, and other phenomena.

Other load terms

Estimating the total residual load at Mallard Island as the product of daily DAYFLOW discharge and mean concentration neglects several terms from the total load equation. The magnitude of the first four terms of the load equation can be estimated via point data at the Mallard Island site. This method estimates the bias produced when the advective load estimate alone is used to compute total load, though the time variation of cross-sectional area must be ignored due to a lack of data. The remaining terms cannot be estimated due to a lack of cross-sectional velocity and concentration data. We estimate these neglected terms in our error calculation.

Term 2 of the load equation represents the residual dispersive load, which can be significant in many systems. Dispersive load essentially is a measure of the correlation between tidal velocity and sediment concentration. The relative contributions of advective and dispersive load to the total load were estimated using point velocity and concentration data at Mallard Island. While the units of these point-loads (mass per unit area and time) are not congruent with the units of advective load in the full load equation (mass per unit time), the exercise here is to estimate the bias involved in computing only an advective load. Although dispersive load is likely to be small during high flow periods, it likely is large during the rest of the annual cycle when tidal flushing is dominant. Therefore, the simplified point-load equation, neglecting the last seven terms of the fully developed load equation, as well as cross-sectional area variations, is as follows:

$$[l]=[[u][c]] + [u'c'] + [[u]c'] + [u'[c]] \qquad (3)$$

where $[[u][c]]$ is the residual advective load and $[u'c']$ is the residual dispersive load. All terms are analogous to terms 1 - 4 in the full load equation. This equation was applied to point velocity and SSC data at Mallard Island.

Three sets of data were available for this analysis; one from WY 1996 (near-surface), and two from WY 1994 (near-surface and mid-depth). An Acoustic Doppler current profiler (ADCP) was deployed near the gage house where SSC data were collected 1 m below the water surface and at mid-depth. The ADCP measured velocity in vertical bins, and load was calculated using the bin closest to the elevation of the optical sensor used to measure SSC. Here we calculate point-load rather than cross-sectionally averaged load, which is valid for comparing advective and dispersive load.

Mid-depth SSC data were not collected during WY 1996 deployment due to vandalism. The ADCP deployments during WYs 1994 and 1996 were at different locations; therefore, the total load cannot be compared between the deployments.

For illustrative purposes, cumulative frequency of flow during WY 1996 were used to identify high, average, and low-flow periods. Flows above the 90 percent cumulative frequency (2,747 m^3/s) were considered high, flows at 50 percent (396 m^3/s) were considered average, and flows below 10 percent (226 m^3/s) were considered low.

Combining advective and dispersive load estimates

To correct the positive bias associated with calculating WYs 1995 - 2003 advective load alone, an equation was fit to the scatter of points created by plotting Delta outflow versus the ratio of dispersive to advective load for the available data (Figure 2.3). At infinitely high flows, the advective load would be wholly responsible for transport, while at zero flow, the advective load should go to zero, resulting in a dispersive/ advective load ratio of plus or minus infinity. The dispersive load is rarely in the same direction as the advective load at Mallard Island (points greater than zero).

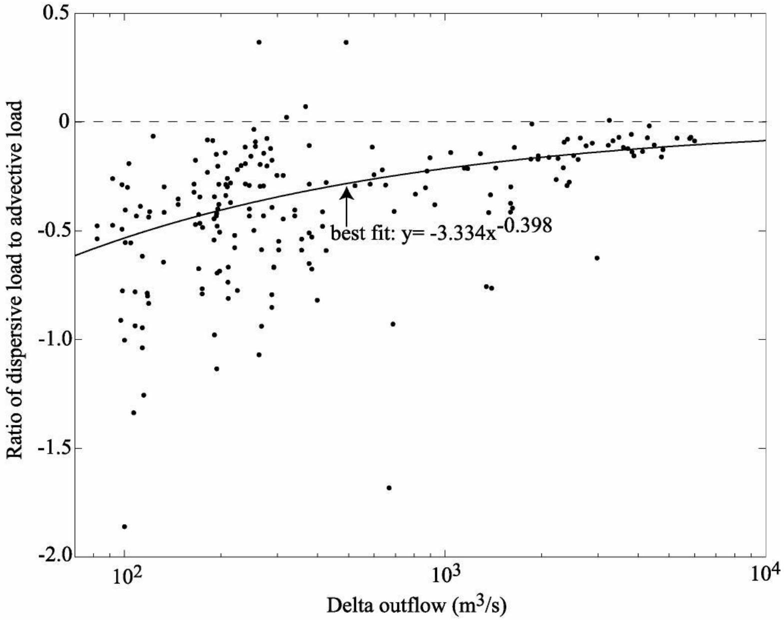

Figure 2.3 Ratio of dispersive-to-advective point-loads vs. Delta outflow, for all three data periods (198 points). A negative ratio indicates opposing directions of dispersive and advective point-loads.

Error analysis

SSC data were averaged for each day (up to 96 data points per day). To determine the error associated with taking the average over the tidally affected 24-hour record, the SSC data were filtered using a low-pass filter with a cutoff period of 30 hours. The record then was integrated daily, and divided by 96 (number of readings per day) to get a filtered, daily-integrated average concentration (cf_{ave}). The mean daily concentrations from the same record (C_{ave}) were used to calculate the percent difference between the filtered average and the daily geometric average [$(cf_{ave}-C_{ave})/cf_{ave}$]. The square root was taken of the sum of the squares of all the percent differences to give an rms error or 0.67 percent.

The error in Delta outflow will be the error associated with all the parameters that are used in the DAYFLOW calculation. The DAYFLOW Delta outflow has been compared to measurements of outflow based on ultrasonic velocity meters (UVM) (Oltmann, 1998). Oltmann found that during the period of high flow that he tested (winter 1996), the two hydrographs matched "fairly well". Given the difficulty with estimating some of the input terms in the DAYFLOW calculation, especially during low flow when water use for drinking and irrigation dominate the calculation (Interagency Ecological Program, 2001a) and when the spring and neap tides partially empty and fill the Delta (Oltmann, 1998), an error of at least ±5 percent is likely. The error associated with laboratory analysis of SSC was set at ±5 percent (Gray *et al.*, 2000). The estimated error associated with the regression between OBS and SSC was ±10 percent [see regressions in Buchanan and Schoellhamer (1996, 1998, 1999), Buchanan and Ruhl (2000, 2001), Buchanan and Ganju (2002, 2003)].

The heterogeneity of SSCs in the water column is a potential error in the study calculations. At this time, data collected near the base of the deep-water channel at Mallard Island (Buchanan and Schoellhamer, 1996, 1998, 1999; Buchanan and Ruhl, 2000, 2001; Buchanan and Ganju, 2002, 2003) have not been included in this analysis of load (reasons explained previously). During WY 1995, Buchanan and Schoellhamer (1996) found that mean near-surface SSC was 43 mg/L and the near-bottom SSC was 41 mg/L (a difference of -5 percent). During WY's 1996, 1997, 1998, 1999, 2000, and 2001, the percent differences between the upper and lower sensors were +27, +11, +2, +10, +30, +27 (Buchanan and Schoellhamer, 1998; Buchanan and Schoellhamer, 1999; Buchanan and Ruhl, 2000, 2001; Buchanan and Ganju, 2002, 2003). In years when the near-bottom concentrations are greater than the near-surface concentrations, a negative bias in load estimation would result during high-flow periods when discharge throughout the water column is downstream (ebb flow). This negative bias may be offset partially by upstream transport of sediment during flood tides at drier times of the year (e.g., Tobin *et al.* 1995). The differences between top and bottom may be an overestimation of the error because not all the top and bottom data are concurrent. In any case, it seems that the error associated with water column heterogeneity either can be positive or negative and on average about 15%. Further, if it is assumed that lateral variations are similar to the vertical, then the total error associated with water column variation will be closer to ±30 percent. Cross-sectional sampling at similar suspended-sediment monitoring stations in the Delta indicates that the typical cross-sectional variability is 25 percent (David Schoellhamer, USGS, unpublished data, 2004), so a 30 percent error appears realistic. The errors (shown in Table 2.2) were calculated as follows and applied to all nine water years:

$$\text{Error} = (0.67^2+5^2+5^2+10^2+30^2)^{0.5}$$

$$= \pm 32 \text{ percent}$$

2.4 RESULTS

2.4.1 Delta Outflow for Water Years 1995 – 2003

DAYFLOW estimates followed an intra-annual cycle typical of Californian Mediterranean (dry summer subtropical) climate, where the majority of flow occurs during the wet season (Figure 2.4). The wet season during WY 1995 to WY 2003 started in December and ended 3 - 6 months hence. For consistency, however, the wet season of each water year was considered December 1 to May 31. On average (WYs 1995 - 2003), 83 percent of the Delta outflow occurred during the wet season and 34 percent occurred during the wettest 30-day period of each year. Discharge varied inter-annually from $8.6\text{x}10^3$ Mm^3 in WY 2001 to $53.6\text{x}10^3$ Mm^3 in WY 1998. This relatively small inter-annual variation does not reflect long-term variability. Discharge during WYs 1971 - 2000 varied from $3.1\text{x}10^3$ Mm^3 to $79.3\text{x}10^3$ Mm^3 (26 times) with a coefficient of variation (CV) of 0.76 (Note that the period 1971 - 2000 was chosen to be consistent with the published United States National Oceanic and Atmospheric Administration [NOAA] National Climate Data Center [NCDC] climatic averages.). Mean annual discharge for WYs 1995 - 2003 was greater than average ($29.6\text{x}10^3$ Mm^3 compared to $24.9\text{x}10^3$ Mm^3 for WYs 1971 - 2000). Of interest, average annual discharge was only $8.5\text{x}10^3$ Mm^3 during the 8 years previous to our study period (WYs 1987 – 1994). This may have decreased the net transport of sediment during those years and increased the amount of storage in the watershed and channels that subsequently could be eroded or resuspended during later years when rainfall, snow melt, and runoff were greater.

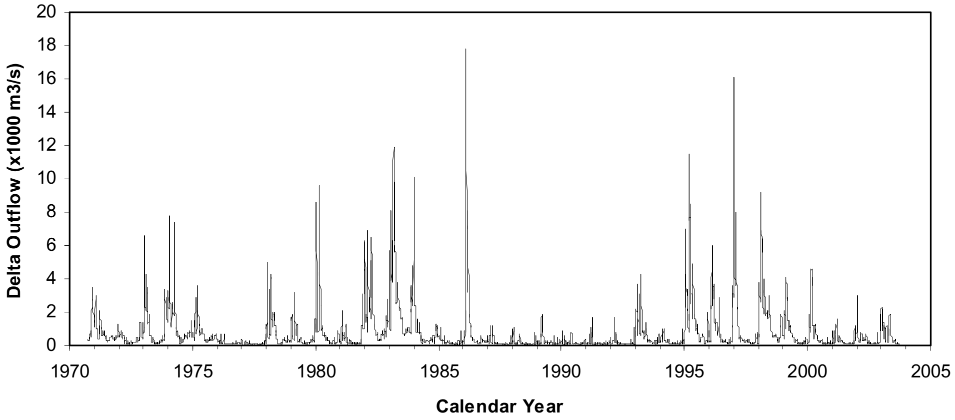

Figure 2.4 Daily water discharge (Delta outflow) at Mallard Island using output from the Department of Water Resources DAYFLOW model.

2.4.2 SSC and Daily Suspended-sediment Load at Mallard Island

Daily average SSC at Mallard Island was highly variable, ranging from 14 mg/L to 223 mg/L. The highest instantaneous concentrations reached 420 mg/L on January 7th 1997 during the largest flood of the study period, approximately 4 days after the peak in Delta outflow. As predicted, advective load of suspended sediment at Mallard Island reflected the intraannual cycle of water discharge. Dispersive point-load (load estimated from point measurements and assumed to be representative of the entire water column) was calculated for the period for which data were available (Figure 2.5, December 17, 1995 - March 5, 1996, near-surface, high Delta outflow). During high flows, the advective point-load dominates (Figure 2.5), which is expected because the large volumes of water moving seaward through the river are responsible for the transport of sediment. Dispersive point-load magnitude averages about 11 percent of the advective point-load magnitude during this above-average flow period (mean discharge=2,116 m^3/s). The direction of the dispersive point-load mainly is in the opposite direction (landward) of the advective point-load at the location of the Mallard Island station.

During a period of low flow (April 15, 1994 - June 4, 1994) (mean discharge = 255 m^3/s), the dispersive point-load magnitude near surface averages about 49 percent of the advective point-load magnitude, and almost always is in the opposite direction (landward) (Figure 2.6). For the same period, the mid-depth dispersive point-load averages 52 percent of the advective point-load. Thus, for lower flows, dispersive load is relatively more important in estimating total load. This result is similar to a scaling analysis of the relative magnitudes of the advective and dispersive load, which calculates the two loads to be on the same order of magnitude for low flows (David Schoellhamer, USGS, unpublished data, 2001).

These results demonstrate that load is overestimated at this location when only the advective term is considered, and the overestimate is largest during low-flow periods. However, the advective load will be strongly dependent on flow, suggesting that at lower flows the overestimate of a small load might not be as important to an estimate of the total annual sediment load from the Delta to the Bay. Figure 2.7 presents the three data sets, displaying the load that would be estimated by using only the advective term, and the total load. The ADCP deployments were in different locations, so the load cannot be compared directly between the WY 1994 and 1996 deployments.

Average dispersive point-load for a given discharge was estimated using the curve shown in Figure 2.3. On an annual basis, tidal dispersive load caused a net flow upstream of about 0.39 Mt during WY 1995, 0.23 Mt during WY 1996, 0.34 Mt during WY 1997, 0.40 Mt during WY 1998, 0.23 Mt during WY 1999, 0.17 Mt during WY 2000, 0.12 Mt during WY 2001, 0.12 Mt during WY 2002, and 0.16 Mt during WY 2003. Thus, if tidal effects had not been taken into account, sediment load from the Central Valley to the Bay would have been over estimated by an average of 0.24 Mt per year or about 20 percent of the total 9-year load.

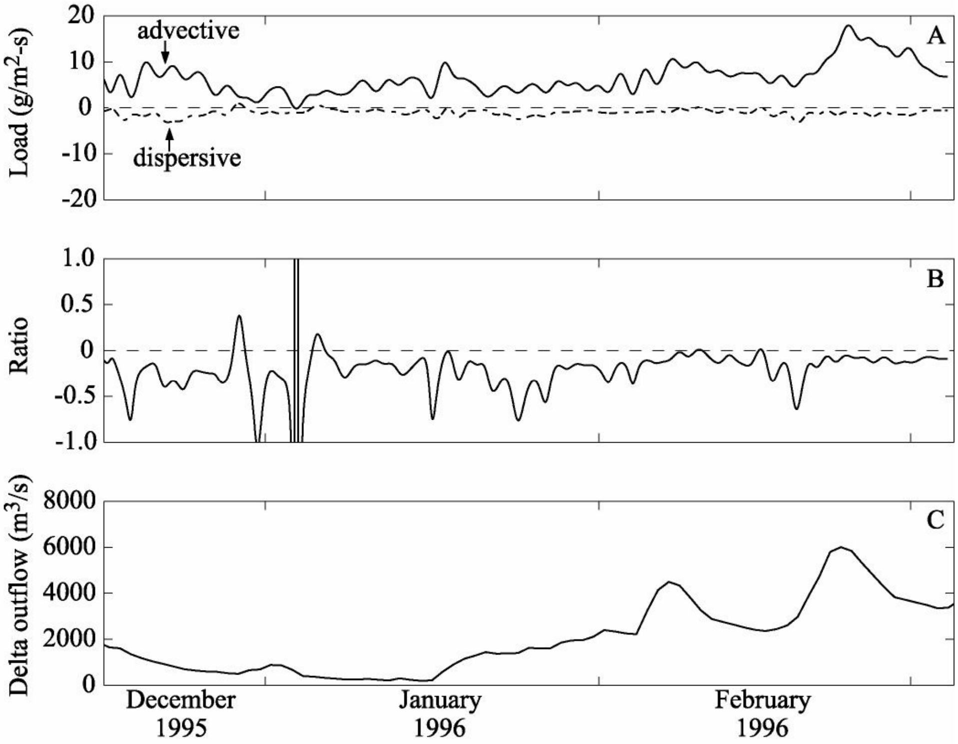

Figure 2.5 Advective and dispersive point-loads at Mallard Island (A), ratio of dispersive-to-advective point-load (B), and Delta outflow (C), December 17, 1995 to March 5, 1996.

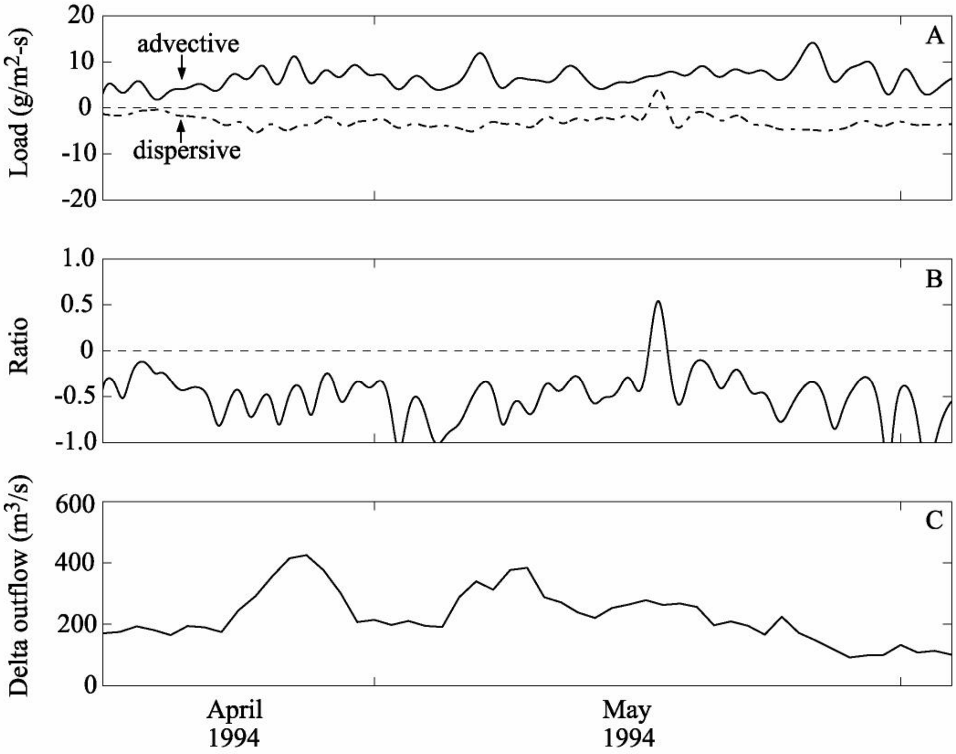

Figure 2.6 Advective and dispersive point-loads at Mallard Island (A), ratio of dispersive-to-advective point-load (B), and Delta outflow (C), April 15, 1994 to June 4, 1994.

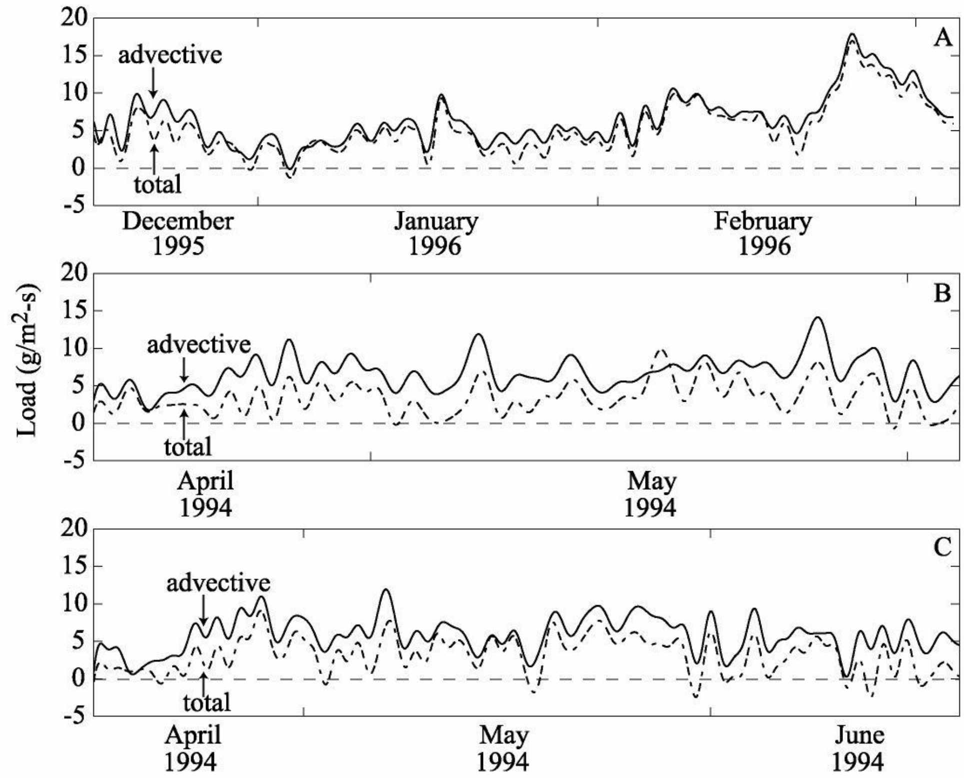

Figure 2.7 Comparison of advective and total point-loads at Mallard Island. December 17, 1995 - March 5, 1996, near surface (A), April 15, 1994 - June 4, 1994, near surface (B), and April 15, 1994 - June 20, 1994, mid-depth (C).

Dispersive loads for each discharge then were added to the advective loads to give the best estimate of suspended-sediment load per day. While the use of point-load data to estimate a bias in average cross-sectional load may not be optimal, the analysis here shows that the dispersive load must be considered even during high-flow periods. On average, (WYs 1995 - 2003) 88 percent of the annual load (dispersive and advective) was discharged through the Delta during the wet season of a water year, 43 percent was discharged during the wettest 30-day period, 19 percent was discharged during the wettest 7-day period, and 3.7 percent of the suspended-sediment load occurred on the wettest 1-day period (Table 2.1). The largest flood during WYs 1995 - 2003 occurred in January 1997. This flood alone transported 1.2 Mt of suspended sediment or about 11 percent of the total accumulated load for the 9 years (10.9 Mt). When the second peak in January 1997 was included, 1.7 Mt of suspended sediment were transported, or about 15 percent of the 9-year total load.

Table 2.1 Intra-annual variation of the sum of advective and dispersive suspended-sediment load at Mallard Island for water years 1995 - 2003. For example, during water year 1995, 22 percent of the total annual suspended-sediment load was transported during seven consecutive days.

Water Year	1-day (percent)	7-day (percent)	30-day (percent)	Wet Season December 1 to May 31 (percent)
1995	6.1	22	38	92
1996	2.5	13	36	88
1997	9.6	44	70	96
1998	2.7	17	45	84
1999	1.6	9	31	81
2000	2.5	16	49	89
2001	3.2	18	41	86
2002	3.1	18	44	86
2003	2	11	37	88
Average	3.7	19	43	88

Annual suspended-sediment load at Mallard Island varied from 0.26±0.08 Mt in WY 2001 to 2.6±0.8 Mt in WY 1995 and averaged 1.2±0.4 Mt (Table 2.2). Given that the water discharge for the 1995 - 2003 period was greater than the average discharge, it seems likely that the average sediment load may be less than 1.2±0.4 Mt. Water year 1996 had an average discharge and, therefore, the WY 1996 suspended-sediment load (1.0±0.3 Mt) may be our best hypothesis of the average annual suspended-sediment load entering the Bay from the Central Valley. However, it should be kept in mind that suspended-sediment load in a system is seldom linear with respect to discharge. Water year 1996 followed a year of greater-than-average discharge that may have left the system low in stored sediment. If the assumption is made that the SSC data and loads presented here are representative of the variability over a wider range of flow conditions and that there is no long term trend in SSC and we extrapolate the WY 1995 - 2003 data, a regression between load and flow (Figure 2.8) can be used to estimate long term loads. Using the annual Delta outflow for WY 1971 - 2000, an average long-term sediment load of 1.0±0.3 Mt is determined (similar to WY 1996 in spite of non-linearity of the equation on Figure 2.8). Regardless of how one chooses to manipulate the data, it is clear that the new loads estimates presented here are less by a factor of about 3 than those previously calculated (Table 2.2).

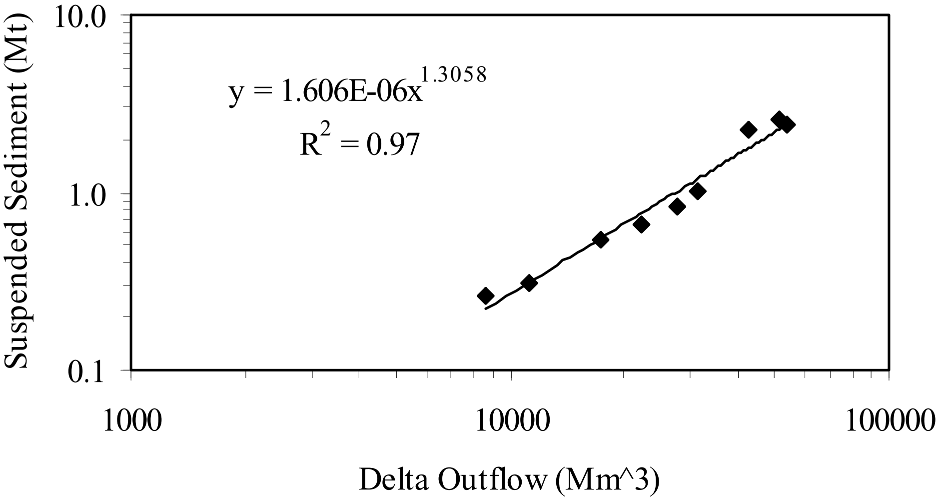

Figure 2.8 The relationship between Delta outflow and suspended sediment load at Mallard Island (WY 1995 - 2003).

