

Estimation of Loads of Mercury, Selenium, PCBs, PAHs, PBDEs, Dioxins, and Organochlorine Pesticides from the Sacramento-San Joaquin River Delta to San Francisco Bay

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**Estimation of Loads of Mercury, Selenium, PCBs, PAHs, PBDEs, Dioxins, and
Organochlorine Pesticides from the Sacramento-San Joaquin River Delta to San
Francisco Bay**

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1. Executive Summary

Contaminant concentrations from the Sacramento- San Joaquin River watershed were determined in water samples during flood flows in an ongoing effort to describe contaminant loads entering San Francisco Bay, CA, USA. The contaminants of concern were predominantly PCBs and mercury with a profile of mercury species to better understand bioavailability. Calculated PCB and total mercury loads during the 6-year observation period ranged between 3.9 and 19 kg/yr and 61 and 470 kg/yr, respectively. Long term average PCB loads were estimated at 7.7 kg/yr and total mercury loads were estimated at 210 kg/yr. PCB loads indicated a mixture of aroclors dominated by Aroclor 1254 with additional contributions of Aroclors 1016/1242, 1248, and 1260. Total mercury was dominated by particulate forms (73%), with methylated and reactive forms making up 1.6 and 6.1%, respectively. Also monitored were PAHs, PBDEs (two years of data), and dioxins/furans (one year of data) with average loads of 392, 11, and 0.15/0.014 (OCDD/OCDF) kg/yr, respectively. Organochlorine pesticide loads were estimated at 9.9 kg/yr (DDT), 1.6 kg/yr (chlordane), and 2.2 kg/yr (dieldrin). Selenium loads were estimated at 16,300 kg/yr. With the exception of selenium, all average contaminant loads described in the present study were close to or below regularly load allocations

established for North San Francisco Bay. The study demonstrates that large river systems can supply very large loads of contaminants to sensitive coastal systems despite rather dilute concentrations. It also demonstrates an ideal methodology that could be applied to other large systems.

2. Introduction

Polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), several organochlorine (OC) pesticides (DDT, chlordanes, and dieldrin), polybrominated diphenyl ethers (PBDEs), and dioxins are highly stable and toxic organic pollutants of concern in San Francisco Bay (She et al. 2002; Holden et al. 2003; She et al. 2004; Oros et al. 2005; Greenfield and Davis 2005; Connor et al. 2007; Davis et al. 2007; Oram et al. 2008; Davis et al. 2011). Despite the fact that the production and sale of some of these pollutants has been prohibited in most countries for many decades, they still pose potential threats to the health of humans and aquatic life. Their widespread use and dispersion has left residues in soils and sediments of the Sacramento and San Joaquin River watersheds that are transported to the Bay mostly during large storm events. Similarly, many studies of methylmercury (MeHg) bioaccumulation and effects have raised concern about mercury (Hg) contamination (Davis et al. 2003; Eagles-Smith et al. 2009; Greenfield and Jahn 2010; Gassel et al. 2011; Davis et al. 2011; Davis et al. in preparation) and resulted in a fish consumption advisory for San Francisco Bay (OEHHA 2011).

Due to these concerns, the San Francisco Bay Regional Water Quality Control Board (Water Board) has allocated loads as a tool toward achieving water quality to support the beneficial uses. Due to uncertainties in loads estimates, the Water Board has called for better quantification of loads from the main sources. Monitoring of contaminants in the Sacramento River, the largest single source for some contaminants, was conducted beginning in January of 2002. The objectives of this monitoring were to characterize water concentrations of suspended sediment concentration (SSC), Hg, selenium (Se), PCBs, PAHs, PBDEs, dioxins and furans, and OC pesticides in response to flood flows, and to estimate annual loads for all measured contaminants. The distribution and temporal trends of these contaminants in San Francisco Bay and its tributaries is complex, and the detailed documentation of concentrations and loads from the Central Valley watershed is valuable for determining potential impacts to water quality.