Table 2.2 Annual suspended-sediment load at Mallard Island calculated for water years 1995 - 2003. Previous estimates are included for comparison.

Author	Data calculation period	Annual suspended-sediment load (Mt/y)
This study	1994/95	2.6 ± 0.8
This study	1995/96	1.0 ± 0.3
This study	1996/97	2.2 ± 0.7
This study	1997/98	2.4 ± 0.8
This study	1998/99	0.84 ± 0.27
This study	1999/00	0.66 ± 0.21
This study	2000/01	0.26 ± 0.08
This study	2001/02	0.31 ± 0.10
This study	2002/03	0.55 ± 0.17
This study	9-year average	1.2 ± 0.4
Krone (1979)	Average for 1960	3
Smith (1963)	?	*3.3
Schultz (1965)	?	*4.5
U.S.A.C.E (1967)	?	*4.0
Porterfield (1980)	1909-66	*3.5
Ogden Beeman & Associates (1992)	1955-90	~2.8

* These estimates include bed-sediment load and suspended-sediment load from local tributaries to San Francisco Bay as well as load from the Central Valley.

2.5 DISCUSSION

2.5.1 Suspended-sediment Concentration and Flow-data Quality

Approximately 26 percent of the days between February 9, 1994 and September 30, 2003 had no data recorded. It happened that the majority of the missing data occurred during low-flow periods, thus 86 percent of the load was measured, and only 14 percent was estimated using linear interpolation. Only during the flood of 1998 were data missing on the rising stage of the hydrograph. In this case, 11 days were missing and linear interpolation was used to estimate the missing data. Although this may have caused an unknown, but significant, error (perhaps 10 percent in addition to the other errors) in the estimate of the load for the 1998 water year, it certainly had little effect on the overall estimate of the average load for the 9-year period.

In most studies of suspended-sediment load, the discharge of water is measured on a smaller time interval than concentration. Thus, the scientific literature concerning measuring and estimating riverine load is rich with methods that interpolate between concentration data points (e.g., Walling and Webb, 1981; Preston *et al.*, 1989; Kronvang and Bruhn, 1996). In contrast, the SSC data collected at Mallard Island have a time interval of 15 minutes (96 data points per day), and thus a potential loss in accuracy results from a 1-day time interval in water-discharge data. The travel time of a flood wave down the Sacramento and San Joaquin River systems may vary, depending on the back push of the daily and bimonthly tidal cycle, antecedent watershed and flow conditions, the magnitude of the rainstorm, and the peak intensity of the rainstorm. Given that the DAYFLOW model does not take into account factors such as these, the absolute timing of the peak flow may be imprecise. The 1-day time step for water discharge undoubtedly influenced the estimation of suspended-sediment load at Mallard Island, but the loss of precision is perhaps random.

The use of the daily time step is satisfactory to estimate load. Large floods pass through the Delta during periods of 7 - 14 days and the Delta is likely to "fill up" with water during floods. As discussed previously, Oltmann (1998) compared DAYFLOW Delta outflow with outflow based in ultrasonic velocity meters and found that the discharge during the 1996 wet season compared "fairly well". Further, daily averaged SSC did not vary greatly between days during the January 1997 flood (35 mg/L to 45 mg/L). Therefore, as a consequence of the size of the system and the relatively low variability of SSC between days, the 1-day time step with no adjustment for varying discharge lag seems to be adequate for analysis of suspended-sediment loads. Additional work to test the use of models to generate flow on a smaller time step could be done if future applications warrant this level of effort.

2.5.2 Dispersive Load

The direction of the dispersive point-load mainly is in the opposite direction (landward) of the advective point-load, at the location of the Mallard Island station. Five explanations can be given for this phenomenon: (1) higher suspended-sediment concentrations in Suisun Bay (seaward end of the study area) as opposed to the lower concentrations in the Sacramento River (landward end) result in a concentration gradient from Suisun Bay to the Lower Sacramento River and, therefore, a net dispersive load in that direction (landward); (2) the relatively shallow depths in Suisun Bay allow for wind-wave resuspension of bed sediment (Ruhl and Schoellhamer, 2004); (3) flood tide induces a higher bed shear stress than ebb tide (enhancing resuspension and SSC on flood tide), and sediment is more erodible at the beginning of flood tide (Brennan *et al.* 2000); (4) a local turbidity maximum previously has been identified seaward of Mallard Island, which is congruent with explanations 1, 2, and 3 (Schoellhamer, 2001); (5) flood/ebb asymmetry in lateral variability of SSC also is possible. A consequence of bidirectional flow and a seaward gradient of increasing SSC at Mallard Island is that there may be net sediment transport upstream during part of the annual, fortnightly, or daily tidal cycles (Tobin *et al.* 1995). Our estimated dispersive load accounts for this upstream transport and for the 9-year study period the landward dispersive load was 20% of the seaward advective load. This has implications for the future estimation of contaminant loads. For example, if concentrations of contaminants such as mercury on resuspended particles downstream from Mallard Island are greater than those upstream, there would be a greater percentage of dispersive load for mercury relative to suspended sediments.

2.5.3 Trends in Suspended-sediment Load

Loads calculated here are lesser in magnitude than those calculated by previous authors (Table 2.2), though differences in methods undoubtedly contribute to some variation (for details on the method of each previous author see Krone, 1979; Smith, 1963; Schultz, 1965; U.S.A.C.E, 1967; Porterfield, 1980; Ogden Beeman & Associates, 1992). In addition, some authors included estimates of bed load, however bed load accounts for only about 1.4 percent of the total annual average load (e.g. Porterfield, 1980). Estimates that include the bed load component of fluvial transport still seem to be higher than the estimates for WYs 1995 - 2003. Given that the discharge during the 1995 - 2003 period ($29.6\text{x}10^3$ Mm^3) was greater than the average for the last 30 years ($24.9\text{x}10^3$ Mm^3), discharge is not the cause of discrepancies.

The most recent of the previous estimates (Ogden Beeman & Associates 1992) estimated suspended sediment loads by use of a rating curve for sediment load versus water discharge using sediment data gathered at Freeport on the Sacramento River and Vernalis on the San Joaquin River. Because no sediment data were available from the tidal channels of the Delta, the rating curve was applied to Delta outflow to estimate load into the Bay. In so doing, Ogden Beeman & Associates (1992) assumed that the relation between water discharge and SSC did not vary in time, no deposition occurred in the Delta, and water exports remove sediment from the Delta. Wright and Schoellhamer (2004) however, show that the water discharge and SSC relation in the Sacramento River has changed with time, Rojstaczer et al. (1991) analyzed depositional cores from the Delta, and deposited sediment is occasionally removed from the forebay used by the water export projects. The loads presented here for WY 1995 - 2003 are not subject to these issues.

Krone (1996) suggested a downward trend over time and made a hypothesis that total sediment load from the Central Valley to the Bay would decrease to 2.1 million yd^3/y (0.85 Mt/y) by the year 2035. Wright and Schoellhamer (2004) found that the sediment yield of the lower Sacramento River has decreased by about one-half from 1957-2001. If this trend continues, perhaps the predictions of Krone (1996) will be realized. The ramifications of this trend are considered in the following sections, that address management considerations.

2.6 CONCLUSIONS AND MANAGEMENT CONSIDERATIONS

2.6.1 San Francisco Bay Sediment Budgets

Load of sediment from the Central Valley previously has been reported to account for approximately 89 - 92 percent of the total input of sediment to the San Francisco Bay sediment budget (Ogden Beeman & Associates, Inc. 1992). Krone (1979) suggested that the ratio of sediment input to the San Francisco Bay is changing mainly due to reductions in sediment load from the Central Valley. Krone reported 76 percent of the total load to the San Francisco Bay was derived from the Central Valley in 1960 and hypothesized that the ratio would reduce to 63 percent in 1990 and 54 percent in 2020, based on increasing water diversions and retention in reservoirs. The present study suggests that the Central Valley supplies about 57 percent of the total load to the San Francisco Bay if the following assumptions are made:

1. Sediment load from local watersheds within the nine Bay area counties has not decreased with time, which was asserted by Krone (1979) and is conceptually possible, given increasing population and ongoing conversion of grazing and open space lands to vineyards and urban land uses in the Bay area.
2. The current estimate of long-term average for sediment load entering the Bay from local tributaries is 0.83 million short tonnes suspended-sediment (Krone 1979) equivalent to 0.75 Mt/y.
3. The estimate calculated in the present study for load of suspended sediments from the Central Valley during WY 1996 is 1.0 Mt/y.

San Pablo Bay and Suisun Bay have undergone erosion in shallow areas since the 1950s (Jaffe *et al.* 1998, 2001; Capiella *et al.* 1999). For example, from 1942 to 1990, more than two-thirds of Suisun Bay was eroding (Capiella *et al.* 1999). The erosion in these bays is likely, in part, a result of reduced sediment supply from the Central Valley (Jaffe *et al.* 1996), although sediment redistribution within these bays, in response to human and climatic changes during the past 80 - 150 years, also may play a role. A further implication of reducing sediment load is that sediment dredging requirements in shipping channels may decrease in the future, once sediment stored in the Bay has redistributed and has found a new equilibrium, relative to reduced sediment inputs, changing runoff patterns, changing salinity, and increasing sea level (Dettinger *et al.* 2001; Knowles 2001). Dredging figures for the period 1955 - 1990 (4.5 Mm^3/yr) versus figures for the period 1995 - 2002 (3.1 Mm^3/yr) indicate that this may already be occurring. Reduction in Central Valley sediment load also implies that sediment derived from local watersheds will become increasingly important as a supply of sediment to the Bay, in general, and in particular to some shipping channels and ports that are affected increasingly by local runoff.

2.6.2 Resuspension of Contaminants Stored in Bottom Sediments

One of the major issues affecting the water quality and biological integrity of the San Francisco Bay is the internal supply of contaminants, such as mercury, from resuspension and biological recycling (Johnson and Looker, 2003). One of the factors influencing the availability of the benthic pool of contaminants is exposure through erosion and redistribution of sediment particles (Jaffe *et al.*, 2001). Erosion apparently is occurring in parts of the Bay where removal through tidal currents and wave action is occurring faster than deposition of new sediment supply from fluvial sources (Jaffe *et al.*, 1996, 2001). There still is more than 100 Mm^3 of mercury-contaminated sediment remaining in San Pablo Bay and tens of millions of cubic meters of mercury-laden debris along the margins of Suisun Bay (equivalent to about 10^5 kg Hg) (Jaffe *et al.*, 2001). Bay sediments also contain high concentrations of many other contaminants, which probably include some whose effects are not yet documented. There are a number of mechanisms by which stored contaminants may enter the food web, including physical, chemical, and biological pathways. The depth of the active sediment mixing layer and the assumption of net deposition or net erosion strongly influence the outcomes of modeling of contaminant processes in the Bay (Davis, 2004).

2.6.3 Sediment Supply for Restoration Projects

Given the decreasing mass of sediment delivered to the Bay from the Central Valley, the implication is that less sediment will be available for restoration of wetlands that require either reuse of dredged material or natural sedimentation through tidal and fluvial supply (Williams, 2001). Furthermore, Williams pointed out that restoration, in itself, also will decrease sediment supply to the Bay as sediment is diverted to wetland areas by deliberate levee breaches and reconnection of the floodplain with the channels. For example, Mount (2001) asserted that “in order to restore lowland rivers in the Central Valley, the winter flood pulses and the smaller, but equally important spring snowmelt pulselets must be able to reach a significant portion of the floodplain” in a way that allows water to move parallel to the stream, thus increasing hydraulic interaction and residence time. Restoring the connectivity of the near-channel floodplain to allow for flow that is parallel to stream channels will undoubtedly capture sediment and related contaminants. Shellenbarger et al. (2004) found that restoring tides to former commercial salt ponds in South San Francisco Bay may greatly reduce sediment deposition elsewhere. Williams (2001) further predicted that a coupling of a decrease in sediment supply and an increase in sea level will result in conversion of some mudflats to shallow subtidal habitats and an increase in shoreline erosion causing losses of fringing marsh and undermining of levees. A ramification of the estimates of upstream flow of sediment associated with tidal advection and dispersion (an average of 0.24 Mt/y) is that this sediment mass may be, in part, available for restoration projects in the Delta.

Concerns have been raised about the adequacy of the regional sediment supply for large-scale tidal marsh restoration (Goals Project, 1999; Williams, 2001), and these concerns are beginning to be addressed. Sediment cores (Byrne et al., 2001), historical maps (Grossinger et al., 1998), and estimates of historical sediment loads (Gilbert, 1917; Kondolf, 2000), when studied together, indicate that marshes depend less on inorganic sediment and more on peat production. Marshes evolve upward through the intertidal zone, and the vast amounts of historical high marsh [there was almost five times as much marshland in the Bay area 200 years ago as exists today (Goals Project, 1999)] was supported by less than one-half the modern sediment supply. It also is expected that the overall demand for sediment to support new marsh restoration can be lessened by starting projects where sediment is abundant and subsidence is moderate, by sizing projects to fit local sediment supplies, and by pacing projects carefully over time (Goals Project, 1999).

2.6.4 Calculation of Contaminant Load from the Central Valley

It has been demonstrated that the sediment concentration data collected at Mallard Island by the USGS are suitable for estimating the annual load of suspended sediments to the San Francisco Bay. Steding et al. (2000) produced compelling evidence of the influence of the Central Valley on contaminant fate and transport in the Bay using lead isotope data. They found that in 20 years since the phasing out of lead in gasoline began, there has been no reduction in supply of lead from the Central Valley to the Bay. This suggests that flushing of the Central Valley watersheds of traditionally persistent contaminants will continue for some time because the Central Valley sink for lead and other contaminants is so large. Several recently released mercury reports, describing current knowledge and data needs for management of the Bay, also highlighted the need for continuing evaluation of contaminant loads entering the Bay from the Central Valley (Johnson and Looker, 2003; Hetzel, 2003). Many substances of concern in the Bay can be directly correlated to SSC (Schoellhamer, 1997). Future studies will likely use the SSC data and estimates of sediment load presented here to improve the understanding of the timing and magnitude of sediment-associated contaminants of current management concern (mercury, PCBs, and organochlorine pesticides) that enter the Bay from the Central Valley.

2.7 REFERENCES

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SECTION THREE

3. POLYCHLORINATED BIPHENYLS, ORGANOCHLORINE PESTICIDES, AND POLYCYCLIC AROMATIC HYDROCARBONS

J.E. Leatherbarrow and L.J. McKee

3.1 ABSTRACT

Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), and several organochlorine (OC) pesticides (DDT, chlordanes, and dieldrin) are organic contaminants of current environmental and regulatory concern in the San Francisco Bay. Their use and/or production and subsequent distribution have left storages of these organic contaminants in soils and sediments of the Sacramento and San Joaquin River watersheds that are available for continued transport to the Bay during large storm events. The magnitudes of mass loading of these contaminants from these major rivers have not been accurately determined and are an important data gap in understanding their long-term fate in the Bay and developing management strategies for improving water quality.

To address this data gap, monitoring was conducted on the Sacramento River at Mallard Island between January 10th, 2002 and May 6th, 2003. Twenty-four water samples were collected for analysis of organic contaminants during varying flow regimes. Concentrations ranged from 200 to 6,700 pg/L of ΣPCBs, 240 to 1,600 pg/L ofΣ DDT, 40 to 180 pg/L of ΣChlordanes, 60 to 250 pg/L of dieldrin, and 12 to 36 ng/L ΣPAHs. Pesticide concentrations were significantly correlated to suspended sediment concentrations (SSC) and displayed a "first flush" effect consistent with that found for sediment. In contrast, ΣPCB and ΣPAH concentrations were influenced to a greater extent by tidal variation and potential urban inputs from localized or episodic sources.

Contaminant mass loads were estimated over the study period using available flow information for the Sacramento-San Joaquin Delta and time-continuous SSC data collected by USGS on 15-minute intervals. Correlations between pesticide concentrations and SSC allowed for estimation of pesticide loads based on an estimated time-continuous record of pesticide concentrations, whereas ΣPCB and ΣPAH loads were estimated based on flow-weighted mean concentrations and flow. Daily contaminant loads varied by 1-2 orders of magnitude for ΣPCBs (1.6 to 550 g), ΣPAHs (58 to 5,200 g), ΣDDT (1.4 to 150 g), ΣChlordanes (0.22 to 22 g), and dieldrin (0.37 to 56 g). Annual loads for WY 2002 and WY 2003 respectively were 6.0 ± 2.3 and 9.7 ± 3.7 kg ΣDDT, 0.93 ± 0.36 and 1.5 ± 0.57 kg ΣChlordanes, 1.8 ± 0.8 and 3.0 ± 1.3 kg Σdieldrin, 6.0 ± 2.0 and 23 ± 18 kg ΣPCBs, and 230 ± 60 and 350 ± 90 kg ΣPAHs. Extrapolation of study data to previous years indicates that annual contaminant loads may vary by up to a factor of eight between wet and dry years. In the context of mass budget models developed for the Bay, study results further indicate that continued loads of PCBs and OC pesticides from the Sacramento-San Joaquin Rivers may significantly delay recovery of water quality by decades.

3.2 INTRODUCTION

Polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and polycyclic aromatic hydrocarbons (PAHs) are organic chemicals of current environmental concern in San Francisco Bay due to their persistence in the environment and their potentially adverse effects on wildlife and human health. These chemicals are hydrophobic organic contaminants that are sparingly soluble in water and tend to partition into particulate material in soil and sediment and lipid tissue in biota (Schwarzenbach *et al.* 1993). The hydrophobic properties allow PCBs, OC pesticides, and PAHs in San Francisco Bay to accumulate and persist in sediment (Phillips and Spies 1988, Flegal *et al.* 1994, Oros and Ross 2004, Pereira *et al.* 1999, Venkatesan *et al.* 1999), benthic organisms (Phillips and Spies 1988, Gunther *et al.* 1999), fish (Fairey *et al.* 1994, Davis *et al.* 2002) and aquatic birds (Hothem *et al.* 1995, Hui *et al.* 2001).

Concerns over the persistence of PCBs and OC pesticides in the Bay and their tendency to biomagnify in the food web have spurred the allocation of considerable resources and effort to monitor these chlorinated hydrocarbons in the Bay over the last few decades. Although these chemicals have been restricted or banned for decades, their concentrations were high enough in Bay sport fish caught in 1994 (Fairey *et al.* 1994) to contribute to the issuance of an interim consumption advisory for sport fish caught in the Bay (OEHHA 1994). This health advisory remains in place and has led to the listing of all segments of San Francisco Bay on the Clean Water Act Section 303(d) list as impaired by PCBs and the OC pesticides DDT, chlordanes, and dieldrin. Since the initial listing in 1998, PCBs have been a high priority concern for the Bay and are currently subject to development of a Total Maximum Daily Load (TMDL) management plan. PAHs also pose a health risk to fish and wildlife in San Francisco Bay (Spies and Rice 1988, Thompson *et al.* 1999). The current levels of PAHs in the Bay have prompted the San Francisco Bay Regional Water Quality Control Board to place PAHs on a regulatory watch list of compounds that require further study to determine whether they are impairing beneficial uses of San Francisco Bay (SFBRWQCB 2001).

PCBs were commercially produced in the United States from 1929 to 1977 and were primarily used in industrial applications as insulating fluids in transformers, capacitors, and electromagnets and were also used for other minor purposes: heat exchanger fluids, chemical stabilizers, plasticizers, adhesives, insulating materials, flame-retardants, lubricants, and other products (ATSDR 2000 and references cited therein). Beginning in the 1940's, OC pesticides were used as insecticides for agricultural purposes and in urban areas for pest control and mosquito abatement (Wong *et al.* 2000, Mischke *et al.* 1985). They were also used in various other industries, such as forestry and transportation (Nowell *et al.* 1999). PAHs originate largely from anthropogenic sources, such as combustion of fuels, vehicular emissions, biomass burning and minor inputs from unburned or crude petroleum (Simoneit 1984, Jones *et al.* 1986). Natural combustion of biomass (*e.g.*, wood) also releases PAHs to the environment (e.g., Blumer and Youngblood 1975).

Persistent sources of PCBs, OC pesticides, and PAHs are dispersed throughout the San Francisco Bay watershed from activities associated with population growth, expansion of urban landscapes, historic and current agriculture, and industrial development. Their persistence in Bay watershed soils and sediments has left a storage of organic contaminants that are available for mobilization and transport to the Bay from local tributaries (Law and Goerlitz 1974, Gunther *et al.* 2001, KLI 2001, Salop *et al.* 2002, KLI 2002, Leatherbarrow and McKee 2004) and from the Sacramento and San Joaquin Rivers (Bergamaschi *et al.* 1997, Bergamaschi *et al.* 2001, Domagalski and Kuivila 1993, Kratzer 1999, Pereira *et al.* 1996, Mischke *et al.* 1985).

The annual mass loading of PCBs, OC pesticides, and PAHs that enters the Bay from surrounding watersheds is an essential element for understanding their long-term fate (Davis 2004, Greenfield and Davis 2005, Leatherbarrow *et al.* 2003) and developing management strategies for improving water quality in the Bay (*e.g.*, Hetzel 2004). In particular, inputs via the Sacramento-San Joaquin River Delta comprise a large portion of total loads of sediment and associated contaminants relative to other routes, or pathways, of contamination in the Bay, such as atmospheric deposition, point-source discharge, runoff from local tributaries, and remobilization of sediment through erosion or dredging. Concentrations and loads of organic contaminants in water entering the Bay from the Sacramento and San Joaquin Rivers are highly dependent on the interacting processes of tidal mixing, river flow, and sediment discharge. However, the variability in organic contaminant concentrations and loads in response to these major processes has not been accurately defined.

This study was implemented through the RMP to improve our understanding of how concentrations of PCBs, OC pesticides, and PAHs vary in response to combined interactions of tidal processes, river flow, and sediment discharged to the Bay from the Sacramento-San Joaquin River Delta. Results from the study were used in conjunction with data collected on sediment transport and hydrology to derive estimates of contaminant fluxes at the study location. This report summarizes the first two years of data collected in water years (WY) 2002 and WY 2003. Data collection will continue with varying intensity from water year 2004 to 2009.

3.3 METHODS

3.3.1 Sample Collection

Twenty-four samples were collected at Mallard Island between January 10th, 2002 and May 6th, 2003 for analysis of organic contaminants (Figure 3.1). Organic contaminants analyzed in this study included selected PCBs, OC pesticides, and PAHs (Table 3.1). Concentrations of forty individual PCB congeners, including co-eluting congeners, were measured and summed to derive total PCB (ΣPCB) concentrations in water samples. Total DDT (ΣDDT) concentrations accounted for concentrations of o,p' and p,p'-isomers of DDD, DDE, and DDT. Total chlordane (Σchlordane) concentrations were comprised of alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide. Dieldrin concentrations were also measured.

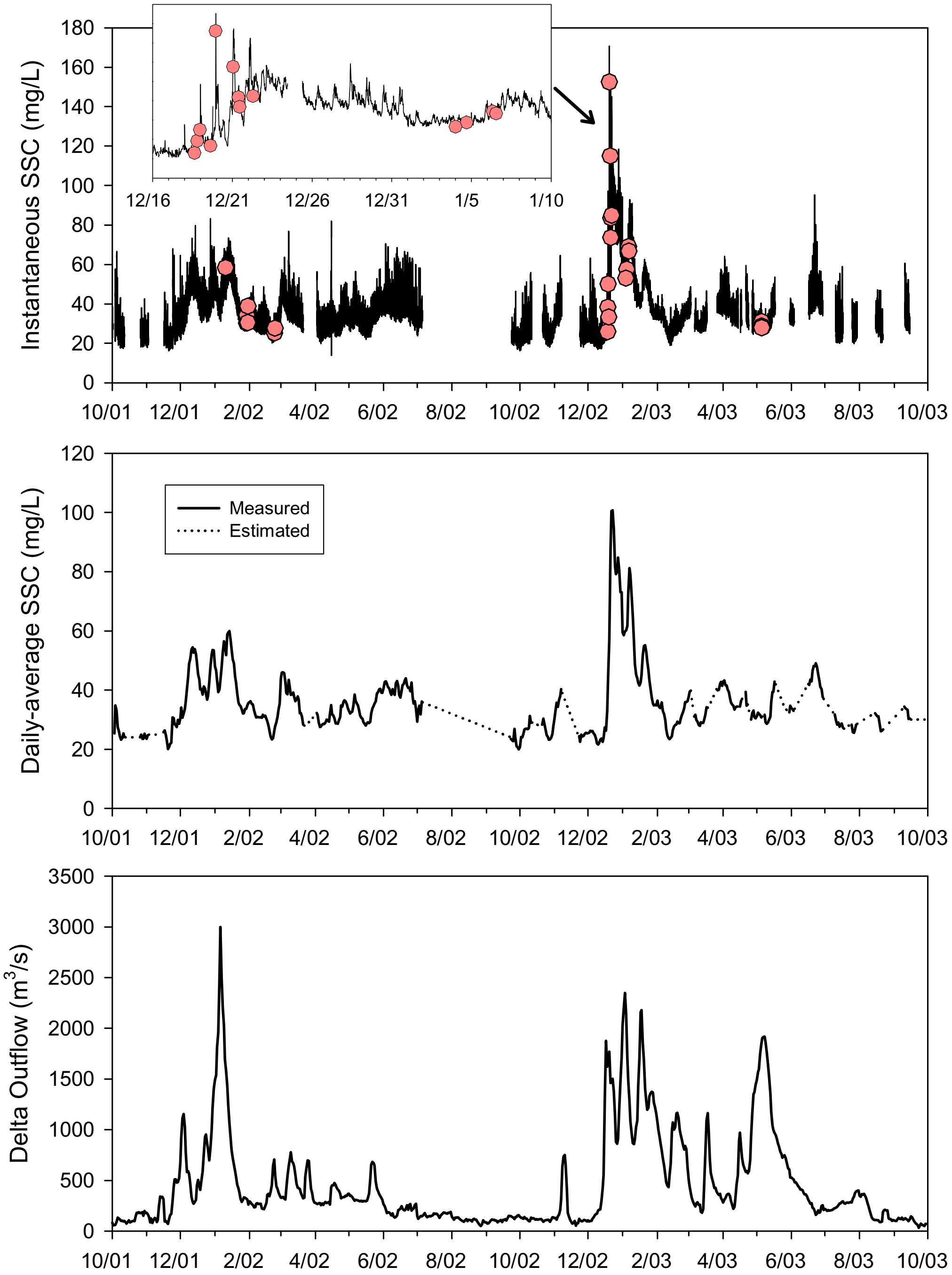

Figure 3.1 Hydrology, suspended sediment concentrations (SSC), and sampling events for organic contaminants at Mallard Island in WY 2002 and WY 2003. Dashed line represents daily-average SSC that was estimated based on linear interpolation (see Section 2).

Table 3.1. Organic contaminants measured at Mallard Island. Listed coeluting PCB congeners have RMP target PCB congeners in bold. Multiple coeluting PCB congeners were added to derive concentrations of target PCB congeners.

ΣPCBs		**ΣPAHs**	**Pesticides**
PCB 008, **008**/5	PCB 118, **118**/106	**ΣLPAHs**	**ΣDDTs**
PCB 018, **018**/30	PCB 128, **128**/166	1-Methylnaphthalene	o,p'-DDD
PCB 028, **028**/20	PCB 132, **132**/168	2,3,5-Trimethylnaphthalene	o,p'-DDE
PCB 031	**132**/153/168	2,6-Dimethylnaphthalene	o,p'-DDT
PCB **033**/020/21, **033**/21	PCB **138**/163/164	2-Methylnaphthalene	p,p'-DDD
PCB 044, **044**/47/65	**138**/129/160/163	Biphenyl	p,p'-DDE
PCB **049**/43, **049**/69	PCB 141	Naphthalene	p,p'-DDT
PCB 052, **052**/73	PCB **149**/139, **149**/147	1-Methylphenanthrene	
PCB 056, **056**/**60**	PCB 151, **151**/135/154	Acenaphthene	**ΣChlordanes**
PCB 060	PCB 153, **153**/168	Acenaphthylene	alpha-chlordane
PCB 066, **066**/80	PCB 156, **156**/157	Anthracene	gamma-chlordane
PCB **070**/**74**/061/76, **070**/76	PCB 158, **158**/160	Fluorene	cis-nonachlor
PCB **074**/61	PCB 170, **170**/190	Phenanthrene	trans-nonachlor
PCB **087**/**97**/86/108/119/125,	PCB 174, **174**/181		heptachlor
087/111/115/116/117,	PCB 177	**ΣHPAHs**	heptachlor epoxide
087/115/116	PCB 180, **180**/193	Benz(a)anthracene	oxychlordane
PCB **095**/93	PCB 183/185	Chrysene	
095/93/98/100/102	PCB 183	Fluoranthene	dieldrin
PCB **097**/86	PCB 187, **187**/182	Perylene	
PCB 099, **099**/83	PCB 194	Benzo(a)pyrene	
PCB **101**/089/90, **101**/090/113	PCB 195	Pyrene	
PCB 105, **105**/127	PCB 201	Benzo(e)pyrene	
PCB 110, **110**/115	PCB 203, 203/196	Benzo(b)fluoranthene	
		Benzo(bjk)fluoranthene	
		Dibenz(a,h)anthracene	
		Benzo(ghi)perylene	
		Indeno(1,2,3-cd)pyrene	

Twenty-five individual PAH congeners were measured to derive concentrations of total PAHs (ΣPAHs), high-molecular weight PAHs (ΣHPAHs), and low-molecular weight PAHs (ΣLPAHs). For each sample, eight liters of water was collected in two 4-liter amber glass bottles.

Samples were also collected for analysis of suspended sediment concentrations (SSC). Turbidity and suspended-sediment data were collected on 15-minute intervals by USGS following methods described in Section 2 of this report. Ancillary water quality data were collected by the Department of Water Resources (DWR) and are available online for Mallard Island (DWR 2004).

3.3.2 Sample Preparation and Analysis

Trace organic contaminants were analyzed by Axys Analytical Services, LTD in Sidney, British Columbia, Canada. Prior to analysis, approximately eight liters for each sample were spiked with $^{13}C_{12}$-labeled standards and filtered. The filtrate was liquid/liquid extracted with dichloromethane (DCM), and the particulate was soxhlet extracted with DCM. Sample extracts were combined and the extract quantitatively split. Approximately one-quarter of the extract was used for PAH analysis, and the remaining three-quarters were used for analyses of PCBs and OC pesticides.

The PAH portion of the extracts was reduced in volume, solvent exchanged to hexane, treated for sulphur and columned on deactivated silica. The extracts were spiked with a labeled recovery (internal) standard prior to instrumental analysis. PAH analyses were performed on extracts using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) performed on an Agilent 6890N GC equipped with an Agilent 5973 MS, an Agilent 7683 Series Autosampler, and an HP Chemstation. A Restek Rt_x-5 chromatography column (30 m, 0.25 mm i.d., 0.25 mm film thickness) was coupled directly to the MS source. The MS was operated at a unit mass resolution in the electron ionization (EI) mode using multiple ion detection (MID) acquiring two characteristic ions for each target analyte and surrogate standard. A splitless/split injection sequence was used.

PCBs and OC pesticides were analyzed following EPA method 1668 revision A (USEPA 1999). The PCB/pesticide portion of extracts was separated into two fractions (fraction E1, containing the PCB congeners and less polar pesticides, and fraction E2, containing the more polar pesticides) using Florisil chromatographic columns. Extracts of the E1and E2 fractions were reduced in volume and separately spiked with labeled recovery (internal) standards prior to instrumental analysis. Analyses of PCB and pesticide extracts were performed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) with a Micromass Autospec Ultima HRMS equipped with an HP 6890 gas chromatograph, a CTC autosampler, and an Alpha data system running Micromass software. PCBs in WY 2002 samples were analyzed using a DB-5 chromatography column (30 m, 0.25 mm i.d., 0.1 µm film thickness) coupled directly to the MS source. PCBs in WY 2003 samples were analyzed using an SPB-Octyl chromatography column (60 m, 0.25 mm i.d., 0.25 µm film thickness) coupled directly to the MS source. Pesticides were analyzed using a DB-5 chromatography column for all samples. The MS was operated at 10,000 (static) mass resolution for PCBs and 8,000 (static) mass resolution for pesticides in the electron impact mode using multiple ion detection, acquiring at least two ions for each target and surrogate compound.

3.3.3 Quality Assurance and Control

Quality assurance and quality control criteria were based on protocols outlined in the RMP Quality Assurance Program Plan (Lowe *et al.* 1999) and in EPA Method 1668, Revision A (USEPA 1999). Quality assurance samples included laboratory blanks, matrix spikes, $^{13}C_{12}$-labeled surrogate recoveries, and duplicate field samples (Table 3.2). Concentrations not measured above limits of quantification were assumed to be zero for calculation of ΣPCBs, ΣDDT, ΣChlordanes, and ΣPAHs. Concentrations in samples with $^{13}C_{12}$-labeled surrogate recoveries outside of method specifications (25-150%) were estimated and qualified (q). Attempts to bring recoveries within the normal range by additional clean-up procedures and reanalysis were not possible for some samples due to complete consumption of the low sample volumes collected in the study. These data have greater uncertainty; however, sample concentrations reported with surrogate recoveries outside of method specifications were not rejected because concentrations fell within the range of reported concentrations in other samples.

3.4 RESULTS

3.4.1 Polychlorinated Biphenyls

Total PCB concentrations ranged from 200 to 6,700 pg/L and exhibited a flow-weighted mean concentration (FWMC) of 1,200 pg/L (Table 3.3). Four samples taken in May 2003 had higher concentrations than samples collected during previous storm events. Review of QA data and ancillary data did not give an explanation for these anomalously high results and did not indicate any blank contamination. In all samples, PCB congeners with less than six chlorine (di, tri, tetra, and pentachlorobiphenyls) comprised 64 to 92% of ΣPCB concentrations. Tetra- and pentachlorobiphenyls were the most predominant congeners in 22 of 24 samples comprising approximately 47 to 85% in those samples. The remaining two samples were dominated by di- and trichlorobiphenyls. Total PCB concentrations were not significantly correlated to SSC ($p > 0.05$; Figure 3.2). Concentrations of individual PCB congeners measured in WY 2002 are listed in Appendix Table 2. Concentrations of individual PCB congeners measured in WY 2003 are listed in Appendix Table 3.

3.4.2 Organochlorine Pesticides

Total DDT concentrations ranged from 240 to 1,600 pg/L and exhibited a FWMC of 720 pg/L (Table 3.3). Total DDT concentrations were comprised primarily of p,p'-DDE (48-66%) with minor contributions from p,p'-DDD (10-30%) and p,p'-DDT (6-20%). Total DDT concentrations were significantly linearly correlated to SSC ($[\Sigma DDT] = 8.4 \times [SSC] + 214$, $r^2 = 0.68$, $p < 0.0001$; Figure 3.2). Total chlordane concentrations ranged from 40 to 180 pg/L with a FWMC of 100 pg/L (Table 3.3). Concentrations of ΣChlordanes were comprised primarily of alpha-chlordane (28-69%) and gamma-chlordane (23-38%). Trans-nonachlor also comprised a large percentage of ΣChlordanes concentrations (21-27%), except in three samples that had concentrations below detection limits. Total chlordane concentrations were significantly linearly correlated to SSC ($[\Sigma Chlor] = 0.70 \times [SSC] + 56$, $r^2 = 0.51$, $p = 0.0002$; Figure 3.2). Dieldrin concentrations ranged from 60 to 250 pg/L with a FWMC of 170 pg/L (Table 3.3) and were significantly correlated to SSC using non-linear regression ($[Diel] = 28 \times [SSC]^{0.43}$, $r^2 = 0.41$, p =

0.0010; Figure 3.2). Concentrations of all pesticide compounds are listed in Appendix Table 4.

3.4.3 Polycyclic Aromatic Hydrocarbons

Total PAH concentrations ranged from 12 to 36 ng/L with a FWMC of 20 ng/L (Table 3.3). High molecular weight PAHs (HPAHs), or PAHs with four aromatic rings or greater, comprised from 38-87% of ΣPAH concentrations. Similar to ΣPCB concentrations, ΣPAH concentrations were not significantly correlated to SSC ($p > 0.05$; Figure 3.2). Concentrations of individual PAH compounds are listed in Appendix Table 5.

Table 3.2 Quality assurance and control summary for organic contaminants. DF = detection frequency, MDL = method detection limit, ND = below detection limit. Accuracy is the range of matrix spike recoveries in QA samples.

Parameter	**MDL Range**	**Lab Blanks**	**Field Samples**	**DF**	**Accuracy**
Pesticides	pg/L	pg/L	pg/L	%	%
o,p'-DDD	1.5 - 18	ND	28 - 87	100	83 - 195
o,p'-DDE	1.1 - 20	ND	ND - 31	87	62 - 115
o,p'-DDT	2.7 - 29	ND	ND - 47	83	79 - 106
p,p'-DDD	1.7 - 24	ND	66 - 200	100	96 - 145
p,p'-DDE	1.8 - 30	ND	150 - 900	100	93 - 108
p,p'-DDT	3.5 - 40	ND	22 - 310	100	95 - 104
alpha-chlordane	3.0 - 34	ND	19 - 61	100	88 - 169
gamma-chlordane	2.6 - 29	ND	14 - 53	100	95 - 156
cis-nonachlor	9.0 - 12	ND	ND - 17	26	98 - 146
trans-nonachlor	3.8 - 41	ND	ND - 49	87	95 - 176
heptachlor	0.58 - 2.6	ND	ND - 3.5	19	94 - 136
heptachlor epoxide	0.38 - 8.3	ND - 3.1	ND - 23	96	51 - 102
oxychlordane	2.8 - 4.2	ND	ND - 7.5	17	89 - 123
dieldrin	1.0 - 12	ND - 16	60 - 240	100	72 - 102
ΣPAHs	ng/L	ng/L	ng/L	%	%
1-Methylnaphthalene	0.075 - 0.38	0.28 - 1.2	0.54 - 2.7	100	86 - 117
2,3,5-Trimethylnaphthalene	0.058 - 0.50	ND - 0.20	0.28 - 1.0	100	114 - 141
2,6-Dimethylnaphthalene	0.049 - 0.34	ND - 0.53	ND - 1.4	91	83 - 113
2-Methylnaphthalene	0.066 - 0.34	0.75 - 1.8	0.98 - 3.7	100	84 - 114
Biphenyl	0.045 - 0.19	ND - 0.46	0.31 - 0.77	100	97 - 123
Naphthalene	0.093 - 0.30	1.4 - 2.9	ND - 4.6	91	83 - 111
1-Methylphenanthrene	0.058 - 0.19	ND - 0.72	ND - 5.9	78	107 - 167
Acenaphthene	0.086 - 0.16	ND - 0.18	ND - 1.8	35	84 - 116
Acenaphthylene	0.054 - 0.15	ND - 0.18	ND - 0.45	43	81 - 99
Anthracene	0.039 - 0.15	ND - 0.13	ND - 0.47	78	67 - 82
Dibenz(a,h)anthracene	0.050 - 0.11	ND	ND - 0.29	26	82 - 121
Fluorene	0.045 - 0.20	ND - 0.89	ND - 1.2	78	56 - 94
Phenanthrene	0.035 - 0.20	0.17 - 0.99	0.80 - 3.3	100	83 - 111
Benz(a)anthracene	0.031 - 0.13	ND - 0.089	ND - 1.3	74	77 - 102
Chrysene	0.024 - 0.16	ND - 0.13	0.56 - 3.4	100	81 - 117
Fluoranthene	0.020 - 0.23	0.063 - 0.24	0.70 - 3.3	100	79 - 113
Pyrene	0.025 - 0.22	0.061 - 0.54	1.2 - 4.3	100	81 - 107
Benzo(a)pyrene	0.081 - 0.42	ND	0.44 - 2.1	100	39 - 101
Benzo(e)pyrene	0.060 - 0.42	ND	0.41 - 2.5	100	89 - 146
Benzo(bjk)fluoranthene	0.055 - 0.47	ND - 0.23	0.77 - 3.7	100	81 - 112
Perylene	0.086 - 0.49	ND	0.75 - 3.0	100	9 - 127
Benzo(ghi)perylene	0.070 - 0.61	ND	ND - 2.5	87	81 - 105
Indeno(1,2,3-cd)pyrene	0.063 - 0.58	ND - 0.091	ND - 1.6	82	80 - 98

Table 3.2 (continued). Quality assurance and control summary for organic contaminants. DF = detection frequency, MDL = method detection limit, ND = below detection limit. Accuracy is the range of matrix spike recoveries in three QA samples.

Parameter	MDL Range	Lab Blanks	Field Samples	DF	Accuracy
ΣPCBs	pg/L	pg/L	pg/L	%	%
PCB 001					98 - 130
PCB 003					98 - 125
PCB 004					105 - 125
PCB 008/5*	0.31 - 0.99	ND - 1.4	1.7 - 140	100	
PCB 015					99 - 118
PCB 018/30*	0.055 - 0.28	0.72 - 1.9	4.9 - 79	100	
PCB 019					101 - 128
PCB 028/20*	0.068 - 0.88	0.84 - 5.3	7.4 - 130	100	
PCB 031	0.066 - 0.73	0.50 - 4.1	4.3 - 130	100	
PCB 033/20/21*	0.068 - 0.41	0.44 - 4.0	2.0 - 66	100	
PCB 037					99 - 121
PCB 044/47/65*	0.047 - 0.38	0.31 - 4.9	8.8 - 410	100	
PCB 049/43/69*	0.043 - 0.32	0.31 - 2.0	6.8 - 230	100	
PCB 052/73*	0.047 - 0.34	0.32 - 2.9	15 - 1,180	100	
PCB 054					100 - 124
PCB 056	0.20 - 1.2	ND -3.3	3.2 - 50		
PCB 060/56	0.15 - 0.27	0.12 - 0.84	2.8 - 16	100	
PCB 060	0.20 - 1.2	ND -1.8	1.7 - 27	100	
PCB 066/80*	0.071 - 1.1	0.21 - 4.5	5.1 - 160	100	
PCB 070/074/61/76*	0.077 - 1.1	0.31 - 7.0	2.9 - 570	100	
PCB 077					96 - 107
PCB 081					97 - 107
PCB 087/86*	0.12 - 1.6	ND -1.9	3.2 - 370	100	
PCB 095/93/98/100/102*	0.11 - 0.95	ND -1.0	ND - 845	96	
PCB 097/87/86/108/119/125*	0.12 - 2.5	ND -1.9	3.4 - 22	100	
PCB 099/83*	0.14 - 1.7	ND -1.2	5.3 - 370	100	
PCB 101/89/90/113*	0.12 - 2.1	0.37 - 1.8	13 - 780	100	
PCB 104					100 - 129
PCB 105	0.15 - 1.2	0.14 - 1.1	2.9 - 50	100	98 - 116
PCB 110/115*	0.096 - 1.6	0.45 - 2.1	11 - 440	100	
PCB 114					99 - 118
PCB 118/106*	0.14 - 1.2	ND - 1.4	7.3 - 190	100	100 - 117
PCB 123					98 - 113
PCB 126					96 - 116
PCB 128/166*	0.12 - 0.75	ND - 0.25	1.4 - 9.7	100	
PCB 132/153/168	0.12 - 0.90	ND - 0.48	3.5 - 54	100	
PCB 138/129/160/163*	0.12 - 0.74	0.38 - 1.2	10 - 82	100	

Table 3.2 (continued). Quality assurance and control summary for organic contaminants. DF = detection frequency, MDL = method detection limit, ND = below detection limit. Accuracy is the range of matrix spike recoveries in three QA samples.

Parameter	MDL Range	Lab Blanks	Field Samples	DF	Accuracy
ΣPCBs	pg/L	pg/L	pg/L	%	%
PCB 141	0.14 - 0.82	ND - 0.31	1.5 - 19	100	
PCB 149/139/147*	0.13 - 0.76	0.29 - 0.85	9.0 - 150	100	
PCB 151/135/154*	0.050 - 0.488	ND - 0.26	2.4 - 70	100	
PCB 153/132/168*	0.10 - 0.65	ND - 1.2	10 - 86	100	
PCB 155					102 - 124
PCB 156/157*	0.095 - 0.76	ND - 0.25	0.71 - 3.8	100	93 - 115
PCB 157					96 - 118
PCB 158	0.095 - 0.59	ND - 0.086	0.75 - 8.9	100	
PCB 167					97 - 119
PCB 169					88 - 111
PCB 170/190*	0.020 - 0.35	ND - 0.30	2.3 - 7.3	100	
PCB 174/181*	0.019 - 0.39	ND - 0.59	ND - 12	96	
PCB 177	0.020 - 0.43	ND - 0.13	1.9 - 6.9	100	
PCB 180	0.016 - 0.38	ND - 0.68	4.9 - 21	100	
PCB 183185*	0.018 - 0.35	ND - 0.20	1.6 - 10	100	
PCB 187/182*	0.017 - 0.36	ND - 0.49	4.2 - 21	100	
PCB 188					98 - 126
PCB 189					93 - 117
PCB 194	0.028 - 0.45	ND - 0.14	1.1 - 4.1	100	
PCB 195	0.031 - 0.54	ND - 0.078	ND - 2.3	88	
PCB 201	0.019 - 0.41	ND	0.26 - 1.5	100	
PCB 202					90 - 123
PCB 203/196	0.022 - 0.50	ND - 0.17	1.2 - 4.6	100	
PCB 205					91 - 116
PCB 206					92 - 114
PCB 208					94 - 117
PCB 209					90 - 113

Table 3.3 Summary of Delta Outflow Index (DOI), suspended sediment concentrations (SSC), and concentrations of selected organic contaminants at Mallard Island. e = estimated, NA = not analyzed, q = concentration estimated based on low surrogate recovery. Q = concentration comprised of greater than 30% of summed individual concentrations estimated based on low surrogate recoveries.

DATE	TIME	DOI m^3/s	SSC mg/L	COND mS/cm	ΣPCB pg/L	ΣPAH ng/L	ΣLPAH ng/L	ΣHPAH ng/L	ΣDDT pg/L	DDD pg/L	DDE pg/L	DDT pg/L	ΣCHL pg/L	ACHL pg/L	GCHL pg/L	TNON pg/L	DIEL pg/L
1/10/02	15:30	1,696	58.3	0.16	309	NA	NA	NA	1,100	273	715	112	111	39	27	25	60
1/29/02	10:40	321	30.2	1.73	433	19	8.9	10	462	134	282	46	41	21	14	ND	63
1/29/02	15:40	321	34.3	5.39	635	25	10	15	519	151	317	51	56	20	16	14	85
1/30/02	11:40	309	30.5	1.52	663	16	8.8	7.4	505	145	317	43	56	19	14	12	80
1/30/02	15:50	309	38.7	4.41	358	33	12	22	530	160	324	46	68	21	18	14	77
2/23/02	11:50	706	25.2	6.98	202	23	14	9.2	342	135	174	e 33	74	24	18	15	119
2/23/02	20:12	706	27.6	1.13	258	23	14	8.7	390	143	208	e 40	72	23	19	16	117
12/18/02	15:04	1,621	25.2	4.61	699	19	Q 7.5	11	460	162	249	49	94	31	27	23	161
12/18/02	19:35	1,621	39.5	3.34	613	14	6.9	6.7	500	162	266	73	113	40	30	27	210
12/18/02	22:55	1,621	52.8	1.57	439	12	Q 1.5	11	1,298	243	788	q 266	168	47	38	37	249
12/19/02	15:17	1,726	33.7	6.08	Q 601	36	Q 10	25	Q 541	q 209	268	q 64	105	38	28	26	164
12/19/02	23:04	1,726	171	1.55	Q 846	21	Q 9.1	12	Q 1,553	q 263	929	q 361	178	55	53	49	240
12/21/02	1:05	1,459	128	0.71	Q 709	23	13	10	Q 1,240	q 189	q 840	q 211	126	36	32	30	225
12/21/02	9:15	1,459	91.3	1.06	475	Q 20	Q 10	Q 9.8	1,136	193	748	q 195	126	40	34	30	227
12/21/02	11:21	1,459	80.0	1.13	503	20	10	10	1,115	194	722	199	135	37	31	32	221
12/22/02	7:35	1,467	92.9	0.98	Q 628	23	Q 11	12	Q 986	q 218	614	q 154	134	46	34	33	219
1/4/03	17:00	2,132	61.5	0.33	476	20	12	8.3	495	125	298	72	75	23	24	16	160
1/5/03	0:13	1,697	58.1	0.32	684	16	Q 8.4	7.2	574	130	366	78	77	22	23	20	183
1/6/03	7:54	1,480	74.7	0.27	318	16	8.6	7.4	575	132	e 367	76	84	26	24	23	179
1/6/03	12:58	1,480	72.1	0.29	370	22	12	9.2	631	129	417	85	87	30	23	21	179
5/5/03	11:30	1,844	31.0	0.17	6,677	Q 17	6.2	Q 10	Q 260	q 100	q 160	NA	Q 88	e 61	q 23	ND	78
5/5/03	14:00	1,844	28.3	0.18	3,853	Q 21	Q 7.1	Q 13	NA	NA	NA	NA	NA	NA	NA	NA	205
5/5/03	14:20	1,844	27.5	0.18	1,828	14	5.9	8.4	Q 241	q 93	q 148	NA	Q 56	q 31	q 21	ND	e 91
5/6/03	12:00	1,904	36.0	0.17	883	23	14	Q 9.5	Q 287	q 105	q 182	NA	Q 72	q 26	q 22	q 16	101

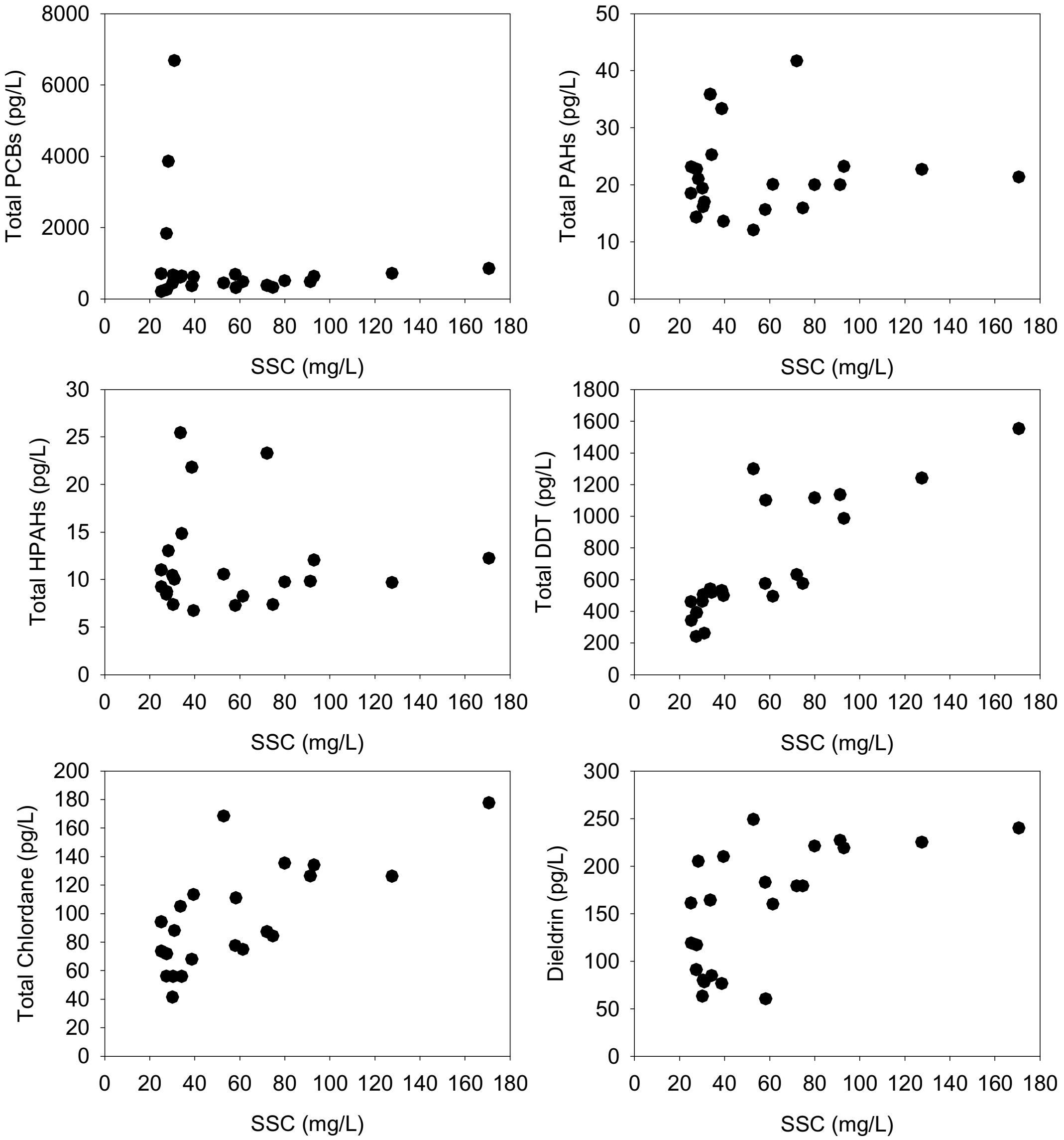

Figure 3.2 Relationships between organic contaminant concentrations and SSC.