3. Methods

3.1 Site Description

San Francisco Bay is located on the Central Coast of California. Numerous small tributaries drain the heavily urbanized area of the Coast Range around the margin of the Bay. However, small tributaries are minor with regard to catchment area and water flow compared to the Sacramento and San Joaquin watersheds that together drain 154,000 km² (about 37% of the State of California). These watersheds include the expansive area of the eastern part of the Coast Range, the western slopes of the southern-most region of the Cascade Range, and the northern region of the Sierra Nevada Mountain Range (David et al. 2009). The Sacramento River drains the northern reaches of the Central Valley and is

characterized by high rainfall and snow pack with relatively reliable winter flows. In contrast, the San Joaquin River drains the southern drier portions of the Central Valley and parts of the San Joaquin River and some of its tributaries often run dry due to more variable rainfall and proportionally greater water diversion of water for urban and agricultural use. Even during storm events, discharge contribution from the San Joaquin River to the Delta only represents approximately 10% of the flow from the Sacramento River, Yolo Bypass, and other associated tributaries (Sacramento-San Joaquin Delta Atlas 1995).

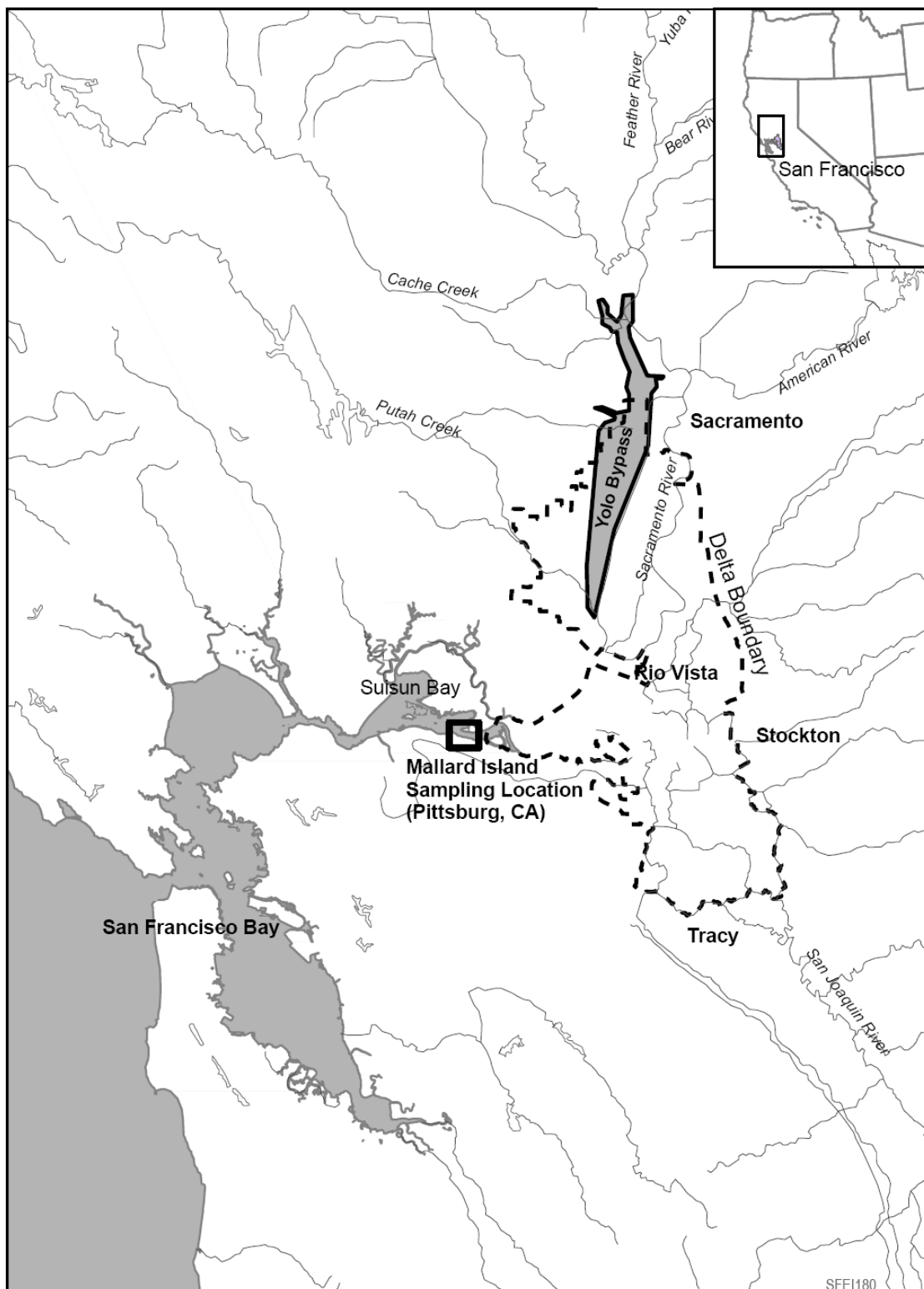


Figure 1. Map of San Francisco Bay and the sampling site at Mallard Island

(38°02'34.06"N, 125°55'12.48"W, WSG 84), where water from the Sacramento-San Joaquin River Delta enters the Bay.

Precipitation in central California is winter dominated, with 94% occurring in the City of Sacramento between October 1st and April 30th (Data: 1941-2010) (NOAA 2011a).

Annual average rainfall in the Sacramento River watershed varies from 340 mm at Mallard Island to 2,500 mm of water equivalent in the higher elevations of northern and eastern California (NOAA 2011b). The largest runoff events typically occur in January, February, or March when storms derived from equatorial regions of the Pacific Ocean drop warm rain onto the winter accumulations of snow. During these types of large runoff events, water is diverted over the Fremont weirs from the Sacramento River into the Yolo Bypass as part of the Sacramento River Flood Protection System when discharge exceeds 1,980 m³/s (Figure 1). Large flows bypass the City of Sacramento, the State Capital, passing through the Yolo Bypass, a leveed floodplain, and flow back into the Sacramento River near Rio Vista, north of the Sacramento-San Joaquin River Delta and 35 km upstream from the sampling site.