3.5 DISCUSSION

3.5.1 Comparisons to Other Studies

Concentrations of organic contaminants measured in this study were compared to results from previous studies conducted in close proximity to Mallard Island to evaluate potential temporal (seasonal and annual) and spatial variability associated with transport processes driving contaminant fluxes between the Sacramento and San Joaquin Rivers and San Francisco Bay. The most suitable water-column concentration data available for comparison were collected by the RMP Status and Trends Program from 1993 to 2001 over a range of hydrologic conditions at nearby locations in Sacramento River (BG20), San Joaquin River (BG30), and Grizzly Bay (BF20) (Table 3.4). In addition, the USGS conducted a study at Mallard Island to measure pesticide concentrations on suspended sediment during the first flush storms of WY 1996 (Bergamaschi *et al.* 2001) (Table 3.5). The USGS also conducted several other studies to measure sediment-associated organic contaminants in the Delta (Domagalski and Kuivila 1993), Sacramento River (Bergamaschi *et al.* 1997), and San Joaquin River (Kratzer 1999, Pereira *et al.* 1996). In all USGS studies, concentrations were measured for pesticides directly associated with suspended sediment (in µg/kg).

Concentrations of OC pesticides in this study were consistent with concentrations previously measured at RMP stations, (Table 3.4). Total DDT concentrations were more reflective of differences in SSC than the other pesticides, which was likely due to the strong dependence of ΣDDT concentrations on SSC observed in Mallard Island samples (Figure 3.2). Concentrations of ΣPAHs measured at Mallard Island were higher than concentrations measured at the RMP river stations (BG20 and BG30), but were more consistent with concentrations measured at Grizzly Bay (BF20). Observed differences in PAH concentrations between Mallard Island and upstream RMP river stations could be attributed to several reasons that were not confirmed in the study. For example, several municipal and industrial facilities discharge into waters between RMP river stations and Mallard Island, which potentially increase PAH concentrations in surface waters (Culp *et al.* 2002). Furthermore, Mallard Island water samples may have been influenced to a greater extent by more contaminated sediments from seaward locations in the Bay [e.g. Grizzly Bay (BF20)] compared to upstream RMP river stations.

For ΣPCBs, highest concentrations were measured at Mallard Island, but were heavily influenced by concentrations measured in the last four samples collected during the final storm of the study period in May 2003. As previously noted, total PCB concentrations in those four samples (883 to 6,700 pg/L) were higher than concentrations measured in the 21 samples collected previously in this study. Excluding May 2003 data, ΣPCB concentrations ranged from 200 to 850 pg/L (with an average of 510 pg/L), which are more consistent with concentrations measured in previous years by the RMP. The source of high ΣPCB concentrations in the May 2003 storm was not identified and will be explored further through subsequent sampling in WY 2004. Total PCB concentrations were not significantly correlated to suspended sediment concentrations ($p > 0.05$) (Figure 3.2). This was also apparent in RMP data (Hunt *et al.* 2004).

Table 3.4. Water column concentrations at Mallard Island compared to RMP Status and Trends monitoring data. Note there has not been a methods comparison completed.

Location	SSC (or TSS) mg/L	ΣPCBs pg/L	ΣPAHs ng/L	ΣDDTs pg/L	ΣChlordanes pg/L	Dieldrin pg/L
Mallard Island - This Study	54 (25 - 152)	980 (200 - 6,700)	22 (12 - 36)	680 (240 - 1,600)	95 (41 - 180)	150 (60 - 250)
RMP - Sacramento River (BG20)	40 (10 - 174)	240 (54 - 790)	8.4 (3.0 - 15)	680 (280 - 1,800)	140 (58 - 300)	130 (2.0 - 380)
RMP - San Joaquin River (BG30)	28 (11 - 70)	200 (66 - 700)	7.1 (2.8 - 15)	450 (180 - 1,000)	130 (26 - 250)	110 (2.0 - 330)
RMP - Grizzly Bay (BF20)	85 (10 - 371)	500 (80 - 2,300)	30 (5.8 - 97)	970 (340 - 3,100)	130 (7.6 - 250)	92 (4.8 - 280)

Table 3.5. Concentrations of OC pesticides on suspended sediment (μg/kg).

Location	Study Period	ΣDDTs	DDD	DDE	DDT	ΣChlordanes
Mallard Island - This Study	1/02 - 5/03	8.4 (5.7 – 11)	0.73 (0.20 – 1.3)	5.5 (3.8 – 7.3)	2.0 (1.4 – 2.6)	0.70 (0.38 – 1.0)
Mallard Island[1]	12/95	8.0 (5.1 - 11)	1.8 (1.0 - 3.3)	4.2 (2.6 - 6.9)	2.0 (0.9 - 4.4)	1.2 (0.30 - 2.7)
Chipps Island[5]	4/91	-	-	6.5 - 10	-	-
Sacramento River at Tower Bridge[2]	3/92 - 2/94	-	-	1.5	-	-
San Joaquin River at Vernalis[2]	12/92	-	0.6	16.6	7.3	-
San Joaquin River at Vernalis[3]	6/94, 1/95	240, 170	16, 17	150, 97	70, 58	21, 43
San Joaquin River at Patterson[4]		75	10	61	4.4	18

[1] Bergamaschi *et al.* 2001
[2] Bergamaschi *et al.* 1997
[3] Kratzer 1999
[4] Pereira *et al.* 1996
[5] Domagalski and Kuivila 1993

Mallard Island concentrations of DDT compounds and ΣChlordanes were compared to USGS suspended sediment concentrations by converting water-column concentrations in this study to particle-normalized concentrations (units in µg/kg dry weight) using the linear relationships between pesticide concentrations and SSC in Figure 3.2. Particle-normalized concentrations were estimated based on slopes of the pesticide-SSC regressions, whereas ranges of concentrations were based on 95% confidence intervals of each slope. This normalization also assumes that the entire mass of pesticides is associated with the particulate fraction. For example, a ΣDDT concentration of 8.4 µg/kg dry wt and range of 5.7 to 11 µg/kg dry wt on suspended sediment at Mallard Island (this study) was estimated based on the slope of the regression in Figure 3.2 and the 95% confidence intervals of the regression. Regressions for DDD, DDE, and DDT (p,p' + o,p'-isomers) are not shown.

Concentrations of DDT compounds and ΣChlordanes associated with suspended sediment derived in this study were consistent with concentrations measured directly by Bergamaschi *et al.* (2001) (Table 3.5). This suggests that processes involved with transporting these pesticides to the Bay from the Central Valley have remained relatively constant over nearly the past decade, as well as on shorter time scales of seasons and storm events. Compared to results from San Joaquin River, concentrations of DDT and chlordane compounds were lower at Mallard Island, Chipps Island, and upstream locations on the Sacramento River. This supports findings from Bergamaschi *et al.* (2001) and indicates that concentrations of pesticides associated with suspended sediment at Mallard Island reflect dominant inputs of suspended sediment to the Bay from Sacramento River.

3.5.2 Concentrations During Sequential Storms

To further understand the influence of storm events on the transport of sediment-associated organic contaminants between the Sacramento-San Joaquin River Delta and the Bay, sediment and contaminant concentrations were evaluated in relation to Delta outflow in samples collected during three storms in WY 2003 (Figures 3.3 – 3.7). A first flush phenomenon, indicated by first storms of the year showing high SSC concentrations relative to later storms, has previously been reported for suspended sediments in the Delta (Goodwin and Denton 1991, Ruhl and Schoellhamer 1998, Oltmann *et al.* 1999) and was demonstrated again in this study (see Section 2 of this report).

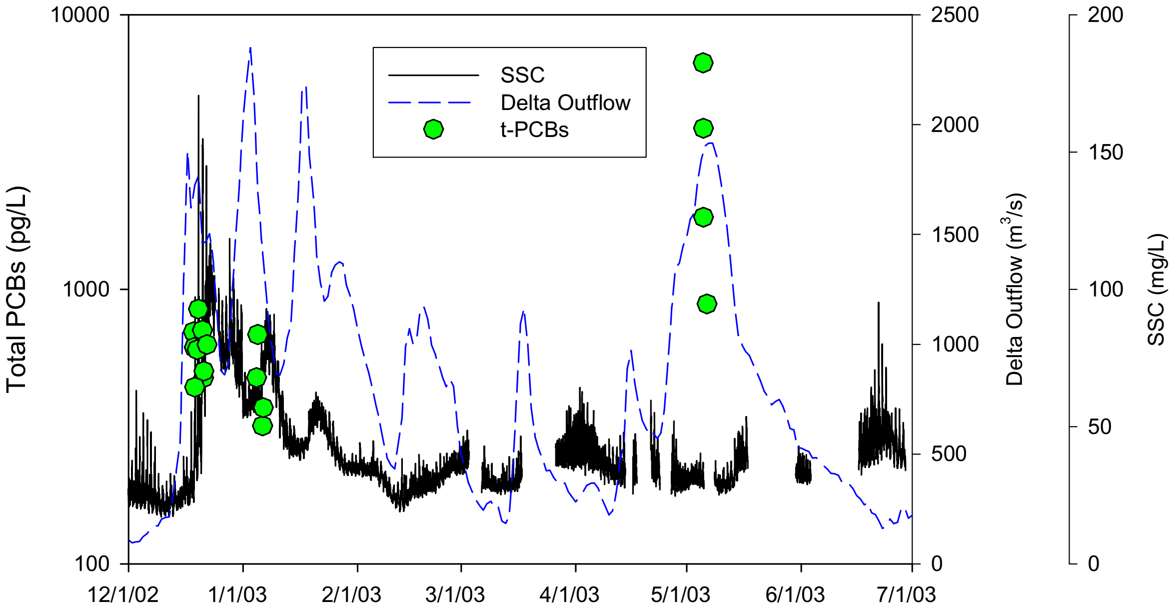

Figure 3.3 Total PCB concentrations relative to suspended sediment concentrations and discharge during WY 2003.

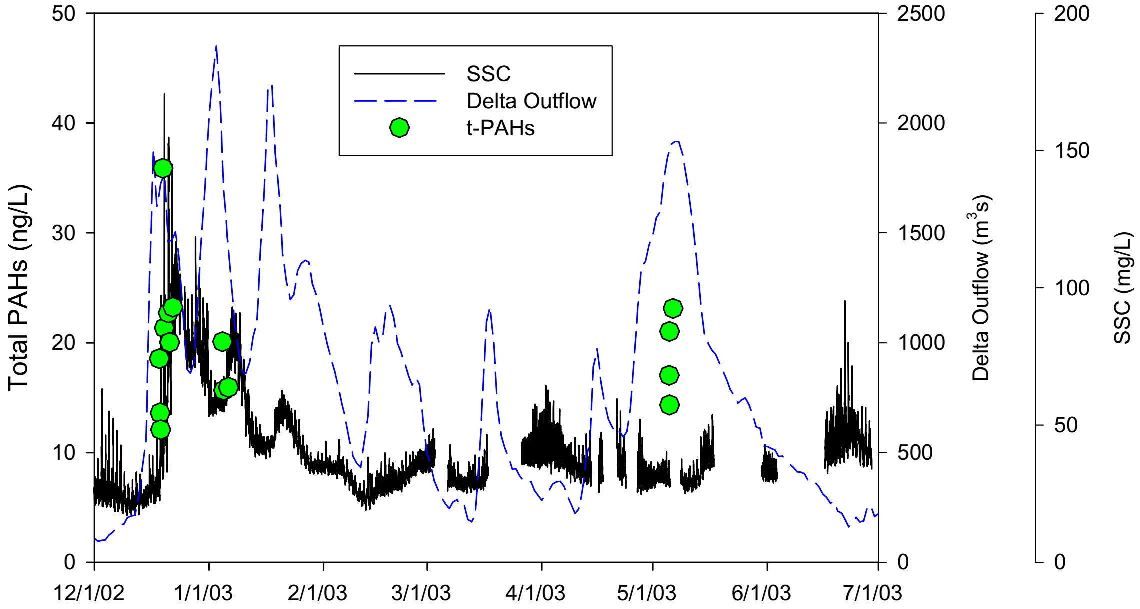

Figure 3.4 Total PAH concentrations relative to suspended sediment concentrations and discharge during WY 2003.

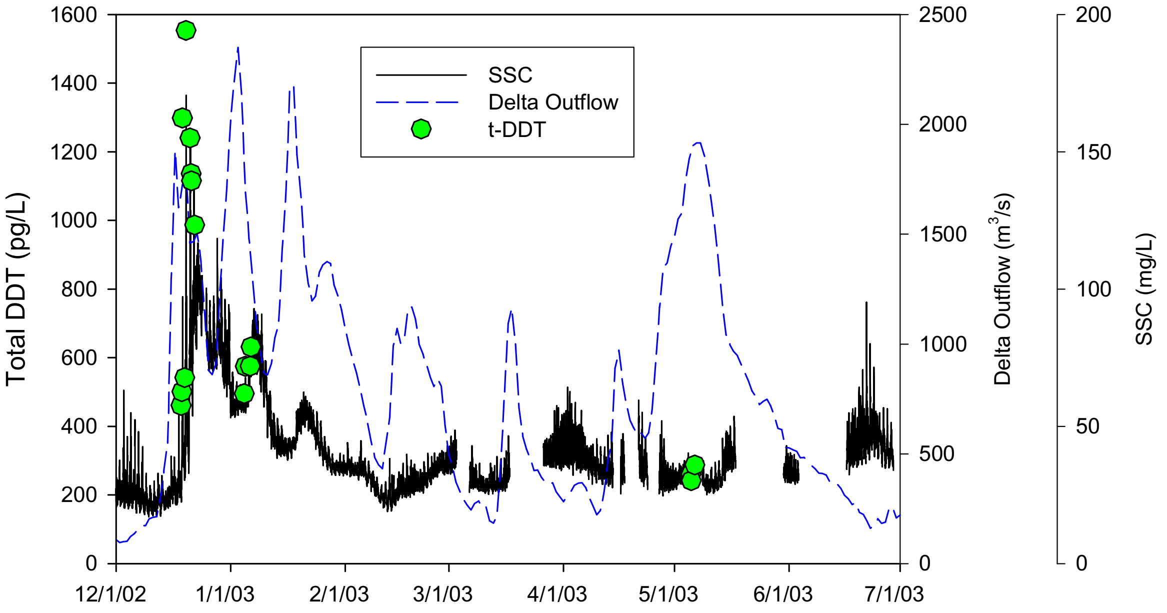

Figure 3.5 Total DDT concentrations relative to suspended sediment concentrations and discharge during WY 2003.

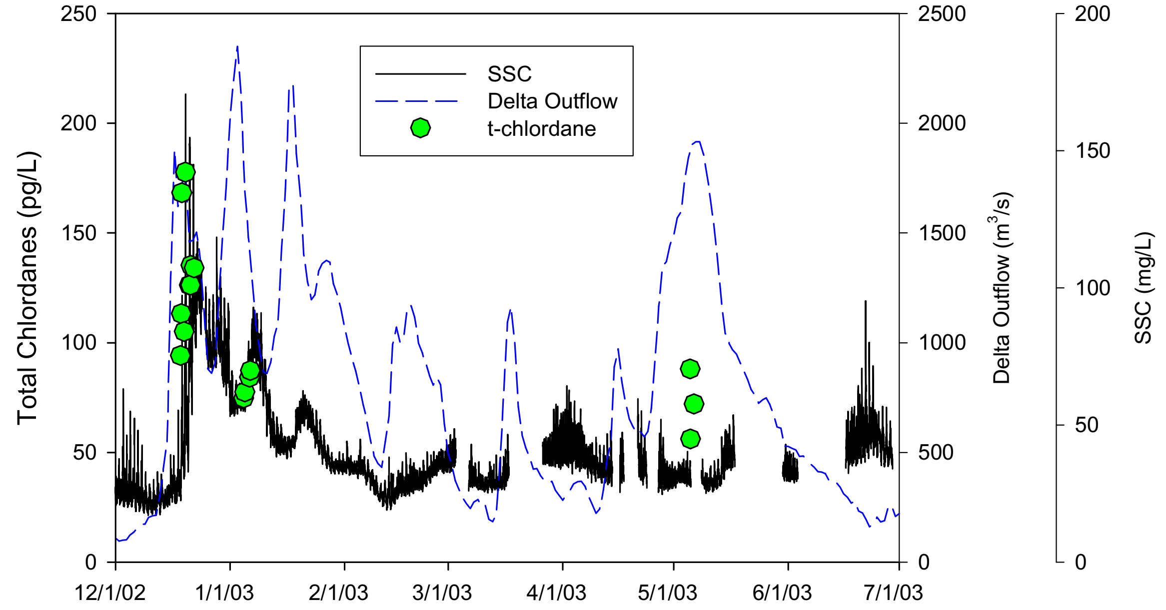

Figure 3.6 Total chlordane concentrations relative to suspended sediment concentrations and discharge during WY 2003.

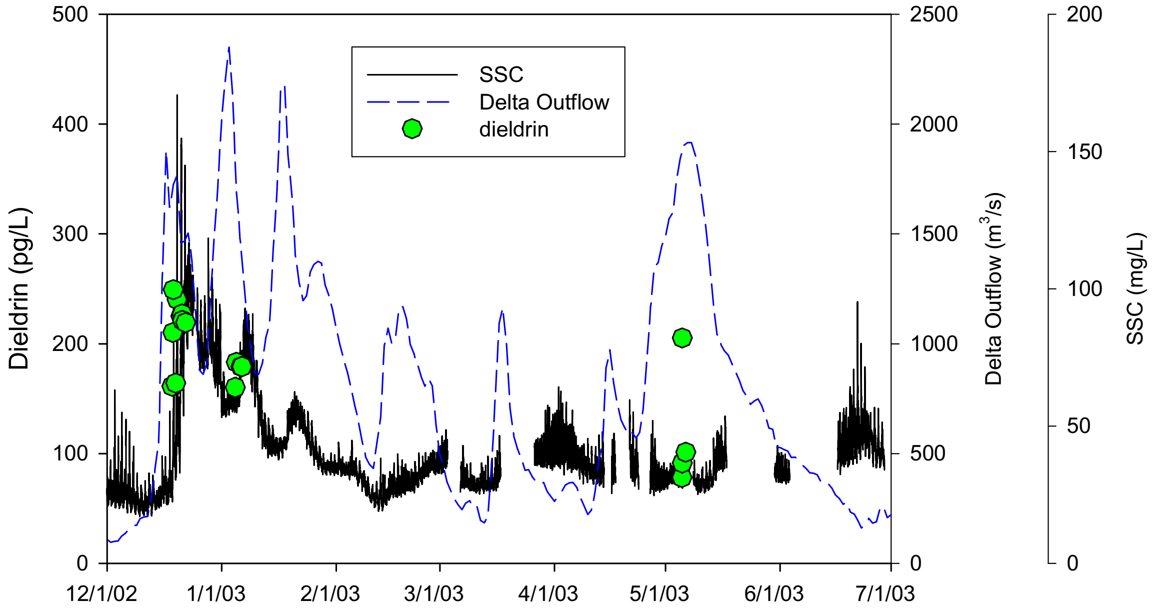

Figure 3.7 Dieldrin concentrations relative to suspended sediment concentrations and discharge during WY 2003.

A first flush effect was not observed for concentrations of ΣPCBs (Figure 3.3) and ΣPAHs (Figure 3.4). As discussed previously, the highest ΣPCB concentrations were measured in early May 2003 during a storm with relatively high discharge, but low SSC. Total PAH concentrations measured in the May 2003 storm were also of similar magnitude to concentrations in previous storms with much higher SSC. The cause of the spikes in PAH and PCB concentrations during the May 2003 storm were not identified but may have been due to an episodic pulse of contaminated material transported to the site, possibly from urban runoff, or longer-term seasonal variability in contaminant behavior at this location.

In contrast, concentrations of OC pesticides were more consistent with patterns of SSC over the course of the different storm events. Highest OC pesticide concentrations were measured during the first storm and decreased in subsequent storms (Figures 3.5 – 3.7). These patterns are consistent with the observed correlations between OC pesticides and SSC (Figure 3.2). Concentrations of dieldrin and ΣChlordanes in one sample collected in May 2003 were similar in magnitude to samples collected during previous storms despite the associated low SSC. The phenomena responsible for increased PAH and PCB concentrations may have had similar effects on dieldrin and chlordane concentrations at Mallard Island.

3.5.3 Tidal Influences

The interaction of tidal and riverine sources of sediment and water at Mallard Island and other estuarine regions of the Bay create highly dynamic conditions that influence the distribution and transport of organic contaminants (Bergamaschi *et al.* 2001, Domagalski and Kuivila 1993). Bergamaschi *et al.* (2001) previously determined that concentrations of several pesticides measured on suspended sediment at Mallard Island during the first flush storm event of WY 1996 differed over tidal cycles in response to varying sources of sediment associated with freshwater flow and tidal mixing.

To determine potential tidal influences on contaminant concentrations in this study, nine samples collected during the first flush storm of WY 2003 (December 18 to December 22, 2002) were evaluated with respect to SSC and conductivity as an indicator of salinity and tidal stage (Figure 3.8). On December 17th, conductivity began decreasing from a range of 6 to 19 mS/cm to a constant value of less than 1 mS/cm from December 23rd to December 28th. In nine samples collected from December 18th to 22nd, conductivity ranged from 6.1 to 0.7 mS/cm with conductivity increasing during flood (or incoming) tides and decreasing during ebb (or outgoing tides). The gradual decrease in conductivity over the period of sampling showed a gradual increase in freshwater (or riverine) influence. For purposes of this evaluation, samples were categorized as primarily river-influenced with conductivity less than 2 mS/cm (6 samples), and the remaining three samples were considered Bay-influenced. This conductivity boundary was selected for this evaluation because samples collected during low tides, which represented the end-member of the tidal cycle most indicative of riverine sources, were dominated by water with conductivity less than 2 mS/cm.

In river-influenced samples, ΣPCB concentrations were significantly linearly correlated to SSC ($r^2 = 0.90$, slope = 3.6, $p = 0.0036$) (Figure 3.8). Bay-influenced samples, however, had higher concentrations than river-influenced ΣPCBs relative to SSC. Less distinct patterns were observed for ΣPAHs and ΣHPAHs; however, the highest concentrations were measured in the sample collected during slack (still water) after the flood tide associated with the highest conductivity. In a previous study at Chipps Island (in close proximity to Mallard Island), PAH concentrations on suspended sediment were approximately 3.5 times greater during flood tide than on the ebb tide (Domagalski and Kuivila 1993). Furthermore, PAH concentrations in spring were lower than in summer likely due to dilution of Bay sediments with incoming agricultural soils low in PAH concentrations (Domagalski and Kuivila 1993). Results from this study in the context of previous studies support the hypothesis that contaminants associated primarily with urban sources and persistent in Bay sediment, such as PCBs and PAHs (and possibly chlordanes) are higher in concentration on sediment transported upstream from the Bay during flood tides compared to incoming sediment from the Rivers.

In contrast to patterns of PCBs and PAHs, concentrations of ΣDDT, ΣChlordanes, and dieldrin did not reveal two separate sources of sediment (Figure 3.8). This could be attributed to greater influence of river sediment on pesticide concentrations measured in the northern regions of the Estuary. Consistent concentrations of ΣDDT over the tidal

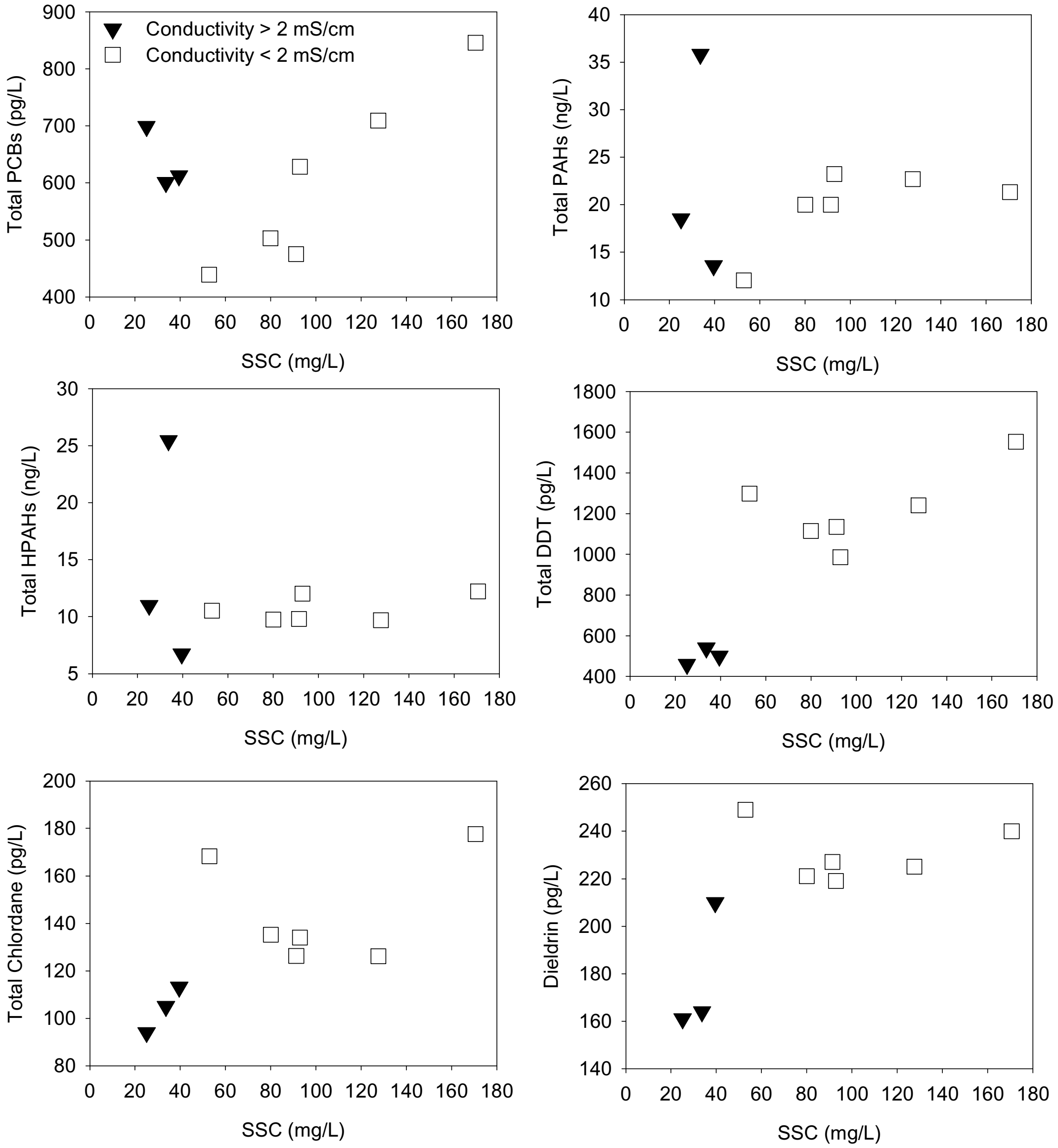

Figure 3.8 Relationships between organic contaminants and SSC in relation to conductivity.

cycle support findings from Bergamaschi *et al.* (2001) in WY 1996; however, that study found that chlordane concentrations varied with the tides and were higher in Bay sediment that was presumably carried upstream with the tides compared to river sediment. Thus, patterns of ΣChlordanes contamination caused by varying sources of sediment are likely to be more complex than for the other pesticides. Nevertheless, ΣDDT and dieldrin concentrations had consistent concentrations relative to suspended sediment over the tidal cycle, suggesting that concentrations of these pesticides have reached a more equilibrated state between Bay and riverine sources of sediment.

In summary, study results indicate that ΣPCB and ΣPAH concentrations are greater in samples comprised predominantly of Bay sediment carried upstream on ebb tides, whereas pesticide concentrations at Mallard Island are influenced to a greater extent by incoming river sediment.

3.5.4 Potential Sources of Organic Contaminants

Previous studies on organic contaminants in the Bay and its watershed have inferred potential contaminant sources and relative degrees of contaminant degradation or dissipation by evaluating the relative abundances of PCB congeners (Jarman *et al.* 1995, Johnson *et al.* 1997), DDT compounds (Pereira *et al.* 1996, Bergamaschi *et al.* 2001, Kratzer 1999), and PAH compounds (Oros and Ross 2004, Ross and Oros 2004). Similar rationale was used in this study to develop hypotheses about the sources of sediment and associated contaminants transported to the Bay via the Sacramento and San Joaquin Rivers.

Results from this study and previous studies indicate that sources of PCBs in the Delta region are relatively unique compared to other regions of the Bay. The relative abundances of individual PCB congeners (or homologs grouped by number of chlorine atoms) in Mallard Island samples were comprised predominantly of low-molecular weight PCBs. As previously noted, PCB homologs with less than six chlorines comprised 64 to 92% of ΣPCB concentrations, whereas tetra- and pentachlorobiphenyls comprised 47 to 85% (Figure 3.9). Even PCB homolog patterns associated with the anomalously high concentrations in the May 2003 storm showed similarly dominant contributions of relatively low-molecular weight PCBs (78-85% tetra-and penta CBs); however, these samples had slightly different homolog patterns than previously collected samples, possibly due to different sources of PCBs sampled during that storm.

RMP water samples collected in previous years in this region showed unique PCB congener distributions indicative of a mixture of multiple Aroclors (original technical mixtures of PCBs) that have been moderately degraded (Jarman *et al.* 1997). Samples had contributions of PCBs associated with highly chlorinated Aroclors 1254 and 1260, but also had substantial contributions of PCBs indicative of less-chlorinated Aroclors, such as Aroclors 1026 and/or 1242 (Jarman *et al.* 1997). This pattern decreased seaward across the northern regions of the Estuary and gave way to patterns indicative of heavier chlorinated Aroclors in the rest of the Bay (Jarman *et al.* 1997). The patterns at Mallard Island and in the Delta are vastly different than those found in water samples collected in an urbanized reach of the Guadalupe River, which drains into Lower South San Francisco Bay (Leatherbarrow and McKee 2004). In Guadalupe River samples, approximately 50 to 75% of total PCB mass was comprised of PCB congeners with six (hexa-) or more chlorines. This suggests that sources and processes driving PCB transport through the Sacramento/San Joaquin River Delta are unique relative to sources of PCB contamination in other regions of the Bay and heavily urbanized watersheds.

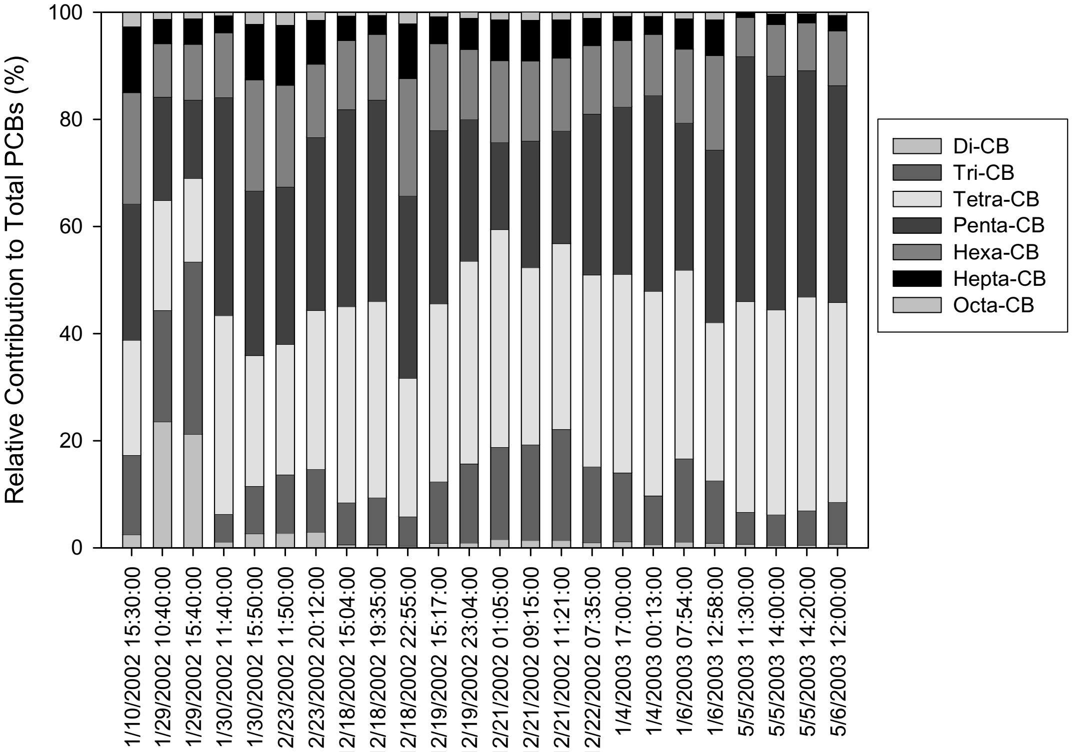

Figure 3.9 Relative abundance of PCB homologs.

The unique signature of PCB congeners and, in particular, the predominance of low-molecular weight congeners, likely reflect either relatively fresh or unweathered sources of PCBs or a large atmospheric contribution to measured concentrations. Given that microbial degradation and volatilization favor rapid removal of less-chlorinated PCBs compared to heavier congeners (Chang *et al.* 2001, Bushart *et al.* 1998, Farley *et al.* 1994), presence of the lower-molecular weight PCB congeners potentially indicates recent introduction of PCBs to the water column. High proportions of less-chlorinated congeners have also been attributed to inputs from direct or indirect (*i.e.* runoff) deposition of PCBs from the atmosphere (Ferreira *et al.* 2003). Studies of atmospheric concentrations of PCBs have shown that gaseous, particulate, and dissolved fractions have commonly been dominated by lower-molecular weight PCB congeners (Tsai *et al.* 2002, Poster and Baker 1994, Park *et al.* 2001). Given that PCB contamination is primarily associated with urban areas (Gunther *et al.* 2001, KLI 2001, KLI 2002) and the Central Valley is less than 2% urban, PCB congener patterns in Mallard Island samples suggest either a localized source of low-molecular weight Aroclors (e.g. 1026 or 1242) or an influence of atmospherically-derived PCBs. Further study is needed to assess the extent to which PCBs from this pathway are bioavailable to fish species of concern compared to other major transport pathways and sources.

The relative abundance of DDE, DDD, and DDT compounds (o,p' and p,p' isomers) provide information on different sources of sediment contributing to ΣDDT contamination in environmental samples (Pereira *et al.* 1996, Bergamaschi *et al.* 2001, Kratzer 1999). Technical DDT was originally prepared in proportions of approximately 80% p,p'-DDT and 20% o,p'-DDT (WHO 1989); however, DDT readily degrades aerobically to DDE and anaerobically to DDD (Corona-Cruz *et al.* 1999). Thus, degraded or weathered DDT residues in aerated sediment tend to be enriched with DDE, whereas anaerobic or flooded sediments tend to have higher proportions of DDD (Castro and Yoshida 1971, Strömpl and Thiele 1997). In contrast, DDT proportions greater than approximately 10% of ΣDDT are thought to be indicative of recent inputs of DDT residues from watershed soils into the aquatic system since DDT degrades more quickly to DDE and DDD in water than in soil (Nowell *et al.* 1999, Agee *et al.* 1986, Castro and Yoshida 1971).

The relative abundances of different DDT compounds measured over the range of SSC at Mallard Island indicated a gradual increase in the contribution of aerated sediment (or soils) as SSC and discharge increased. At low SSC, samples were dominated by DDE and DDD, suggesting that water samples collected at lower discharge streamflows (and greater tidal influence) were representative of highly weathered or degraded DDT residues (Figure 3.10). As SSC increased, proportions of DDE and DDT increased, whereas the contribution of DDD decreased. In fact, in the two samples with the highest SSC, ΣDDT mass was comprised of a greater percentage of the parent compound DDT than its anaerobic breakdown product DDD. This pattern leads to the hypothesis that as runoff increases, the proportion of eroded watershed soils with unweathered DDT residues increases in samples collected at Mallard Island. Thus, results suggest that the reservoir of watershed soils in the Central Valley continue to contribute relatively fresh supplies of DDT to San Francisco Bay decades after its use was restricted and banned.

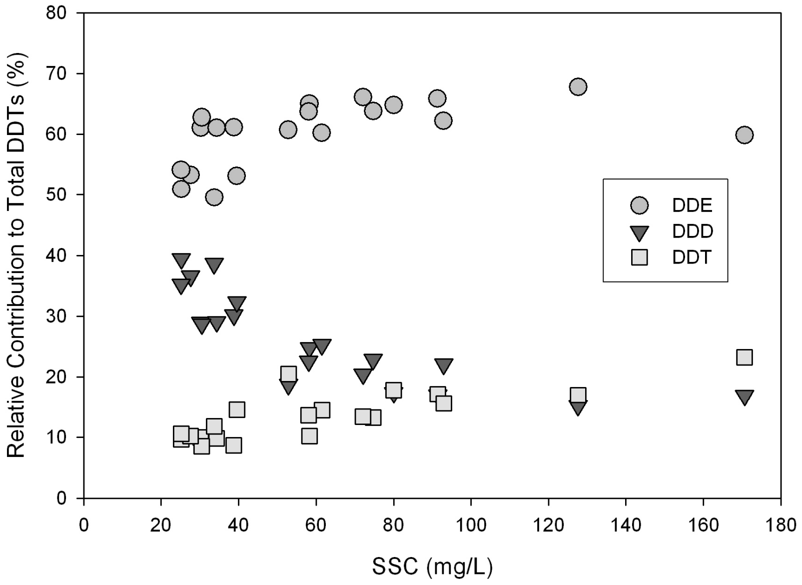

Figure 3.10 Relative abundance of DDE, DDD, and DDT (o,p' and p,p'-isomers) in relation to SSC.

PAHs. Several studies have reported that the dominant source of PAHs to San Francisco Bay is combustion (Pereira *et al.* 1996, Oros and Ross 2004). Sources of PAHs to the Bay have previously been inferred in RMP water (Ross and Oros 2004) and sediment samples (Oros and Ross 2004) by comparing ratios of specific PAH congeners with ratios previously determined from various PAH sources by Yunker *et al.* (2002). In the same manner as in the two previous Bay studies, PAH isomer ratios were evaluated in this study using the following four ratios: anthracene / anthracene + phenanthrene (An/178); benz[a]anthracene / benz[a]anthracene + chrysene (BaA/228); fluoranthene / fluoranthene + pyrene (Fl/Fl + Py); and indeno[1,2,3-c,d]pyrene / indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene (IP/IP+BghiP) (Table 3.6). It should be noted that these ratios are informal indicators of potential sources and do not necessarily reflect the original source signature due to possible chemical and physical alterations in the environment and mixture between two or more sources (Oros and Ross 2004).

Ratios of PAH congeners reflected predominant sources of both unburned and combusted petroleum (Table 3.6). An/178 ratios suggest there were large contributions from sources of both unburned petroleum (in 42% of samples) and combustion (in 58% of samples). Fl/Fl+Py ratios indicate similar proportions of petroleum (43%) and combustion (57%) sources and more specifically from petroleum combustion (0.4 < Fl/Fl+Py < 0.50). BaA/228 ratios suggest that 70% of the samples reflected mixed sources of petroleum and combustion (0.02 – 0.35) and 30% indicated combustion sources. IP/IP+BghiP ratios indicated that all samples were from petroleum combustion (IP/IP+BghiP = 0.20 – 0.50), as opposed to combustion of biomass, such as grasses, coal, and wood. Average ratios determined in this study were generally lower than average ratios measured in water and sediment collected from RMP River stations (Oros and Ross

2004, Ross and Oros 2004). As discussed previously, Mallard Island is located downstream of the RMP River stations and several municipal and industrial dischargers, which may have contributed greater amounts of petroleum-derived PAHs to Mallard Island samples. Previous studies have detected biomarker compounds (triterpanes and steranes) that are indicative of crude oil or petroleum in samples collected in the Delta and northern Estuary (Domagalski and Kuivila 1993). Thus, whereas PAH congener patterns indicate that combustion is likely the dominant source of PAHs to Mallard Island samples, patterns also reflect possible inputs from unburned sources of petroleum.

Table 3.6. PAH compound ratios in Mallard Island water samples. Ranges of ratios indicate potential sources of PAHs from petroleum (P), a mixture of petroleum and combustion (P + C), combustion of petroleum (PC), and combustion of biomass (BC).

	P	*P + C*	*PC*	*BC*	**Mallard Island This study**	**RMP River Sed 1993-2001[1]**	**RMP River Water 1993-2001[2]**
An/178	< 0.1	.	> 0.10		0.12 (0.06 - 0.22)	0.19 (0.11 - 0.26)	0.09 (0.02 - 0.41)
Fl/Fl + Py	< 0.4	.	0.4 - 0.5	> 0.5	0.39 (0.15 - 0.49)	0.43 (0.30 - 0.51)	0.51 (0.34 - 0.64)
BaA/228	< 0.2	0.2 - 0.35	> 0.35		0.32 (0.25 - 0.45)	0.42 (0.27 - 0.60)	0.44 (0.08 - 0.67)
IP/IP + BghiP	< 0.2	.	0.2 - 0.5	> 0.5	0.40 (0.35 - 0.45)	0.43 (0.23 - 0.90)	0.66 (0.45 - 0.85)

[1] Oros and Ross 2004
[2] Ross and Oros 2004

3.5.5 Estimated Loads

Continuous records of SSC and daily estimates of Delta outflow facilitated estimation of fluxes of sediment and contaminants at Mallard Island on a daily, monthly and annual basis for WY 2002 and WY 2003 (Table 3.7). Suspended-sediment fluxes at Mallard Island were estimated based on methodology described in McKee *et al.* (2002) and in section 2 of this report. This method takes into account particle dispersion and reverse flow due to tidal action. Since Delta outflow is available on a daily basis only, the continuous SSC record was converted to daily-average SSC values to estimate fluxes. Daily-average pesticide concentrations were derived using the daily-average SSC record and the regression relationships in Figure 3.2. Daily pesticide fluxes were then estimated by multiplying daily-average pesticide concentrations by Delta outflow.

Given that ΣPCBs and ΣPAHs were not correlated to SSC, using a regression model was not appropriate for deriving daily loads throughout the study period. For this reason, PAH fluxes were estimated using daily discharge and a flow-weighted mean concentration of 20 ng/L. Due to the unexplained increase in ΣPCB concentrations measured in May 2003, PCB fluxes were estimated by stratifying data before and after the onset of the storm associated with those concentrations. Thus, for the extended period of increased Delta outflow from April 10 to June 18, 2003, daily PCB fluxes were estimated using a FWMC of 3,300 pg/L. Before and after that period, PCB fluxes were estimated using a FWMC of 530 pg/L. PCB fluxes are presented as preliminary estimates. Continued monitoring in WY 2004 may provide greater insight into the causes of the intra-annual variability in concentrations and resulting flux estimates and improve our confidence in these and future load estimates.

Flux estimates were subject to several potential errors, the magnitudes of which were estimated for individual sources of error. During the development of the method for estimating sediment fluxes (see Section 2 of this report), errors from the following sources were included: daily-averaging of continuous SSC data (± 0.67%); calculation of Delta Outflow (± 5%); laboratory analysis of SSC (± 5%); regression between optical backscatter (OBS) data and SSC (± 10%); heterogeneity of SSC in the water column (± 30%).

Additional errors were associated with regressions between SSC and pesticide concentrations, as well as errors associated with laboratory analyses of all contaminants. Regression errors for OC pesticides were approximately ± 8.6% for ΣDDT, ± 14% for ΣChlordanes, and ± 29% for dieldrin. Based on QA data (Table 3.3), analytical accuracy was estimated to be ± 18% for ΣDDT, ± 17% for ΣChlordanes, ± 7% for dieldrin, ± 16% for ΣPAHs, and ± 6% for ΣPCBs. Error estimates for PAH and PCB fluxes were assumed to include errors associated with measured concentrations represented by coefficients of variation (CV = standard deviation/mean). The CV for PAH concentrations was ± 27%. The CV for PCB concentrations in samples collected before May 2003 was ± 34%, whereas the CV for samples collected in May 2003 was ± 77%. Estimates of total errors were calculated through propagation of errors. Total error estimates were ± 38% for ΣDDT, ± 39% for ΣChlordanes, ± 44% for dieldrin, ±27% for ΣPAHs, ±77% for ΣPCBs during the period from April 10 to June 18, 2003, and ±34% for PCBs on other days.

Daily contaminant loads over the two-year study period varied from 1.6 to 550 g ΣPCBs, 58 to 5,200 g ΣPAHs, 1.4 to 150 g ΣDDTs, 0.22 to 22 g ΣChlordanes, 0.37 to 56 g dieldrin. Over a 20-day period (12/28/2001 – 1/16/2002) during the largest storm of WY 2002, approximately 27 to 32% of the annual pesticide loads occurred. Approximately 25% of the annual ΣPAH and ΣPCB loads also occurred during that time. Similarly, in WY 2003, approximately 19 to 27% of annual pesticide loads occurred during a 20-day period of the first flush storm event (12/20/02 – 1/8/03). Approximately 15% of the annual PAH load occurred during the December-January storm in WY 2003. Due to the stratification methods used for estimating PCB loads in WY 2003, approximately 57 g ΣPCBs (73% of annual load) was estimated between April 10 and June 18, 2003.

Table 3.7. Estimated sediment and contaminant loads at Mallard Island in WY 2002 and WY 2003.

WY 2002	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	**TOTAL**
SS (x1000 t)	4.1	10	60	113	16	33	18	24	13	8.1	4.1	3.7	**309 ± 99**
ΣDDT (kg)	0.14	0.26	1.1	1.8	0.38	0.66	0.42	0.51	0.30	0.21	0.13	0.13	**6.0 ± 2.3**
ΣCHLOR (kg)	0.024	0.045	0.16	0.26	0.063	0.10	0.068	0.081	0.045	0.034	0.022	0.022	**0.93 ± 0.36**
DIEL (kg)	0.034	0.068	0.34	0.59	0.10	0.20	0.12	0.15	0.092	0.062	0.036	0.032	**1.8 ± 0.80**
ΣPCB (kg)	0.12	0.23	0.79	1.3	0.32	0.52	0.34	0.41	0.22	0.17	0.11	0.11	**6.0 ± 2.0**
ΣPAH (kg)	6.5	12	38	59	16	26	17	20	11	8.6	5.7	6.0	**230 ± 60**

WY 2003	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	**TOTAL**
SS (x1000 t)	4.3	12	110	166	48	30	42	85	22	14	9.3	3.7	**546 ± 175**
ΣDDT (kg)	0.14	0.27	1.6	2.5	0.95	0.61	0.82	1.6	0.46	0.34	0.24	0.12	**9.7 ± 3.7**
ΣCHLOR (kg)	0.024	0.043	0.22	0.36	0.16	0.096	0.13	0.25	0.071	0.056	0.040	0.020	**1.5 ± 0.57**
DIEL (kg)	0.036	0.078	0.58	0.86	0.26	0.18	0.24	0.45	0.14	0.091	0.066	0.034	**3.0 ± 1.3**
ΣPCB (kg)	0.17	0.29	1.2	2.1	1.1	0.63	4.6	10	2.2	0.39	0.28	0.13	**23 ± 18***
ΣPAH (kg)	6.3	11	44	78	41	24	32	64	17	15	10	5.1	**350 ± 90**

*An annual PCB load in WY 2003 was estimated based on a flow-weighted mean concentration of 530 pg/L for all days excluding the period between April 10, 2003 and June 18, 2003, for which daily loads were estimated using a flow-weighted mean concentrations of 3,300 pg/L.