Before it flows back into the Sacramento River near Rio Vista, the Bypass receives additional flow from several tributaries draining the Coast Range Mountains, an area known for historic Hg mining and environmental Hg contamination. One of these tributaries, Cache Creek, has Hg concentrations in water exceeding 250 ng/L and in bed sediment exceeding 500 ng/g dry weight (Domagalski et al. 2004). During years of very

high river discharge, such as the El Nino events of 1998 and 2006, as much as 85% of the total flow of the Sacramento River is channeled through the Yolo Bypass. Our field monitoring program was designed to capture samples in relation to this complex upstream hydrology.

Sacramento River discharge has been estimated since water year (WY) 1956 by the California Department of Water Resources (DWR) (Note a WY begins October 1st and ends September 30th of designated year). DWR uses a water balance model, called DAYFLOW, to calculate a variety of inputs and outputs relevant to the management of the California Water Project (irrigation and drinking water supply) (DWR 2010). Greater than 80% of the annual flow occurs between the months of December and May and the wettest month typically yields 30% or more of the total annual flow. For the study period when only SSC was measured (WY 1995-2001), flow varied from 8,600-53,600 10^6 m^3 with a mean of 34,000 10^6 m^3 . Discharge varied from 11,300-50,000 10^6 m^3 with a mean of 21,400 10^6 m^3 during the period when both SSC and contaminant observations were made (WY 2002-2006, and 2010). These volumes are only slightly less than the ones observed over a longer period that captures a better characterized climatic variation (WYs 1971-2010: 3,100-79,300 10^6 m^3 ; mean = 22,700 10^6 m^3).

3.2 Field Methods

The sampling site at Mallard Island is approximately 8 km downstream of the confluence of the Sacramento and the San Joaquin Rivers. At this location, SSC was estimated since WY 1995 by the United State Geological Survey (USGS) using automated optical

backscatter measurements logged at 15-minute intervals with self-cleaning optical sensors. Samples were collected about 1 m below the water surface at the end of a pier near a deep water ship channel (17 m deep) and analyzed for SSC using established methods (ASTM 1999). All data were retrieved using an automated data processing system and edited utilizing MATLAB software. These optical backscatter data were converted to SSC using linear regression (e.g., Buchanan and Morgan 2010).