The order of magnitude differences in daily contaminant loads translated into considerable variation between estimated monthly loads, which reflected the large influences of streamflow and sediment transport during the wet seasons (Table 3.7). The greatest monthly loads of pesticides and PAHs occurred in January of both years carrying approximately 23 to 37% of the annual loads.

Pesticide loads were estimated over a nine-year period using existing SSC data available from Mallard Island and Delta Outflow (Table 3.8). Using the regression equations for pesticides and SSC in Figure 3.2, estimated annual pesticide loads ranged between dry (e.g., WY 2001) and wet (e.g. WY 1995) years from 5.0 to 36 kg ΣDDT, 0.7 to 4.9 kg ΣChlordanes, and 1.6 to 13 kg dieldrin. PCB and PAH loads were not extrapolated over the nine-year period considering that sufficient data have not been collected to characterize intra- and inter-annual variability in concentrations measured at Mallard Island. It is important to note that there are considerable difficulties associated with extrapolating contaminant data from this study to previous years since water quality conditions in WY 2002 and WY 2003 may not accurately represent conditions in years with above average rainfall and runoff (e.g., 1995 or 1997). Subsequent monitoring at Mallard Island during larger floods will provide further information on inter-annual variability and the range of influences of sediment and hydrology on transport of hydrophobic organic contaminants to the Bay from the Central Valley Rivers.

Table 3.8. Estimated long-term sediment and contaminated loads from WY 1995 to WY 2003.

Water Year	Delta Outflow (Mm3)	Susp. Sed. (Mt)	ΣDDT (kg)	ΣCHLOR (kg)	DIEL (kg)
1995	51,559	2.6±0.83	36±14	4.9±1.9	13±5.5
1996	31,436	1.0±0.32	17±6.5	2.6±1.0	5.3±2.3
1997	42,307	2.2±0.72	31±12	4.2±1.6	11±4.8
1998	53,639	2.4±0.77	35±13	5.0±1.9	12±5.3
1999	27,805	0.84±0.27	15±5.7	2.3±0.90	4.5±2.0
2000	22,394	0.66±0.21	12±4.5	1.8±0.71	3.5±1.6
2001	8,565	0.26±0.08	5.0±1.9	0.74±0.29	1.6±0.71
2002	11,303	0.31±0.10	6.0±2.3	0.93±0.36	1.8±0.80
2003	17,330	0.55±0.17	9.7±3.7	1.5±0.57	3.0±1.3
Nine-Year Average		1.2±0.39	18±7.0	2.7±1.0	6.2±2.7

3.6 CONCLUSION AND IMPLICATIONS

Results from the first two years of monitoring led to several hypotheses concerning the influence of flow, tidal mixing, and sediment dynamics on the transport of hydrophobic organic contaminants to the Estuary from the Sacramento and San Joaquin Rivers. The following general hypotheses will be further explored in the subsequent years of monitoring from WY 2004 to 2009.

Hypothesis 1: The positive correlations between organochlorine pesticide concentrations and SSC measured in varying flow regimes and tidal stages over several storm events indicate that pesticide concentrations measured at Mallard Island and in the Bay are driven by sediment entering the Bay from the Sacramento River.

Hypothesis 2: Bay sediment concentrations of PCBs and PAHs (and possibly Chlordanes) that originate primarily from urban sources are diluted by less-contaminated sediment entering the Bay from the Rivers.

Hypothesis 3: PCBs transported to Mallard Island likely originate from sources of predominantly low-molecular weight Aroclors that have not degraded to a great extent and/or reflect an atmospheric input of PCBs.

Hypothesis 4: Contributions of DDT from different sources vary with streamflow (and SSC) with low flows dominated by highly degraded DDT residues (as depicted by high proportions of DDE and DDD) from aquatic sediments and high flows dominated by more recent inputs of less weathered material from aerated watershed soils (high proportions of DDE and DDT).

Contaminant loads are most informative when placed into context of contaminant mass budgets for SF Bay and compared to contaminant concentrations and loads from other major pathways. For example, according to results from a simple box modeling effort that describes the long-term fate of PCBs in the Bay (Davis 2004), as little as 10 kg per year of PCBs is predicted to significantly delay the recovery of water quality by decades. The estimated PCB loads of 6 and 23 kg per year in WYs 2002 and 2003 indicate that sustained PCB loads from the Sacramento and San Joaquin Rivers may continue to contribute to water quality impairment of the Bay.

Although these loads are significant inputs, the particles themselves are less contaminated by PCBs than sediment already in the Bay and sediment entering the Bay from urbanized watersheds. This situation might have a positive influence on Bay water quality through the burial of contaminated sediment with cleaner or less contaminated sediment; however, the deposition of cleaner sediment is highly variable and may not necessarily occur in areas that are having the greatest impact on biota. Furthermore, the extent to which organic contaminants transported to the Bay from the major rivers are bioavailable to Bay fish is not well known. Thus, a complex array of factors needs to be considered in determining the impact of contaminant loads from important transport pathways on water quality in the Bay. Some of these include the magnitudes of contaminant loading, the degree of contamination on sediment entering the Bay compared to sediment already in the Bay, and the processes within the Bay that control contaminant fate and uptake into the food web.

Contaminant monitoring at Mallard Island in WY 2002 and WY 2003 occurred during years with relatively low annual discharge and small floods. As a result, variability in contaminant concentrations and loads has not been characterized during years with above average runoff and sediment discharge (*e.g.* WY 1997). Another year of monitoring at Mallard Island will be conducted in WY 2004 that will potentially provide further insight into seasonal and tidal variability observed in WY 2003 and improve the accuracy of loading estimates. These improvements in our current state of knowledge of PCB distribution, and the future application of accurate loading estimates of OC pesticides and PAHs to similar fate models, will provide better information for future development and refinement of TMDLs and other strategies to improve water quality.

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SECTION FOUR

4. MERCURY

L.J. McKee, J.E. Leatherbarrow, and A.R. Flegal

4.1 ABSTRACT

San Francisco Bay is listed by the State of California as impaired for mercury. Mercury in the Bay is mainly derived from runoff issuing from historic mercury and gold mining areas of the California Central Valley. There is presently no reliable estimate of the annual or long-term average load of mercury yet, such an estimate is an important informational component for determining how to improve water quality. To resolve this information gap, storm sampling was carried out on the Sacramento River at Mallard Island between January 10th 2002 and May 6th 2003. Thirty total mercury (Hg_T) and 7 dissolved mercury (Hg_{TF}) analyses were carried out on water column samples taken during 6 storm flow peaks. Hg_T concentrations ranged from 4-14 ng/L and Hg_{TF} concentrations ranged between 0.8-1.6 ng/L. These concentrations were similar to those found is previous studies, and indicative of dry climatic conditions. Observations suggest that the Delta exhibits a "first flush" phenomenon for mercury indicated by greater Hg_T concentrations during the first flood of a season despite the subsequent floods having a greater discharge magnitude. Tides were also found to influence mercury concentrations. Suspended sediment particles in water of higher salinity on an incoming tide are more enriched with mercury indicative of mercury sources in Suisun Bay downstream. Despite Hg_{TF} concentrations making up between 11-24% of the Hg_T concentrations a relationship ($[Hg_T] = 0.0973*[SSC] + 3.5049$: $r^2=0.80$) was found between instantaneous suspended sediment concentrations (SSC) and Hg_T. This relationship was used to estimate daily Hg_T concentrations using time-continuous suspended sediment data. Hg_T concentrations were then combined with daily estimates of Delta outflow to estimate daily advective Hg_T loads for water year (WY) 2002 and 2003. Advective Hg_T loads were adjusted using an advective: dispersive flux model developed for suspended sediments and modified for the influence of tides on mercury. Daily Hg_T loads varied from 3-1,803g and annual Hg_T loads were 58±20 and 97±33 kg, respectively for WY 2002 and WY 2003. There are identified uncertainties associated with the applicability of the relationship between SSC and Hg_T during years with larger floods. Despite these uncertainties, a long-term average annual Hg_T load of 201 ± 68 kg was estimated. This estimate is bias low if the particle concentrations of mercury (mg/kg) are greater during larger floods (the present standing hypothesis). Ongoing study will help to resolve this remaining data gap.

4.2 INTRODUCTION

Recent studies of the sublethal effects of mercury on both wildlife and human health (National Research Council 2000) have elevated concerns about mercury contamination in San Francisco Bay (Schwarzbach and Adelsbach 2003, Davis *et al.* 2003). There is a human health advisory on catching and eating fish caught in the Bay (OEHHA 1997, 1999) and the Bay is listed as impaired for mercury by the State of California in compliance with Section 303(d) of the Clean Water Act administered by the U.S. Environmental Protection Agency (USEPA).

Mercury contamination in the Bay is primarily attributed to gold mining with liquid mercury during the gold rush of the mid nineteenth century and mercury mining (1840s-1970s; peak 1870s) (Domagalski 1998, Alpers and Hunerlach 2000, Domagalski 2001, Foe and Croyle 1998, Foe 2002, Conaway *et al.* 2002, 2004). Much of the mercury-laden sediment from these activities probably entered the Bay in the late 18th and early 19th century (Schoellhamer *et al.*, 2003) but some is still being transported into the Bay today during the seasonal floods in rivers of the Central Valley (Foe and Croyle 1998, Foe 2002) and from local contaminated tributaries (Thomas *et al.* 2002, McKee and Leatherbarrow 2004). Other input pathways include atmospheric deposition (Tsai and Hoenicke 2001, Steding and Flegal 2002), industrial and municipal wastewaters, and resuspension and diagenetic remobilization of mercury from legacy bed sediment in the Bay (Johnson and Looker 2003). The magnitude of mercury loads emanating from the Central Valley via the Bay-Delta remains a large uncertainty in the mass balance of the Bay (Davis *et al.* 1999, Johnson and Looker 2003).

Mercury concentrations in excess of 1,000 ng/L have been observed in some tributaries of the Sacramento River basin (Foe and Croyle 1998, Domagalski *et al.* 2003, Ganguli *et al.* 2000, Domagalski *et al.* 2004). Domagalski (1998) sampled water column total mercury at 11 locations in the Sacramento basin and determined that mercury concentrations exceeded the USEPA criteria (12 ng/L) on at least one sampling occasion at every location. Foe and Croyle (1998) suggested that the USEPA criteria would be exceeded on the Sacramento River at Freeport at flows > 850 cubic metes per second (m^3/s). Domagalski (1998) also noted greater mercury concentration under winter flow conditions and that mercury concentrations were more variable at more contaminated locations.

Mercury concentrations appear to be primarily associated with suspended sediments (Domagalski, 1998). Domalgalski (2001) noted a second order polynomial equation could describe 96% of variability between mercury and suspended sediment concentrations (SSC) across large distances in Central Valley waters, despite orders of magnitude differences in mercury concentration (e.g., < 10 ng/L in the upper Sacramento and American rivers and 2,250 ng/L in Cache Creek). The work by Foe and Croyle (1998) demonstrated strong correlations between suspended sediment and total mercury concentrations for Cache Creek at Yolo (r^2=0.83), the Yolo Bypass at Prospect Slough (r^2=0.97) and the Sacramento River at Greens Landing (r^2=0.87), indicating that most mercury during floods is bound to sediment.

Suspended sediment loads at Mallard Island vary from about 0.3 – 2.6 Mt per year (see Section 2 of this report). Given relationships between mercury and suspended sediment concentrations, it follows that annual mercury loadings to the Bay will likely vary greatly with climate. Climatic influences on mercury loads have been demonstrated for Cache Creek. Foe and Croyle (1998) estimated mercury loads of 1.2, 980, and 221 kg for Cache Creek at Yolo during water years (WYs) 1994, 1995, and 1996. A later study estimated mercury loads for WY 2000 (12.3 kg) and WY 2001 (4.9 kg) (Domagalski *et al.* 2004). These order of magnitude differences in estimated annual loadings attest to the pronounced influence of climatic year on transport of sediment and mercury in the Sacramento-San Joaquin river system.

Beginning 1989, mercury concentration data has been collected in waters of the lower Sacramento and San Joaquin Rivers using routine sampling (Flegal *et al.* 1991, SFEI 2003, Foe 2002). With the exception of 1997, all of these data have been generated during low flow conditions. There was no intent to collect samples during high flow when the majority of mercury transport occurs. To-date, loading estimates have been made by incorporation of concentration data collected for various reasons and various locations in the Delta system without taking into account the potential for storage or sources within the system (e.g. Foe and Croyle 1998, Abu-Saba and Tang 2000). An exception was the study by Foe (2002) that made a mercury load estimate of 119 kg at X2 for WY 2001 but the use of a monthly sampling scheme and monthly discharge estimates probably reduced the accuracy of the annual load estimate.

Despite a growing understanding of sources of mercury to rivers and creeks in the Central Valley and a variety of measurements of concentrations and estimates of loads, there remains little information on the dynamic nature of concentrations in the lower Sacramento River in response to large storms that transport and resuspend mercury laden sediment in the Delta system. Measurement of mercury concentrations during storms will enable accurate estimates of average mercury loads or annual variability, an important data gap identified in the San Francisco Bay mercury total maximum daily loads (TMDL) report (Johnson and Looker 2003). To begin to address TMDL management needs, this study assesses the influences of water and sediment runoff and tidal processes on Hg_T concentrations and loads during WY 2002 and 2003 in the Sacramento River at Mallard Island. First order estimates of long-term average loads and variability are presented.

4.3 METHODS

4.3.1 Sample Collection and Analysis

Sampling was conducted at Mallard Island instrument shelter, which is the location of long term monitoring by both the California Department of Water Resources (DWR) and the United State Geological Survey (USGS), at the upstream end- member of San Francisco Bay. Samples were collected from the concrete block instrument shelter at the end of a 400 m wooden walkway that crosses the sometimes-submerged marshlands of Mallard Island. The walkway connects the shelter to a levee road on the property of Mirant Delta, LLC power generation plant. During the study period salinity at Mallard Island ranged from 0.0-19.4 (mean = 5.7) during June-November and 0.0-15.4 (mean = 1.4) during December-May. The channel adjacent to Mallard Island conveys runoff from 154,000 km^2 [>37 percent of the land area of California (411,000 km^2)]. The channel depth at the Mallard Island gage is approximately 7.6 m, whereas the adjacent shipping channel has a depth of about 17 m, the total channel width is approximately 940 m and the location has an average tidal range (DWR unpublished data) of 1.25 m.

Mallard Island is approximately 8 km downstream of the confluence of the Sacramento and San Joaquin Rivers. Upstream from the sampling location, the channel broadens into a complex system of sloughs, modified channels, and reclaimed islands many of which are productive farming lands that together make up the "San Francisco Bay Delta". There are two deepwater channels that connect the city of Stockton on the San Joaquin River and state capital of Sacramento on the Sacramento River to the Bay for shipping purposes. In addition, during high flows, floodwaters are diverted north of Sacramento through the Yolo Bypass (a broad channel bounded by levee that is used for agriculture during the growing season). The Yolo Bypass only conveys Sacramento River water when river stage at the Fremont Weir (DWR station Code *FRE*) exceeds 33.5 ft (10.8 m), but in most years receives runoff from small local coast range tributaries including Cache Creek (DWR station Code *CCY*), a watershed with known mercury contamination.

Sampling was conducted focusing on floods during WY 2002 and 2003 (Figure 4.1). The largest flood during this period peaked on January 6th 2002 and had a return interval of ~1.7 years. The largest flood in WY 2003 occurred on January 3rd 2003 and had a return interval of ~1.6 years. Since discharge in the Sacramento River rises and falls over a period of 5-10 days, a sampling frequency of 1-3 samples a day was deemed appropriate for characterizing trace contaminant variation in response to floods.

Water samples for the analysis of unfiltered total mercury (Hg_T) and filtered total dissolved mercury (Hg_{TF}) were collected with established methods (Flegal *et al.* 1991, Conaway *et al.* 2003) using trace metal clean protocols (e.g., USEPA 1996). Briefly, water samples were collected 1 m below the surface on the upstream side of the instrument shelter using a sample collection system consisting of a 5 m aluminum pole fitted with acid-cleaned Teflon tubing, a 110 v Cole-Palmer Masterflex Dual Head peristaltic pump fitted with acid-cleaned C-Flex tubing, and an acid cleaned 0.45 m polyethylene filter cartridge (Hg_{TF} only). Prior to sampling and between samples, the sample collection system was flushed with river water for 5 minutes. Labeled double-bagged (Ziploc™) sample bottles were extracted from the bags, filled, and re-bagged over a period of 15 minutes per sample. Field blanks were un-bagged, un-capped, re-capped, and re-bagged in the same manner. Unfiltered and filtered samples and field blanks for mercury analysis were snap-frozen using dry ice and transported to the laboratory in frozen condition. Samples for SSC were then taken using the same sample collection system, double labeled and placed in a cooler (4ºC) in the dark.

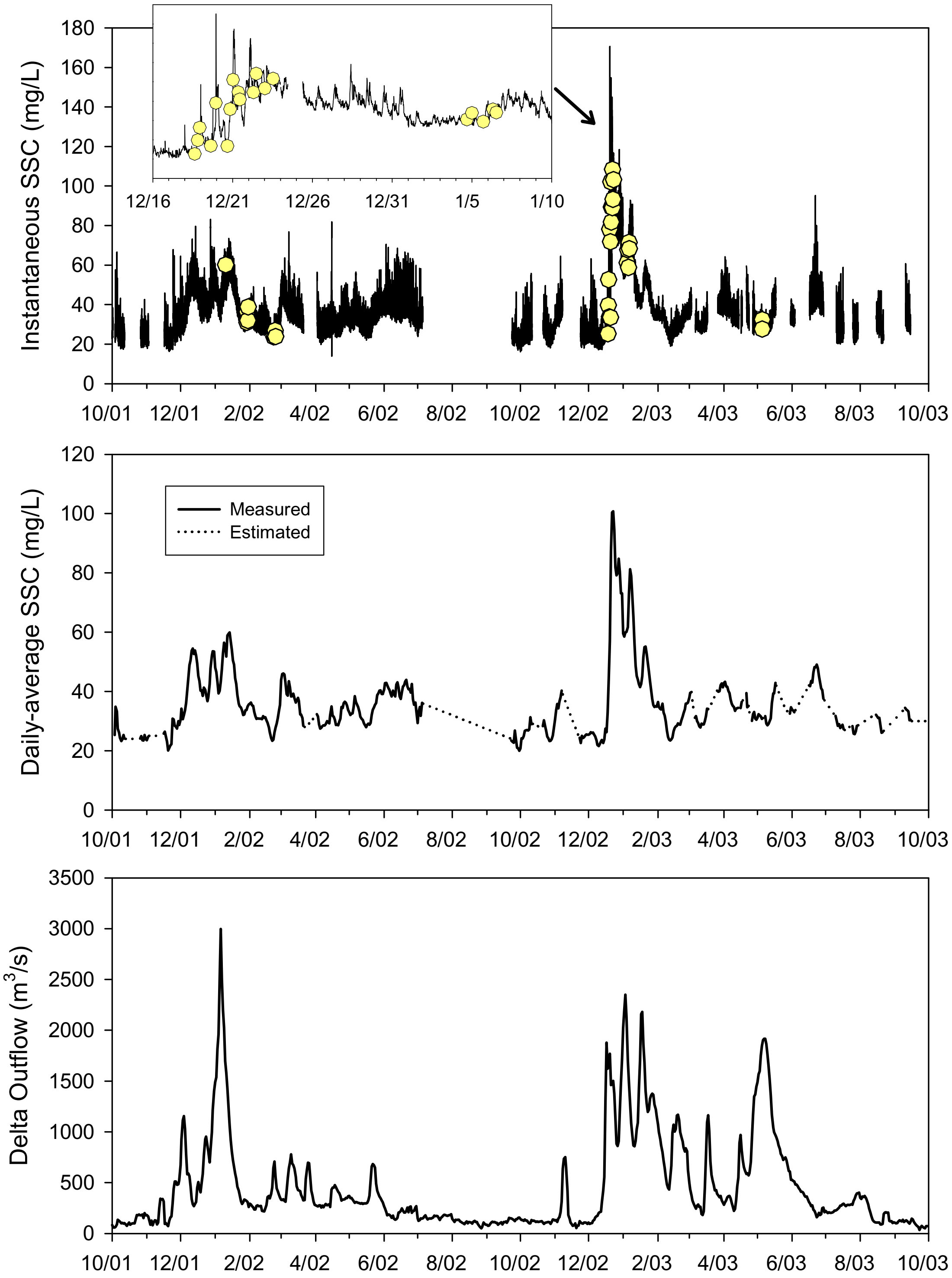

Figure 4.1 Sampling at Mallard Island relative to suspended sediment concentrations and discharge over WY 2002 and 2003.

Analysis for mercury was carried out using cold vapor atomic fluorescence spectrometry (CVAFS), using established protocols (EPA 2002, Conaway *et al.* 2003). Briefly, the frozen water samples were thawed at room temperature, oxidized with bromine monochloride solution (BrCl) for two hours, and then sequentially reduced with hydroxylamine hydrochloride. Stannous chloride ($SnCl_2$) was then used to convert Hg(II) into volatile Hg(0) and analysis carried out using gold amalgamation and CVAFS.

Suspended sediment concentration was determined using standard methods promulgated by the United States Geological Survey (e.g., Gray *et al.* 2000). Samples were passed through pre-weighed 0.45 µm filters. If filters became blocked, a second filter was used so that the entire water sample was filtered. The filters were then dried at 110ºC to a consistent weight and weighed using an analytical balance capable to measuring 0.01 milligrams.

4.3.2 Quality Assurance and Control

The quality assurance program consisted of field components and laboratory components including field duplicates, field blanks, instrument blanks, standard reference material, and sample spike replicates. Samples were run in three batches. Method detection limits were <0.3 ng/L for each batch, defined as three times the standard deviation of the method blank. Field blanks taken on four occasions were typically <0.3 ng/L. Field duplicates were taken as consecutive field samples rather then splitting a single field sample. Relative percent difference (RPD) on field duplicates was <5%. Concurrent analyses of standard reference materials PACS-2, NIST 2709, NIST 1646a yielded recoveries of 89-96%. Analyses of field samples with matrix spikes were also 89-96%.

4.4 RESULTS

Between January 10th 2002 and May 6th 2003, 35 water samples were taken at Mallard Island on the Sacramento River during 6 storm flow peaks. Due to a batch of defective bottles, only 86% of the samples were analyzed because of bottle breakage. In total, 30 sample analyses were completed for Hg_T ranging in concentration from 4-14 ng/L (Table 4.1). Analysis for Hg_{TF} was carried out on seven samples. Hg_{TF} concentrations ranged between 0.8-1.6 ng/L. Despite dissolved concentrations making up between 11-24% of the Hg_T concentration (Table 4.1), it showed a strong relationship ($[Hg_T] = 0.0973*[SSC] + 3.5049$: $r^2=0.80$) to instantaneous SSC estimated by the USGS (see Section 2 of this report) (Figure 4.2). The scatter about the regression line seems appropriate considering the analytical errors associated with estimating SSC (±15%) and measuring Hg_T (±15%), in addition to the variance attributed to separate collections for SSC and Hg_T.

Table 4.1 Total and dissolved (<0.45 µm) mercury concentrations (ng/L), suspended sediment (mg/L) concentrations, electrical conductivity (mS/cm), and Delta Outflow (m^3/s) at Mallard Island during the study period (January 10, 2002 – May 6, 2003).

Sample	Date	Time	Delta Outflow	Conductivity	SSC	HgT	HgTF	HgTF
			m^3/s	mS/cm***	mg/L****	ng/L	ng/L	%
MI01*	1/10/2002	14:40	1,696	0.16	60	-	-	-
MI02	1/29/2002	10:22	321	1.63	31	-	-	-
MI03	1/29/2002	15:26	321	5.42	36	10	1.5	15
MI04	1/30/2002	10:20	309	1.63	32	-	1.6	-
MI05	1/30/2002	16:00	309	4.41	39	9	1.3	14
MI06*	2/22/2002	11:10	645	6.97	24	4	0.9	22
MI07	2/22/2002	18:20	645	1.62	25	5	0.8	16
MI08	2/23/2002	11:30	706	6.65	26	6	-	-
MI09	2/23/2002	19:40	706	1.25	27	-	-	-
MI10	2/24/2002	7:30	552	1.42	24	-	-	-
MI11	12/18/2002	14:55	1,621	4.61	25	5	-	-
MI12	12/18/2002	19:29	1,621	1.83	40	6	-	-
MI13	12/18/2002	22:40	1,621	1.57	53	7	-	-
MI14*	12/19/2002	15:10	1,726	6.08	34	7	-	-
MI15	12/19/2002	22:55	1,726	1.55	78	12	-	-
MI16	12/20/2002	16:05	1,769	4.15	33	6	-	-
MI17	12/20/2002	20:26	1,769	2.03	72	11	-	-
MI18	12/21/2002	0:39	1,459	0.71	102	13	-	-
MI19	12/21/2002	8:48	1,459	1.06	89	11	-	-
MI20	12/21/2002	10:53	1,459	1.13	82	12	-	-
MI21	12/22/2002	7:10	1,467	1.03	89	13	-	-
MI22	12/22/2002	11:34	1,467	0.75	108	14	-	-
MI23	12/23/2002	0:48	1,502	0.92	93	13	-	-
MI24* **	12/23/2002	13:06	1,502	0.62	103	13	-	-
MI25	1/4/2003	16:50	2,132	0.32	61	12	-	-
MI26	1/4/2003	23:56	2,132	0.33	68	10	-	-
MI27	1/5/2003	17:18	1,697	0.29	59	11	-	-
MI28	1/6/2003	7:50	1,480	0.27	71	11	-	-
MI29* **	1/6/2003	12:50	1,480	0.29	68	12	-	-
MI30	5/5/2003	11:19	1,844	0.16	32	5	-	-
MI31	5/5/2003	13:52	1,844	0.18	27	4	-	-
MI32	5/6/2003	11:57	1,904	0.17	36	9	1	11
MI33	5/6/2003	15:08	1,904	0.18	30	5	1.1	24

* Average of a duplicate or triplicate SSC field sample

** Average of a duplicate mercury field sample

*** Data collected by DWR at Mallard Island (station code *MAL*)

**** USGS SSC calculated using 15-minute turbidity data and a regression between SSC and turbidity (see Section 2 of this report)

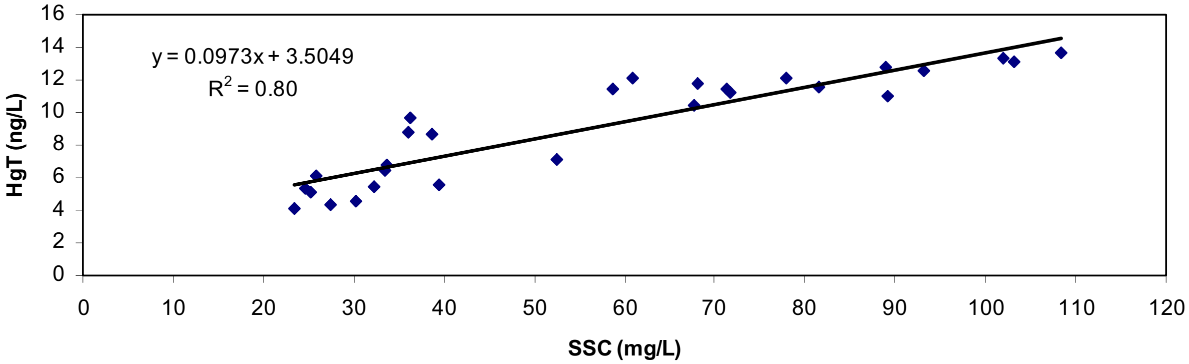

Figure 4.2 The positive relationship ($R^2 = 0.80$, simple linear regression) between Hg_T and SSC for surface water (1 m) samples collected at Mallard Island during WY 2002 and WY 2003.

4.5 DISCUSSION

4.5.1 Comparisons to Other Studies

A number of other studies have collected mercury data in the vicinity of Mallard Island (Foe and Croyle 1998, Domagalski 1998, 2001, Foe 2002, SFEI 2003) that provide some context for the current study and provide insights into processes that might occur during years with different climatic forcing (Table 4.2). Generally, Hg_T concentrations measured for this study appear to be comparable to or slightly lower than Hg_T reported in those previous studies. Maximum concentrations at Mallard Island during WY 2002 and WY 2003 were less than all other studies except data collected by the RMP at the San Joaquin River location in the Delta (SFEI 2003). Greater concentrations have been observed particularly during years when Delta outflow was greater (WY 1995-2000). In fact, during the last nine years (WY 1995-2003), only WY 2001 had a lower Delta Outflow than WY 2002 and WY 2003. Data collected by Foe (2002) for WY 2001 ranged from 4-24 ng/L with a mean of 12 ng/L, more similar to data collected during this study. Concentrations on particles in the present study are also less than those previously reported near Mallard Island and in upstream locations (Table 4.2). Again the reason for this appears to be climatic. The data in Table 4.2 supports the hypothesis that the slope of the relationship between SSC and Hg_T varies depending on discharge. During years when flow is greater, the slope probably resembles a combination of the signal from Yolo Bypass and the Sacramento River in the middle and upper Delta. At what flows the slope (and therefore particle concentration) change is presently unknown, but is the subject of subsequent years of observation.

Table 4.2. Tabulation of mercury data collected during this study and in previous studies at or near Mallard Island.

			Number	Hg_T ng/L			Hg_T mg/kg
Author	**Location**	**Date**		**Mean**	**Min**	**Max**	**Mean**
This study	Sacramento R. at Mallard Island	10/2001-9/2003	30	9	4	14	0.1
SFEI (2003)	Grizzly Bay BF20	1993-2001	22	19	3	41	0.23
	Honker Bay BF40	1994-2001	20	18	4	46	0.25
	Sacramento R. BG20	1993-2001	23	8	1	38	0.2
	San Joaquin R. BG30	1993-2001	23	7	2	16	0.19
Foe (2002)	Sacramento R. X2	3/2000-10/2001	18	18	4	49	0.32
Domagalski (2001)	Sacramento R. at Freeport	2/1996-4/1998	27	7*	3	~11	-
	Yolo Bypass at Hwy 880	2/1996-4/1998	?	30*	~17	~120	-
Domagalski (1998)	Sacramento R. at Freeport	2/1996 – 2/1997	13	8*	3	18	-
	Yolo Bypass at Hwy 880	1/1997	1	30	-	-	-
Foe and Croyle (1998)	Sacramento R. at Greens Landing	1/1995-7/1995	46	21	8	87	0.23
	Yolo Bypass at Prospect Slough	1/1995-7/1995	20	90	7	696	0.19

* Median concentration

4.5.2 Concentrations During Sequential Storms

Samples collected during three storms in WY 2003 provided an opportunity to look at variation in SSC and Hg_T concentrations between storms (Figure 4.3). Consistent with the strong relationship ($R^2 = 0.80$, simple linear regression) between SSC and Hg_T (Figure 4.2), both of those variables show a similar trend in concentrations over the flood season. The Hg_T concentrations (peak = 14 ng/L) were greatest during the first flood of the season (12/22/2002) despite the second flood (01/06/02) having a 1.2 times greater discharge magnitude. Similarly, Hg_T concentrations peaked at only 9 ng/L during a subsequent flood in May that had a peak in discharge (1,900 m^3/s) larger than the first flood of the season (1,770 m^3/s).

These observations suggest that the Delta exhibits a "first flush" phenomenon for mercury. This phenomenon has been previously reported for suspended sediments in the Delta (Goodwin and Denton 1991, Ruhl and Schoellhamer 1998, Oltmann *et al.* 1999), and it appears that early storms of the season also "clean out" the standing reservoir of mercury leaving relatively clean sediment for transport in later storms. The ultimate origin of the "dirty" first flush sediment is still debated and might be from Suisun Bay, from mercury derived from small floods that deposits in the system rather than being flushed through, or from release from bed sediments stored within the Delta.

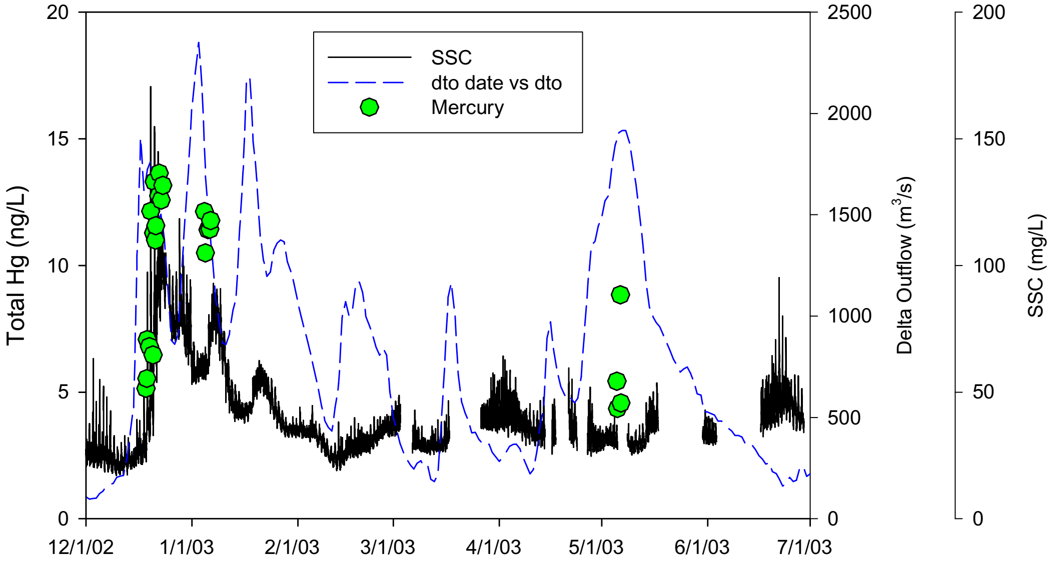

Figure 4.3 Mercury concentrations (ng/L) relative to suspended sediment concentrations (mg/L) and discharge (m^3/s) at Mallard Island during WY 2003.

4.5.3 Tidal Influences

As mentioned previously, there is a tidal influence on waters at the Mallard Island sampling location, which are chronicled by fluctuations in salinity (measured as EC by DWR) in response to twice daily uneven tides. Even during floods, reverse flow is normally observed at Mallard Island at high tide. Downstream from Mallard Island, the Bay opens up into wide expanses known as Honker, Grizzly, and Suisun Bays before the channel narrows again as water passes through Carquinas Straight. Upstream from Mallard Island, the channel remains relatively narrow until it splits in a complex manner near the confluence of the Sacramento and San Joaquin Rivers.

Based on that channel geometry and bathometry, it is hypothesized that particulate mercury transport and resuspension processes are different upstream and downstream. The hypothesis is consistent with reported variations in suspended sediment concentrations in Honker Bay, that are associated with seasonal variations in wind-wave action and associated wind shear stress at the sediment-water interface (Ruhl and Schoellhamer 1998). This variation is attributed to unconsolidated bottom sediments being resuspended when wind increases during the spring and summer months. The effect reduces in magnitude as the summer progresses, and sediments consolidate and coarsen due to selective winnowing and transport of fines. In addition, a turbidity maximum has been observed in Suisun Bay (Schoellhamer and Burau 1998) in the "Null Zone" associated with stratified bi-directional flow in areas where salinity gradient-induced gravitational circulation exists. Similarly, there is evidence that mercury concentrations in the Suisun Bay may be greater than those observed in the lower Delta possibly due to net erosion from sediments (Foe, 2002). Net erosion of contaminated sediment might result in a considerable transport of mercury from Suisun Bay to the Delta (perhaps 200-300 kg total mercury annually) (Foe 2002).

Mercury data collected during this study were tested for a tidal influence. The data appear to form two separate populations based on electrical conductivity EC > 2 mS/cm and EC< 2 mS/cm (Figure 4.4). This breakpoint does not relate to a particular magnitude of Delta Outflow because EC at a particular sampling moment is influenced by tide as well and Delta Outflow in the days before the measurement and how these two phenomenon influence the salinity and origin of water in the downstream Suisun, Honker and Grizzly Bays. Mercury on suspended particles has an average concentration of 0.29 mg Hg/kg suspended sediment when EC>2 mS/cm and an average concentration of 0.11 mg/kg when EC<2 (Figure 4.4). The particle concentration of 0.29 mg/kg is more similar to other studies completed during low flow periods (Foe 2002: 0.32 mg/kg; SFEI 2003: 0.22 mg/kg) and near-surface concentrations (0.3 mg/kg) in a sediment core taken in Grizzly Bay (Hornberger *et al.* 1999). The slope of the relationship between Hg_T and SSC for EC<2 mS/cm (0.11 mg/kg) appears to be more similar to particle concentrations (0.14 mg/kg) reported for upstream locations on the Sacramento River during low flow conditions (Greens Landing, Foe 2002) and that (~0.1 mg/kg) derived from a consolidation of data from multiple locations in the Sacramento River Basin (Domagalski 2001). In contrast, greater particle concentrations have been observed during high flows at the upstream location Greens Landing (0.17-0.41 mg/kg) on the Sacramento River and in the Yolo Bypass (0.19 mg/kg) during high flow (Foe and Croyle 1998). The latter values are consistent with those of fine (<63 μm) depositional zone bed sediments in the <63 μm fraction at Verona (0.24 mg/kg) and at Bend Bridge (0.16 mg/kg) on the Sacramento River (Domagalski 1998).

Although particulate mercury concentrations during high flow periods at Mallard Island are unknown, they are likely to be greater than those observed during WY 2002 and WY 2003 (this study). Determining nature of mercury and suspended sediment concentrations during high flows is, consequently, needed for an accurate understanding of long-term average loads and annual variability in mercury fluxes to the Bay. In addition, if sediment entering the Bay from the Central Valley is "cleaner" than sediment already in the Bay, it may be a net benefit by providing a cap over some "dirtier" Bay sediments in areas of net deposition and/ or diluting mercury in the water column derived from resuspension of Bay sediments (see Johnson and Looker 2003).

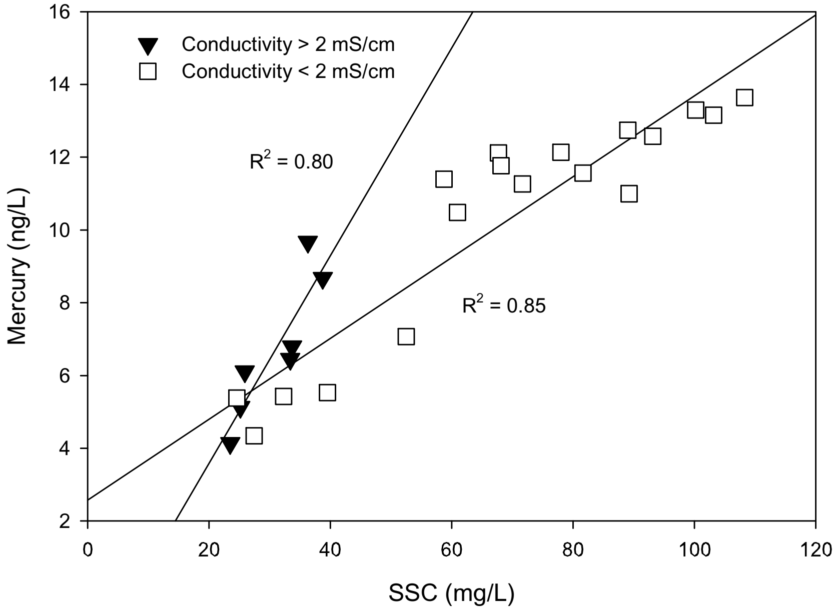

Figure 4.4 The influence of tidal fluctuation and associated salinity (represented here by electrical conductivity) on the relationship between total mercury (Hg_T) concentrations and suspended sediment concentrations (SSC) at Mallard Island. Regression equation (1) for conductivity < 2 mS/cm is: $y = 0.111x + 2.574$ ($R^2 = 0.85$, simple linear regression). Regression equation (2) for samples with conductivity > 2 mS/cm is: $y = 0.286x - 2.128$ ($R^2 = 0.80$; simple linear regression). The two equations are statistically different from each other ($p<0.05$).

4.5.4 Estimated Loads

As the preceding analysis demonstrates, estimates of mercury loads at Mallard Island at the head of San Francisco Bay are confounded by the influences of tidal processes on particle dispersion and salinity. The influence of diurnal tides on particle dispersion has already been discussed by McKee *et al.* (2002), who developed a model for adjusting advective sediment loads based on ADCP data collected during WY 1994 and WY 1996. Their model confirmed the intuitive hypothesis that flow conditions have a large influence on particle dispersion and flux at Mallard Island. The model also provided an estimate of an advective: dispersive flux ratio based on flow conditions. This ratio can be used to adjust the suspended sediment advective load effectively reducing it by an average of about 20% over WY's 1995-2003 (see Section 2 of this report). This same method can be used for estimating loads of other particle bound substances, including mercury.

To estimate mercury loads, the methods described by McKee et al (2002) were modified to account for the influence of tide and salinity on mercury:

Step 1. Use time continuous daily averaged SSC data (or estimates based on interpolation when data is missing) to estimate daily Hg_T concentration (see sediment chapter in this progress report).
Step 2. Use the regression equation (1) between SSC and Hg_T for <2 mS/cm to estimate Hg_T concentration on days when average conductivity at Mallard Island (DWR data) was <2 mS/cm (flood-flow conditions).
Step 3. Use the regression equation (2) between SSC and Hg_T for >2 mS/cm to estimate Hg_T concentration on days when average conductivity at Mallard Island (DWR data) was >2 mS/cm (low-flow conditions).
Step 5. Combine estimated daily Hg_T concentration (ng/L) with daily Delta outflow (Mm^3) to estimate daily fluvial advective Hg_T load (kg).
Step 6. Adjust 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; see sediment section of this progress report)
Step 7. Errors are estimated using the same method as outlined for suspended sediment (McKee *et al.* 2002; see sediment section of this progress report) with the addition of an error for laboratory analysis of Hg_T (±5%) and an error for the regression relationship between SSC and Hg_T (±10%) giving a total error of ±34%.

Using these methods, mercury loads were estimated for WY 2002 and 2003. Daily loads varied from 3-1,803g over WY 2002 and WY 2003. The maximum daily load occurred on December 20th 2002 and was associated with the first flush flood during the WY 2003. Over a 23-day period, the rising and falling stage of that flood transported 13.5 kg of Hg_T or 14% of the total load for WY 2003. Monthly loads varied considerably between wet and dry seasons of each year reflecting the strong influence of rainfall and snow melt on discharge character in the Central Valley Rivers (Table 4.3). Annual Hg_T loads for each water year were 58±20 and 97±33 kg, respectively for WY 2002 and WY 2003.

SSC data is available for Mallard Island for 9 water years (1995 – 2003) and can be used to estimate long-term variability and long-term average mercury loads. However, there are difficulties associated with extrapolating the Hg_T data beyond WY 2002 and WY 2003 because of the uncertainty of the applicability of the relationship between SSC and Hg_T during years with larger floods when the Yolo Bypass is the conduit for a greater percentage of the Delta Outflow (see discussions above). This uncertainty comes about because Cache Creek, a known area of high mercury contamination and load (Foe and Croyle 1998, Domagalski *et al.* 2002), flows directly into the Yolo Bypass. In addition, concentrations in excess of 30 ng/L (compare this to 14 ng/L, the maximum concentration found in this study) have been found in other parts of the Sacramento River

Basin (Domagalski 1998), and concentrations up to ~200 ng/L have been measured in the Yolo Bypass (Domagalski 2001). Given these uncertainties, long-term estimates of loads presented here are likely to change when more data are available.

Table 4.3 Monthly and annual loads of suspended sediment (t) and Hg_T (kg) at Mallard Island over WY 2002 and WY 2003.

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Total
Water Year 2002													
Susp. sediment (x1000 t)	4.1	10	60	113	16	33	18	24	13	8.1	4.1	3.7	309
Percent annual (%)	1.3	3.3	20	37	5.3	11	6	7.7	4.2	2.6	1.3	1.2	100
HgT (kg)	0.82	2.1	12	19	3.5	6.2	3.8	4.7	2.9	1.8	0.89	0.74	58
Percent annual (%)	1.4	3.6	21	32	5.9	11	6.5	8.0	5.0	3.1	1.5	1.3	100
Water Year 2003													
Susp. sediment (x1000 t)	4.3	12	110	166	48	30	42	85	22	14	9.3	3.7	546
Percent annual (%)	0.8	2.2	20	30	8.8	5.5	7.7	16	4.1	2.5	1.7	0.70	100
HgT (kg)	0.88	2.7	18	27	9.3	5.6	8.0	16	4.1	2.9	2.0	0.82	97
Percent annual (%)	0.9	2.8	18	28	9.6	5.8	8.2	17	4.2	3.0	2.0	0.80	100

Using the regression equations (Figure 4.4) and daily EC data available for WY 1996-2003 (DWR), annual loads estimates were made for WY 1996-2001. An estimate for WY 1995 was made using regression equation (1) only because there is no EC data available for that year. The estimated annual Hg_T load varied from 52±11 - 399±88 kg and averaged 201±44 kg (Table 4.4). The load of 399±88 kg for WY 1995 was approximately half the load previously estimated for a similar period by Foe and Croyle (1998). The load of 52±11 kg for WY 2001 was approximately half the load previously estimated for the same period by Foe (2002).

Both Foe and Croyle (1998) and Foe (2002) calculated mercury loads combining mercury concentrations with estimates of discharge, so their over estimates of sediment loads were not the cause of discrepancies between this study and theirs. The cause is related to the slope of the regression equations that are bias for conditions during WY 2002 and WY 2003 that probably do not represent long-term conditions. Data collection during WY 2004 and subsequent years will likely reduce uncertainties associated with the estimation of long-term variability and mean Hg_T loads entering the Bay from Central Valley.

Table 4.4 A comparison of estimated long term annual and average Hg_T loads (kg) and loads calculated from this study and in previous studies.

	This study			**Other studies**		
	Water	**Sediment**	**Hg**		**Sediment**	**Hg**
Water Year	**Mm^3**	**Mt**	**kg**		**Mt**	**kg**
1995	51,559	2.6 ± 0.5	399 ± 136	Foe and Croyle (1998)*	4	800
1996	31,436	1.0 ± 0.2	184 ± 63			
1997	42,307	2.2 ± 0.4	351 ± 119			
1998	53,639	2.4 ± 0.5	389 ± 132			
1999	27,805	0.84 ± 0.16	156 ± 53			
2000	22,394	0.66 ± 0.13	123 ± 42			
2001	8,565	0.26 ± 0.05	52 ± 18	Foe (2002)	0.46	119
2002	11,303	0.31 ± 0.06	58 ± 20			
2003	17,330	0.55 ± 0.10	97 ± 33			
Average =	29,593	1.2 ± 0.2	201 ± 68			

*May 1994 – April 1995.

4.6 SUMMARY, HYPOTHESES, AND CONCLUSIONS

This report presents the first two years of data for a three-year study on mercury concentrations and loads in the Sacramento River at Mallard Island. The following summarizes the results to-date:

- Hg_T in 30 samples varied from 4-14 ng/L.

- Hg_{TF} in 7 samples varied from 0.84-1.59 ng/L (11-24% of the Hg_T concentration).

- Hg_T show a strong relationship to SSC.

- Water column Hg_T concentrations (ng/L) measured in this study were less than those previously for the study area, probably due to climatic differences.

- Water column particulate mercury concentrations (mg/kg) also were less that other reported data, probably due to climatic differences.

- The Delta exhibits a "first flush" phenomenon for Hg_T similar to suspended sediments, indicated by decreasing concentrations over a flood season.

- The origin of water (predominantly from upstream during floods or a mixture of water from the Delta and Suisun Bay during low-flow) influences the particulate mercury concentration in the water column. The average concentration was 0.11 mg/kg when EC<2 (high flow), whereas that average concentration was 0.29

mg/kg when EC>2 (low flow). It remains unknown what happens to that concentration during larger floods (see hypotheses below)

- Daily Hg_T loads varied from 3-1,803g over WY 2002 and WY 2003.

- Annual Hg_T loads for each water year were 58±13 for WY 2002 and 97±21 kg for WY 2003.

- Long terms estimates of mercury loads to the Bay are confounded by the choice of what particle concentration to use during years with flood larger than those observed during WY 2002 and WY 2003. Long terms estimates presented in this study appear to be about half those of previous authors.

The following hypotheses are based on those preliminary data and analyses:

Hypothesis 1: Water column Hg_T concentrations (ng/L) at Mallard Island are highest in years when a greater proportion of total Delta Outflow at Mallard Island passes through the Yolo Bypass.

Hypothesis 2: Water column particulate mercury concentrations (mg/kg) at Mallard Island are highest in years when a greater proportion of total Delta Outflow at Mallard Island passes through the Yolo Bypass.

In conclusion, observations of mercury during this study occurred during flow years with relatively low annual discharge and relatively small floods (< 2 year return interval). Estimates of mercury loads for WY 2002 and WY 2003 are considered reliable, however long term estimates of those loads based on suspended sediment data (WY 1995-2003) and EC data (WY 1996-2003) are confounded by a lack of understanding of flood characteristics at discharge beyond 2,600 m^3/s. Given that the Sacramento River at Mallard Island is capable of a daily discharge in excess of 16,000 m^3/s, which occurred in WY 1997, there still are serious gaps in our understanding of the riverine flux of mercury to San Francisco Bay. Filling these data and knowledge gaps is the topic of further study at Mallard Island.

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APPENDIX TABLES

Appendix Table A1. PCB concentrations in Mallard Island samples, WY 2002. ND = concentration was below detection limit. Cxxx = coelution, where xxx is the lowest number of the coeluting congeners where the value is stored. K = peak detected but did not meet quantification criteria, reported result represents estimated maximum possible concentration.