Additionally, over 300 samples were collected between January of 2002 and June of 2010 and analyzed for contaminants (Table 1). Whole water samples were collected using a peristaltic pump with tubing (PTFE with a short section of Masterflex C-Flex at the pump head) extended to ~1m below the water surface using clean hands sample handling (US EPA 2002). Dissolved fraction samples were collected using the same techniques, but with an acid-cleaned 0.45 μm cartridge filter in-line on the outlet. Trace elements analyzed included various Hg species (total Hg in whole water (HgT) and dissolved (HgD) fractions, MeHg, and acid labile Hg) and Se. Organic contaminants analyzed included selected PCBs, OC pesticides, PAHs, PBDEs, dioxins, and furans. Samples collected for analyses of organic compounds were placed in coolers with ice in the field and samples for selenium and various mercury species were preserved in accordance with their respective analytical specifications (described below).

Table 1. Summary of the number of water samples collected at Mallard Island on the Sacramento River from water year 2002 to 2010.

Water Year	HgT	HgD	MeHg	Acid Labile Hg	PCBs	PAHs	OC Pest	PBDEs	Se	Dioxins
2002	10	6	-	-	10	10	10	-	-	-
2003	23	23	-	-	23	23	23	-	-	-
2004	31	-	-	-	31	31	31	-	-	-
2005	10	-	-	-	10	10	-	10	10	-
2006	25	-	-	-	25	25	-	25	25	-
2010	36	18	18	18	36	-	-	-	-	16
Total	135	47	18	18	135	99	64	35	35	16

3.3 Analytical Methods and Quality Assurance

Water samples collected from WY 2002 to 2006 were analyzed for HgT by the University of California Santa Cruz using methods similar to EPA method 1631 (Bloom and Fitzgerald 1988, US EPA 2002). In WY 2010, total and dissolved phase water samples were analyzed for Hg by Brooks Rand Laboratories using a lab specific variant of EPA Method 1631 Revision E. Samples collected and frozen in the field (only UCSC) were thawed in the lab, oxidized with addition of 1% BrCl (only UCSC), and immediately before analysis pre-reduced using $\text{NH}_2\text{OH}\cdot\text{HCl}$. Analyses were then performed using tin chloride reduction, gas purge, gold trap amalgamation, thermal desorption, and quantification by cold vapor atomic fluorescence spectrophotometry (CVAFS).

Detection limits for HgT were sufficiently low (0.04 to 0.8 ng/L) that only a small fraction (<3%) was less than the method detection limit (MDL). Recoveries on reference materials and matrix and blank spikes were good, all within 25% of target or expected concentrations. Precision on replicate analyses was also good, with RPDs (relative

percent differences) averaging <25% in samples in a quantitative range (at least 3x MDL).

Samples analyzed for acid labile Hg were immediately chilled on ice (not frozen) and kept chilled in the dark during shipping. On receipt at the lab, samples were preserved by addition of 0.8% v:v HCl, then stored refrigerated for 21 days before analysis. Analyses then proceeded by a method similar to that for HgT analysis, but skipping the initial BrCl oxidation step to derive what is often referred to as reactive or “easily reducible” Hg under mild reducing conditions (in this case SnCl₂) (Bloom and Fitzgerald, 1988). Acid labile Hg measurements had greater uncertainty with about a third of all samples returning non-detects (<0.15 ng/L) and most were detected but not quantified (DNQ) and flagged accordingly. DNQ concentrations were used as reported by the lab as the best estimate of their actual concentrations. Recoveries on blank and matrix spikes were somewhat more variable, ranging from 60-112% (up to 40% error) but not censored. RPDs were also higher, up to 50%, as would be expected given the non-quantitative range of most results. Results were not censored but should not be considered fully quantitative.

Samples for dissolved methylmercury (MeHgD) and total methylmercury (MeHgT) were collected into bottles pre-acidified with hydrochloric acid (HCl) to a final concentration of 0.4% v:v. MeHg samples were shipped and stored in the dark at 4°C until analysis. Samples were analyzed by Brooks Rand Laboratories method BR-0011, a lab specific variant of EPA Method 1630. Sample aliquots were distilled to pre-concentrate samples,

distillates collected, and ethylated using sodium tetraethyl borate, purged from solution onto a graphitic carbon trap, then thermally desorbed, with detection and quantification by CVAFS. MeHg was not detected in one sample (<0.01 ng/L), with five more results DNQ (<0.03 ng/L). Recovery on CRM, matrix and blank spike samples was generally good, averaging within 35% of target concentrations, no analytical batches were flagged or censored. Precision on replicates was also good, with average RPDs or RSDs $<35\%$ and thus no results were censored.