Date	Time	∑PCBs	PCB 008/5	PCB 018	PCB 028	PCB 031	PCB 033/20/21	PCB 044	PCB 049/43	PCB 052/73	PCB 056/60	PCB 066/80	PCB 070/76	PCB 074/61	PCB 087/111/115/116/117	PCB 087/115/116	PCB 095/93	PCB 097/86	PCB 099	PCB 101/89/90	PCB 105/127	PCB 110	PCB 118/106
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
1/10/2002	15:30	309	7.9	12	14	12	7.4	11	8.8	16	5.6	8.2	12	4.8		6.4	13	4.5	6.3	17	4.8	16	11
1/29/2002	10:40	433	102	33	23	18	15	17	12	28	5.1	7.9	14	5.2	5.5		20	5.4	6.8	20	3.3	14	8.4
1/29/2002	15:40	635	135	66	57	41	39	20	16	25	5.6	10	16	k 6.3	5.4		18	5.7	8.3	20	4.8	18	12
1/30/2002	11:40	663	7.6	10	11	8.2	4.9	41	39	48	16	50	24	28	21		43	22	36	67	8.5	41	32
1/30/2002	15:50	358	10	9.1	10	7.6	5.1	15	11	26	4.3	10	15	5.6	6.4		24	6.4	11	25	4.9	20	14
2/23/2002	11:50	202	5.5	7.2	7.4	4.3	3.2	8.8	6.8	15	2.8	5.1	8.2	2.9	3.2		13	3.4	5.3	13	3.0	11	7.3
2/23/2002	20:12	258	7.6	10	9.3	6.4	4.6	14	10	27	3.3	6.1	12	4.0	5.2		21	5.3	6.9	19	2.9	15	7.7

Date	Time	∑PCBs	PCB 128	PCB 132/168	PCB 138/163/164	PCB 141	PCB 149/139	PCB 151	PCB 153	PCB 153/132/168	PCB 156	PCB 158/160	PCB 170/190	PCB 174/181	PCB 177	PCB 180	PCB 183	PCB 187/182	PCB 194	PCB 195	PCB 201	PCB 203/196
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
1/10/2002	15:30	309	3.3	3.7	19	2.7	12	3.0	18		1.6	1.8	4.5	8.7	3.6	10	2.7	8.4	2.9	k 1.3	k 0.43	3.6
1/29/2002	10:40	433	1.9	C153	11	1.9	9.0	2.5		15	0.92	1.0	2.8	2.2	2.3	6.6	1.6	4.7	1.6	k 0.61	0.43	2.6
1/29/2002	15:40	635	3.0	C153	17	2.7	13	3.8		23	1.3	1.7	3.8	3.7	3.1	10	2.9	7.5	2.3	0.78	0.55	3.7
1/30/2002	11:40	663	2.5	C153	20	3.2	17	5.9		29	1.0	1.6	2.3	ND	2.5	7.0	2.4	7.2	1.1	ND	0.44	2.4
1/30/2002	15:50	358	3.1	C153	20	2.8	15	4.1		26	1.5	1.7	4.6	4.4	3.9	12	3.3	10	2.8	ND	0.73	4.3
2/23/2002	11:50	202	k 1.9	C153	12	1.5	10	2.4		8.8	0.86	0.90	2.7	4.3	2.1	6.1	2.1	5.6	r 1.7	0.67	0.44	k 2.0
2/23/2002	20:12	258	1.7	C153	11	1.5	9.5	2.4		7.9	0.71	0.75	2.4	4.6	2.3	4.9	1.9	5.1	1.4	ND	0.34	2.1

Appendix Table A2. PCB concentrations in Mallard Island samples, WY 2003. ND = concentration was below detection limit. Cxxx = coelution, where xxx is the lowest number of the coeluting congeners where the value is stored. K = peak detected but did not meet quantification criteria; reported result represents estimated maximum possible concentration. E = Exceeds calibrated linear range, dilution data provides new result. Q = Accuracy unknown.

Date	Time	∑PCBs	PCB 008	PCB 018/30	PCB 028/20	PCB 031	PCB 033/21	PCB 044/47/65	PCB 049/69	PCB 052	PCB 056	PCB 060	PCB 066	PCB 070/74/61/76	PCB 074	PCB 087/97/86/108/119/125	PCB 095/93/98/100/102	PCB 097	PCB 099/83
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
12/18/2002	15:04	699	4.2	10	19	16	11	45	23	97	10	4.9	19	56	C70	32	76	C87	28
12/18/2002	19:35	613	3.8	11	19	15	9	40	20	86	8.1	4.2	17	49	C70	29	67	C87	25
12/18/2002	22:55	439	1.7	4.9	12	5.5	2.0	20	10	50	3.2	k 1.66	e 8.44	20	C70	e 17.5	36	C87	16
12/19/2002	15:17	601	5.3	12	24	18	15	q 35.9	q 17.1	q 56.3	q 13.5	q 6.8	q 21.8	q 48.2	C70	q 25.8	q 45.1	C87	q 21.4
12/19/2002	23:04	846	8.1	22	41	34	27	q 57.1	q 28.7	q 80.9	q 23.4	q 12.9	q 37.5	q 80	C70	q 30.3	q 53.3	C87	q 25.5
12/21/2002	1:05	709	q 11.5	q 21.7	q 38.9	q 33.4	q 28	q 107	q 20.7	q 42.2	q 20.6	q 10.3	q 31.3	q 56.1	C70	q 19.9	ND q	C87	q 15.7
12/21/2002	9:15	475	6.7	17	29	22	16	30	15	35	13	7.5	20	37	C70	15	23	C87	13
12/21/2002	11:21	503	7.1	19	35	28	22	34	16	34	16	9.0	23	43	C70	15	20	C87	12
12/22/2002	7:35	628	q 6.54	17	31	24	17	q 45.2	q 19.4	q 61.2	q 14.4	q 8.19	q 24.2	q 51.9	C70	q 25	q 44.7	C87	q 22
1/4/2003	17:00	476	5.8	12	20	18	12	31	17	56	9.1	4.9	17	42	C70	19	41	C87	17
1/5/2003	0:13	684	4.7	13	21	18	11	46	24	96	10	5.3	20	60	C70	32	73	C87	27
1/6/2003	7:54	318	3.6	12	15	14	8.7	21	11	37	5.7	3.3	10	24	C70	11	22	C87	10
1/6/2003	12:58	370	3.3	10	15	12	7.2	20	11	36	5.7	3.1	10	24	C70	16	27	C87	13
5/5/2003	11:30	6677	48	79	126	127	66	412	232	1180	50	27	e 158	566	C70	e 370	845	C87	373
5/5/2003	14:00	3853	20	46	72	70	33	243	135	646	29	15	93	311	C70	210	486	C87	188
5/5/2003	14:20	1828	10	23	38	38	19	120	67	315	14	7.1	42	163	C70	e 94.7	221	C87	90
5/6/2003	12:00	883	6.5	15	24	21	10	55	30	140	6.6	4.0	21	72	C70	e 44.2	100	C87	39

Appendix Table A2 (continued). PCB concentrations in Mallard Island samples, WY 2003. Q = Accuracy unknown. K = Peak detected, but did not meet quantification criteria; reported result represents estimated maximum possible concentration.

Date	Time	∑PCBs	PCB 101/90/113	PCB 105	PCB 110/115	PCB 118	PCB 128/166	PCB 132	PCB 138/129/160/163	PCB 141	PCB 149/147	PCB 151/135/154	PCB 153/168	PCB 156/157	PCB 158	PCB 170	PCB 174	PCB 177	PCB 180/193
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
12/18/2002	15:04	699	58	5.8	41	16	2.3	8.3	19	3.7	24	11	19	1	1.7	3.8	4.2	3.2	10
12/18/2002	19:35	613	51	5.1	38	15	2.4	7.1	16	3.0	20	9	15	1	1.6	2.6	2.9	2.3	6.3
12/18/2002	22:55	439	31	6.8	26	17	4.1	7.4	25	4.1	19	8.7	23	1.9	k 2.61	k 5.43	5.8	4.1	14
12/19/2002	15:17	601	q 39.3	q 7.8	q 37.8	q 17.4	q 3.87	q 8.62	q 24.6	q 3.85	q 21.4	q 9.01	q 21.2	q 2.07	q 2.43	3.8	4.0	3.3	8.8
12/19/2002	23:04	846	q 46	q 9.1	q 39.7	q 19.7	q 3.55	q 8.98	q 28.6	q 5.07	q 25.5	q 11	q 22.5	q 2.26	q 2.61	6.6	7.3	5.2	15
12/21/2002	1:05	709	q 25.1	q 9.4	q 26.1	q 19.4	q 4.8	k q 7.05	q 33.5	k q 3.99	q 19.4	k q 8.75	q 24.3	q 3.11	q 2.79	7.3	7.3	6.7	17
12/21/2002	9:15	475	21	6.1	22	13	q 3.09	q 5	q 19.1	q 2.78	q 14.6	q 6.04	q 16.8	q 1.61	q 1.78	4.6	5.5	4.2	11
12/21/2002	11:21	503	19	6.0	21	13	q 2.61	q 5.33	q 19.5	q 2.88	q 14.5	q 5.72	q 14.4	q 1.66	q 1.62	4.9	5.9	3.9	11
12/22/2002	7:35	628	q 39.8	q 7	q 33.9	q 16.1	2.8	6.6	20	3.1	18	7.6	19	1.8	1.9	3.9	4.8	3.1	10
1/4/2003	17:00	476	33	4.3	24	11	1.9	5.3	14	2.5	15	6.6	12	1.0	1.2	2.7	3.0	k 2.49	6.3
1/5/2003	0:13	684	56	5.9	40	17	2.3	7.6	17	3.2	21	9.2	15	1.2	1.5	2.5	3.1	2.5	6.9
1/6/2003	7:54	318	18	3.4	15	8	k 1.41	3.5	10	1.8	10	4.4	10	1.0	1.0	2.3	2.5	k 1.88	5.8
1/6/2003	12:58	370	24	5.0	23	12	2.5	5.6	17	3.1	14	5.6	14	1.9	1.5	3.1	3.5	2.5	7.7
5/5/2003	11:30	6677	780	50	440	193	10	54	82	19	151	70	86	3.5	8.9	4.8	10	5.5	14
5/5/2003	14:00	3853	383	33	259	124	q 9.24	q 39.1	q 69.3	q 14.1	q 103	q 50.6	q 71.7	3.8	q 7.15	k 7.08	12	6.9	21
5/5/2003	14:20	1828	179	15	119	55	3.9	16	31	6.6	47	22	31	1.5	3.1	2.9	4.4	2.7	8.3
5/6/2003	12:00	883	81	8.1	58	28	2.6	8.6	18	3.3	23	12	19	1.3	2.0	k 2.97	3.4	2.9	7.5

Appendix Table A2 (continued). PCB concentrations in Mallard Island samples, WY 2003. K = Peak detected, but did not meet quantification criteria; reported result represents estimated maximum possible concentration.

Date	Time	∑PCBs	PCB 183/185	PCB 187	PCB 194	PCB 195	PCB 201	PCB 203
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
12/18/2002	15:04	699	3.5	7.4	2.1	0.86	0.51	1.5
12/18/2002	19:35	613	2.4	k 5.38	1.5	0.58	k 0.369	1.2
12/18/2002	22:55	439	5.1	11	3.8	1.4	0.51	3.4
12/19/2002	15:17	601	3.3	7.3	2.1	k 0.786	0.43	1.6
12/19/2002	23:04	846	4.5	11	4.1	1.8	0.73	3.0
12/21/2002	1:05	709	5.5	11	k 4	1.9	0.73	3.0
12/21/2002	9:15	475	3.4	7.2	3.1	1.0	k 0.395	k 2.31
12/21/2002	11:21	503	3.3	7.5	3.1	1.2	0.41	2.1
12/22/2002	7:35	628	3.1	7.6	2.9	1.1	0.48	2.1
1/4/2003	17:00	476	2.1	4.8	1.6	0.66	k 0.356	k 1.19
1/5/2003	0:13	684	2.6	5.7	2.0	k 0.812	k 0.37	1.8
1/6/2003	7:54	318	k 1.77	4.2	1.6	0.64	0.26	1.2
1/6/2003	12:58	370	2.4	k 5.81	1.9	0.87	k 0.329	1.9
5/5/2003	11:30	6677	9.2	18	2.0	0.92	1.1	2.7
5/5/2003	14:00	3853	10	21	3.9	2.3	1.5	4.6
5/5/2003	14:20	1828	4.5	9.1	k 1.8	0.91	0.62	2.0
5/6/2003	12:00	883	k 2.88	6.6	1.8	0.89	k 0.541	1.7

Appendix Table A3. OC pesticide concentrations in Mallard Island water samples. ND = concentration was below detection limit. K = peak detected but did not meet quantification criteria; reported result represents estimated maximum possible concentration. Q = Accuracy unknown. NA = result not available.

Date	Time	∑DDT	o,p'-DDD	o,p'-DDE	o,p'-DDT	p,p'-DDD	p,p'-DDE	p,p'-DDT	∑Chlordanes	alpha-chlordane	gamma-chlordane	cis-nonachlor	trans-nonachlor	heptachlor	heptachlor epoxide	oxychlordane	dieldrin
		pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
1/10/2002	3:30:00 PM	1100	78	ND	k 22	195	715	90	111	39	27	r 13	25	ND	6.8	ND	60
1/29/2002	10:40:00 AM	462	38	10	13	96	272	33	41	21	14	ND	ND	ND	6.2	ND	63
1/29/2002	3:40:00 PM	519	38	11	13	113	306	38	56	20	16	ND	14	ND	k 5.86	ND	85
1/30/2002	11:40:00 AM	505	44	10	12	101	307	31	56	19	14	ND	12	ND	k 5.84	k 5	80
1/30/2002	3:50:00 PM	530	40	12	12	120	312	34	68	21	18	ND	14	ND	k 7.84	k 7	77
2/23/2002	11:50:00 AM	342	32	7.1	k 11.4	103	167	22	74	24	18	k 8.1	15	ND	8.5	ND	119
2/23/2002	8:12:00 PM	390	42	9.0	k 12.1	101	199	k 27.4	72	23	19	k 6.46	16	ND	7.5	ND	117
12/18/2002	3:04:00 PM	460	47	13	ND	115	236	49	94	31	27	ND	23	k 3.37	k 9.8	ND	161
12/18/2002	7:35:00 PM	500	50	11	20	112	255	53	113	40	30	ND	27	ND	17	ND	210
12/18/2002	10:55:00 PM	1298	70	11	39	173	777	q 227	168	47	38	17	37	k 0.957	22	7	249
12/19/2002	3:17:00 PM	541	q 62.5	9	q 15.5	q 146	259	q 48.4	105	38	28	ND	26	ND q	13	ND	164
12/19/2002	11:04:00 PM	1553	q 86.9	31	47	q 176	898	q 314	178	55	53	ND	49	ND	21	ND	240
12/21/2002	1:05:00 AM	1240	q 67.7	q 22.8	q 39.3	q 121	q 817	q 172	126	36	32	k 12.6	30	ND q	15	ND	225
12/21/2002	9:15:00 AM	1136	65	23	36	128	725	q 159	126	40	34	ND	30	ND	23	ND	227
12/21/2002	11:21:00 AM	1115	66	21	39	128	701	160	135	37	31	k 14.5	32	ND	21	ND	221
12/22/2002	7:35:00 AM	986	q 75.4	16	q 32.7	q 143	598	q 121	134	46	34	ND	33	ND q	17	k 4.77	219
1/4/2003	5:00:00 PM	495	41	ND	19	84	298	53	75	23	24	ND	16	ND	12	ND	160
1/5/2003	12:13:00 AM	574	39	15	21	91	351	57	77	22	23	ND	20	ND	13	ND	183
1/6/2003	7:54:00 AM	575	42	k 13.1	17	90	354	59	84	26	24	ND	23	ND	11	ND	179
1/6/2003	12:58:00 PM	631	39	14	20	91	403	65	87	30	23	ND	21	ND	13	ND	179
5/5/2003	11:30:00 AM	260	q 29.6	q ND	q ND	q 70	q 160	NA	88	kq 61.3	q 23.4	q ND	q ND	3	ND	ND	78
5/5/2003	2:00:00 PM	NA	NA	NA	NA	NA	NA	NA	15	NA	NA	NA	NA	q ND	15	q ND	205
5/5/2003	2:20:00 PM	241	q 27.5	q 3.23	q ND	q 65.6	q 145	NA	56	q 30.5	q 20.7	q ND	q ND	2	k 3.13	ND	k 91.3
5/6/2003	12:00:00 PM	287	q 31	q 4.49	q ND	q 73.7	q 178	NA	72	q 25.9	q 21.5	q ND	q 15.6	ND	9	ND	101

Appendix Table A4. PAH concentrations in Mallard Island water samples. ND = concentration was below detection limit. K = peak detected but did not meet quantification criteria; reported result represents estimated maximum possible concentration. Q = Accuracy unknown. NQ = not quantifiable. NA = not available

Date	Time	TPAHs	LPAHs	1-Methylnaphthalene	2,3,5-Trimethylnaphthalene	2,6-Dimethylnaphthalene	2-Methylnaphthalene	Biphenyl	Naphthalene	1-Methylphenanthrene	Acenaphthene	Acenaphthylene	Anthracene	Fluorene	Phenanthrene
		ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
1/29/2002	10:40	19	8.9	0.93	0.43	0.49	1.5	0.52	2.2	0.48	0.45	NDk 0.336	0.37	NDk 0.32	1.6
1/29/2002	15:40	25	10	0.98	0.54	0.47	1.5	0.63	2.5	0.54	0.59	NDk 0.352	0.38	0.49	1.8
1/30/2002	11:40	16	8.8	0.83	0.44	0.44	1.4	0.55	2.2	0.40	0.40	NDk 0.327	0.27	0.33	1.5
1/30/2002	15:50	33	12	1.01	0.51	0.49	1.6	0.67	2.9	0.69	0.72	NDk 0.401	NDk 0.561	0.51	2.4
2/23/2002	11:50	23	14	2.47	0.57	1.4	3.6	0.71	NDk 4.38	2.2	NDk 0.452	0.30	0.47	NDk 0.889	2.3
2/23/2002	20:12	23	14	2.68	0.75	1.3	3.7	0.77	NDk 4.76	1.9	NDk 0.623	NDk 0.275	0.35	NDk 0.965	2.5
12/18/2002	15:04	19	7.5	0.68	0.36	0.49	0.98	0.34	k 2.64	0.69	ND	ND	0.12	0.21	1.0
12/18/2002	19:35	14	6.9	0.59	0.47	0.50	0.98	0.31	2.6	0.20	ND	ND	k 0.0989	0.23	0.84
12/18/2002	22:55	12	1.5	NQ	kq 0.564	NDq	NQ	NQ	NQ	ND	ND	k 0.132	ND	ND	0.82
12/19/2002	15:17	36	10	0.96	0.53	0.54	k 1.89	0.41	k 3.19	0.40	ND	ND	0.41	0.35	1.7
12/19/2002	23:04	21	9.1	0.90	0.49	0.67	k 1.81	0.31	k 2.82	0.35	ND	ND	0.14	0.25	1.4
12/21/2002	1:05	23	13	1.54	1.0	0.85	k 2.64	0.50	3.2	0.67	ND	k 0.164	k 0.128	0.35	2.0
12/21/2002	9:15	20	10	0.98	0.68	0.56	k 2.06	0.39	k 2.83	0.41	0.18	ND	0.16	0.42	1.6
12/21/2002	11:21	20	10	1.02	0.84	0.77	k 2.14	0.45	2.6	0.43	ND	k 0.135	k 0.124	k 0.244	1.5
12/22/2002	7:35	23	11	1.16	0.70	0.72	k 2.53	0.41	k 3.09	0.41	ND	k 0.14	0.15	k 0.268	1.6
1/4/2003	17:00	20	12	1.34	0.53	0.60	2.0	0.49	4.2	0.29	k 0.163	k 0.451	0.13	k 0.353	1.3
1/5/2003	0:13	16	8.4	0.90	0.42	0.51	1.7	0.45	k 2.85	0.27	ND	ND	k 0.112	0.25	0.97
1/6/2003	7:54	16	8.6	0.90	0.58	0.61	1.4	0.35	3.0	0.30	ND	ND	k 0.109	0.22	1.1
1/6/2003	12:58	22	12	1.09	0.71	0.85	1.7	0.54	3.7	NA	ND	ND	0.25	0.34	3.3
5/5/2003	11:30	17	6.2	0.60	0.31	0.28	1.0	0.45	1.9	ND	k 0.195	k 0.169	ND	k 0.128	1.2
5/5/2003	14:00	20	7.1	0.66	k 0.32	ND	k 1.34	k 0.432	2.6	ND	ND	k 0.173	ND	k 0.604	1.0
5/5/2003	14:20	14	5.9	0.54	k 0.28	k 0.263	1.0	k 0.36	2.5	ND	ND	k 0.142	ND	ND	0.80
5/6/2003	12:00	23	14	1.10	k 0.379	0.47	1.6	k 0.515	4.6	ND	1.8	k 0.176	0.37	1.2	1.3

Appendix Table A4 (continued). PAH concentrations in Mallard Island samples. ND = concentration was below detection limit. K = peak detected but did not meet quantification criteria; reported result represents estimated maximum possible concentration. Q = Accuracy unknown.

Date	Time	TPAHs	HPAHs	Benz(a)anthracene	Chrysene	Fluoranthene	Perylene	Benzo(a)pyrene	Pyrene	Benzo(e)pyrene	Benzo(bjk)fluoranthene	Dibenz(a,h)anthracene	Benzo(ghi)perylene	Indeno(1,2,3-cd)pyrene
		ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
1/29/2002	10:40	19	10	NDk 0.726	1.1	2.5	q 1.05	q 0.731	2.6	0.71	1.9	ND	NDk 0.864	NDk 0.595
1/29/2002	15:40	25	15	NDk 0.638	1.2	2.5	q 2.21	q 1.13	3.1	0.94	2.2	ND	1.7	NDk 1.06
1/30/2002	11:40	16	7.4	NDk 0.327	0.67	1.6	q 1.19	q 0.44	2.0	0.41	1.1	ND	NDk 0.8	NDk 0.521
1/30/2002	15:50	33	22	NDk 0.928	1.5	3.3	q 3.01	q 1.6	4.1	1.3	2.9	ND	2.5	1.57
2/23/2002	11:50	23	9.2	NDk 0.5	1.1	2.0	1.09	0.60	2.6	0.59	1.3	ND	NDk 1.07	NDk 0.604
2/23/2002	20:12	23	8.7	NDk 0.373	0.71	1.7	0.87	0.50	2.3	0.57	1.1	ND	0.93	NDk 0.576
12/18/2002	15:04	19	11	k 0.355	0.85	1.1	1.18	0.80	2.9	0.77	1.2	ND	1.1	k 0.775
12/18/2002	19:35	14	6.7	k 0.236	0.56	0.70	0.90	0.49	1.4	0.54	0.77	ND	k 0.702	k 0.443
12/18/2002	22:55	12	11	k 0.407	0.83	0.98	1.43	0.90	1.6	0.90	1.3	ND	1.2	k 1.01
12/19/2002	15:17	36	25	k 1.25	3.4	3.0	1.65	2.14	4.3	2.5	3.7	k 0.293	1.8	1.5
12/19/2002	23:04	21	12	k 0.485	1.3	1.2	1.30	0.99	2.0	1.2	1.5	k 0.122	1.3	0.91
12/21/2002	1:05	23	10	k 0.34	0.95	1.1	1.16	0.60	1.5	0.98	k 1.12	k 0.144	1.1	0.67
12/21/2002	9:15	20	10	k 0.391	0.91	k 1.17	k 1.24	k 0.635	1.6	k 0.939	k 1.16	ND	1.0	0.71
12/21/2002	11:21	20	10	k 0.342	0.95	1.1	1.30	0.67	1.7	0.89	1.1	k 0.122	1.0	0.60
12/22/2002	7:35	23	12	k 0.418	1.1	1.3	1.49	1.00	1.8	1.2	1.4	k 0.118	1.3	0.84
1/4/2003	17:00	20	8.3	k 0.338	0.79	0.90	0.87	0.57	1.5	0.64	1.0	k 0.121	k 0.91	k 0.572
1/5/2003	0:13	16	7.2	k 0.334	0.83	0.72	0.75	0.56	1.2	0.64	0.96	ND	k 0.747	k 0.501
1/6/2003	7:54	16	7.4	k 0.273	0.83	0.79	0.89	0.46	1.4	0.61	0.85	ND	k 0.818	k 0.442
1/6/2003	12:58	22	9.2	k 0.39	1.0	2.5	1.07	0.61	NA	0.72	1.3	ND	k 1.01	k 0.606
5/5/2003	11:30	17	10	k 0.637	0.98	1.5	k 1.11	k 0.859	1.9	k 0.7	k 1.25	ND	k 0.956	k 0.645
5/5/2003	14:00	20	13	kq 0.57	0.95	1.3	kq 1.68	kq 0.881	2.5	kq 0.955	q 1.57	NDq	k 1.53	kq 1.2
5/5/2003	14:20	14	8.4	k 0.36	0.63	0.88	1.14	k 0.638	1.4	0.65	1.1	ND	k 0.951	k 0.718
5/6/2003	12:00	23	10	k 0.59	0.72	1.2	k 1.24	k 0.598	1.7	0.70	1.2	ND	k 0.922	k 0.766

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