Total selenium samples were transported to the lab refrigerated ($<4^{\circ}\text{C}$) and analyzed using method BR-0060, a lab specific implementation of EPA Method 1638. Selenium was reported as detected in all analyzed samples (>0.08 $\mu\text{g/L}$). Recoveries were good for CRMs, matrix and blank spikes, within 25% of their target concentrations, and precision on replicates was good, with RPDs $<25\%$.

Samples for trace organic contaminants were transported to the lab refrigerated ($<4^{\circ}\text{C}$) and analyzed by AXYS Analytical Services, LTD in Sidney, British Columbia, Canada. Prior to analysis, 8-liter samples were spiked with ^{13}C -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 remainder for analyses of PCBs and OC pesticides. The PAH extract was reduced in volume, solvent exchanged to hexane, treated for sulphur and placed on a deactivated silica column. The extracts were spiked with a labeled recovery (internal) standard prior

to instrumental analysis. PAHs were analyzed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) using splitless/split injection to a Restek Rt_x-5 chromatography column (30 m, 0.25mm i.d., 0.25mm film thickness) with the MS operated in the electron ionization (EI) multiple ion detection (MID) mode. Detection limits for PAHs varied by compound, ranging from around 20 to 1500 pg/L. For most PAHs <10% of the results were non-detects, with a handful of 25-50% non-detects (none over 50%). Blank contamination was detected in at least one batch for nearly all the PAHs. Where the blank accounted for over one third of the field sample concentration, the result was flagged and censored (not used for any data analysis); for some analytes this occurred in over half the samples. If the censored analytes accounted for over 30% of the typical sum of PAHs in a given sample, a sum of PAHs was not reported for that sample. Precision on replicate analyses was good, with only acenaphthylene showing any RPDs or RSDs over the 35% target. Recoveries on blank spike samples had average errors >35% for about half the analytes, which were flagged but not censored (still used in data analysis).

PCBs and OC pesticides were analyzed following EPA method 1668 revision A (USEPA 1999). The PCB/pesticide extract was separated into two extract fractions (E1, with PCBs and less polar pesticides, and E2, with more polar pesticides) using Florisil chromatographic columns. E1 and E2 fractions were reduced in volume, separately spiked with internal standards prior to instrumental analysis. Analyses were performed using HRGC/HRMS. PCBs were analyzed using a DB-5 column (30 m, 0.25 mm i.d., 0.1 µm film thickness) for WY 2002 samples, and with an SPB-Octyl chromatography column

(60 m, 0.25 mm i.d., 0.25 μ m film thickness) for WY 2003 and later. Pesticides were analyzed using a DB-5 column for all samples. The MS was operated in the EI mode using MID, acquiring at least two ions for each target and surrogate compound.

Although many of the minor PCB congeners were below detection limits (0.002 to 7 pg/L, varying by congener) in all samples, the more abundant congeners were generally found. About half the PCBs were detected in blanks from one or more batches. In some instances concentrations exceeded field samples by more than 30%; these samples were flagged and censored. Precision on replicates was good, with all RPDs and RSDs averaging <35%, and recoveries on blank spikes were generally within 35% of their target concentrations, with only a few congeners flagged for being outside that range but none were censored.

Detection limits ranged from 0.04 to 120 pg/L for OC pesticides, with some not detected in about one third of the samples. Half the pesticides were detected in blanks from one or more batches, with blank contamination accounting for one third or more of the concentration in some samples, which were censored as a result. Precision on replicates was good, averaging <35% RPD or RSD, and recoveries on blank spikes samples averaged within 35% of their target concentrations except for a handful of analytes, flagged but not censored.

PBDE samples were analyzed by AXYS Method MLA-033, a lab-specific implementation of EPA Method 1614. Samples were spiked with isotopically labeled

BDE surrogate standards, solvent extracted and cleaned up on a series of chromatographic columns which could include layered acid/base silica, Florisil, and alumina columns. The final extract was spiked with isotopically labeled recovery (internal) standards prior to instrumental analysis by HRGC/HRMS using a DB-5HT column (30 m, 0.25 mm i.d., 0.10 μ m film thickness), with the MS operated in EI mode using MID. One third of the reported PBDEs were not detected for at least half the samples (below limits of detection of 0.1 to 30 pg/L for various congeners). About half the PBDEs were found in blanks from one or more batches, and blanks were over one third of the concentration in field samples for many of those congeners, which were censored for those samples. Replicate precision was good for most PBDEs, with RPDs or RSDs >35% for only three congeners which were flagged but not censored. Recoveries on blanks spikes averaged within 35% of their target concentrations except PBDE 209, which was censored for large recovery errors averaging over 70% in some batches. Sums of PBDEs were not calculated for those samples because PBDE 209 usually constitutes a large proportion of the sum.

Dioxins and furans were analyzed by AXYS Analytical Method MLA-017, equivalent to EPA Method 1613B with some lab-specific modifications. Samples were spiked with a suite of isotopically labeled surrogate standards prior to analysis, solvent extracted, and cleaned up through a series of chromatographic columns that may include gel permeation, silica, Florisil, carbon/Celite, and alumina columns. The extract was concentrated and spiked with an isotopically labeled internal standard. Analysis was performed by HRGC/HRMS on a DB-5 capillary chromatography column (60 m, 0.25

mm i.d., 0.1 μm film thickness) with the MS operated in EI mode with MID. A second column, DB-225 (30 m, 0.25 mm i.d., 0.15 μm film thickness), was used for confirmation of 2,3,7,8-TCDF identification. For dioxins and furans, one quarter of the analytes was below detection limits (0.05 to 0.4 pg/L for various isomers) for over half the samples. Most of the analytes were found in blanks from one or more batches, with concentrations over 1/3 of those in field samples, which were censored and not reported for those analytes. Precision on replicates was good with average RPDs or RSDs <35%, and recoveries on blank spikes were all within 35% of their target and thus reported without flags.

3.4 Calculating mean concentrations and loads

Suspended sediment loads were calculated using methods previously described without modification (McKee et al. 2006). Some contaminant loads (HgT and MeHg) were calculated using a modification of the methods originally developed for suspended sediment (McKee et al. 2006) and further developed for Hg (David et al. 2009). HgT concentrations were estimated for 15-minute intervals using equations derived from simple linear regression between SSC and unfiltered HgT or MeHg concentrations. HgT relationships were developed for three flow classes; high flow (above 4,200 m^3/s), low flow (below 4,200 m^3/s), and high salinity (water moving upstream from San Francisco Bay with electrical conductivity above 2 mS/cm) (David et al. 2009). One regression equation was used for MeHg load calculation due to a small sample set of 18 collected during just one year.

Estimated 15-minute concentrations derived from these regressions (ng/L equivalent to g/Mm^3) were averaged for each day and combined with daily Delta Outflow (DWR, 2010) (converted from cubic feet per second to Mm^3/d) to derive daily advective loads of HgT (g). A correction factor was applied to this daily advective load to account for dispersive load using the same method described for suspended sediment (McKee et al. 2006; David et al. 2009). Dispersive load at this location is always negative (upstream); neglecting this would cause a high bias in the load estimates rather than an error about the mean (McKee et al. 2006). Since the methods are consistent with previous work, the error bounds associated with the loads estimates that were previously reported for suspended sediments ($\pm 32\%$, McKee et al. 2006) and for HgT ($\pm 36\%$, David et al. 2009) remain valid.

Flow-weighted mean concentrations (FWMC) were calculated for each year for those contaminants where the use of a regression estimator method for loads calculation was not possible (i.e., PCBs, PAHs, PBDEs, dioxins, furans, Se, and OC pesticides). FWMC were calculated by multiplying each instantaneous contaminant concentration and the corresponding flow measurement for that day, summing the results and dividing it by the combined sum of the discharge from all of the samples. Loads for these contaminants were then calculated for each year by multiplying the year-specific FWMC with the total annual discharge for that year. With this method certain simplifications were assumed (e.g., no dispersive flux, no change in source of contaminants) that helped to estimate loads for contaminants that did not strongly correlate with SSC. In the case of PCBs, there was one storm (May 2003) when concentrations were greater than encountered

during any other storm. These data were treated separately in the loads calculations and then added back into the loads estimate for the year.

The high and low flow FWMCs have uncertainties in their estimates: the flow-weighted standard deviations for various pollutants ranged from 0.6 to 9.5 % of their respective FWMCs. Typically the uncertainties around the higher flow FWMCs were larger due to inclusion of a wider range of events in that stratum. Additional uncertainties also arise from the representativeness of the events sampled for the FWMC estimate; the sampling program was designed to especially capture the highest flow events, which typically account for the majority of annual loads. For the period for which estimated loads were calculated, 88% of the samples were collected during high flow intervals accounting for the top 25% of cumulative flow ($>430,000 \text{ m}^3/\text{s}$), 11% of samples were from the middle 50% of total flow ($46,000$ to $190,000 \text{ m}^3/\text{s}$), and 1% of samples were collected from periods accounting for the lowest 25% of cumulative flow ($<12,000 \text{ m}^3/\text{s}$). This distribution suggests that the flow periods (low/middle/high) were somewhat under/over proportionally sampled. Application of the “high flow” FWMC to intermediate and moderately low flows (down to $1,000 \text{ m}^3/\text{s}$) may mis-estimate the annual load for individual contaminants, depending on how much the “low flow” FWMC is lower or higher, discussed in the later sections detailing load estimates for individual pollutants.

In order to check the potential bias associated with the FWMC estimator resulting from these and other issues, the loads were calculated both ways for HgT. To ensure the comparison was valid, the dispersive flux adjustment (McKee et al. 2006), was also

applied on an annual basis to the outcome of the FWMC estimator. This step was particularly important because of the known inverse relationship between dispersive flux and flow (McKee et al., 2006). The bias (the difference between the two methods as a percent of the regression method) for the six water years was between 89 to 194%. With the exception of WY 2005, the six years were within errors for Hg calculations ($\pm 36\%$). Given the average bias was 133%, the two methods appear to be comparable and reliable for multi-year average load calculations.

In order to remove the bias associated with our few monitoring years of data, a climatically adjusted average load was calculated. To do this, we assumed the flow variation observed in the past 40 years is representative of the present day. A power function between flow and load for years where we have data was then derived and applied to the annual flow record and the mean of the results calculated.

4. Results and Discussion

4.1 Sediment

Sediment concentrations

Continuously estimated SSC concentrations for WYs 1995-2010 varied from 8.6 - 420 mg/L with the highest concentrations occurring in response to the largest flood in the last 40 years (flood peak January 3, 1997) (Figure 2). During WYs 1995-2001 when only SSC was measured, daily averaged SSC ranged from 14 to 220 mg/L. During the water years when sampling for SSC and contaminants was completed (WY 2002-06, and WY 2010), instantaneous SSC ranged between 11 and 140 mg/L and averaged 53 mg/L. The

similarity of the sediment concentrations between the two periods (WY 1995-2001 and 2002-2006 and 2010) provides support for the assumption that the relationships between SSC and Hg concentrations are applicable for the entire 16-year sediment record despite the likelihood that source areas of sediment could differ between the two periods due to spatial variation in rainfall.

Sediment loads

Annual suspended sediment load varied from 0.26×10^6 metric t in WY 2001 to 2.6×10^6 metric t in WY 1995 and averaged 0.92×10^6 metric t. In years with similar flows (following below-average rainfall years) the average suspended sediment load was reduced by approximately 30%, suggesting that the amount of sediment transported through the system is decreasing, consistent with previous interpretations (Wright and Schoellhamer 2004). This is also consistent with Schoellhamer (2011) who found that annual average SSC has decreased at Mallard Island from 45 mg/L in the 1990s to 25 mg/L in the late 2000s, a drop of 37.5%. The climatically adjusted mean annual suspended sediment load is 0.83×10^6 metric t. Since a trend has been determined, this estimate may be bias high because the data from the 90s were included, but there is no way at this time to know if the trend will continue.

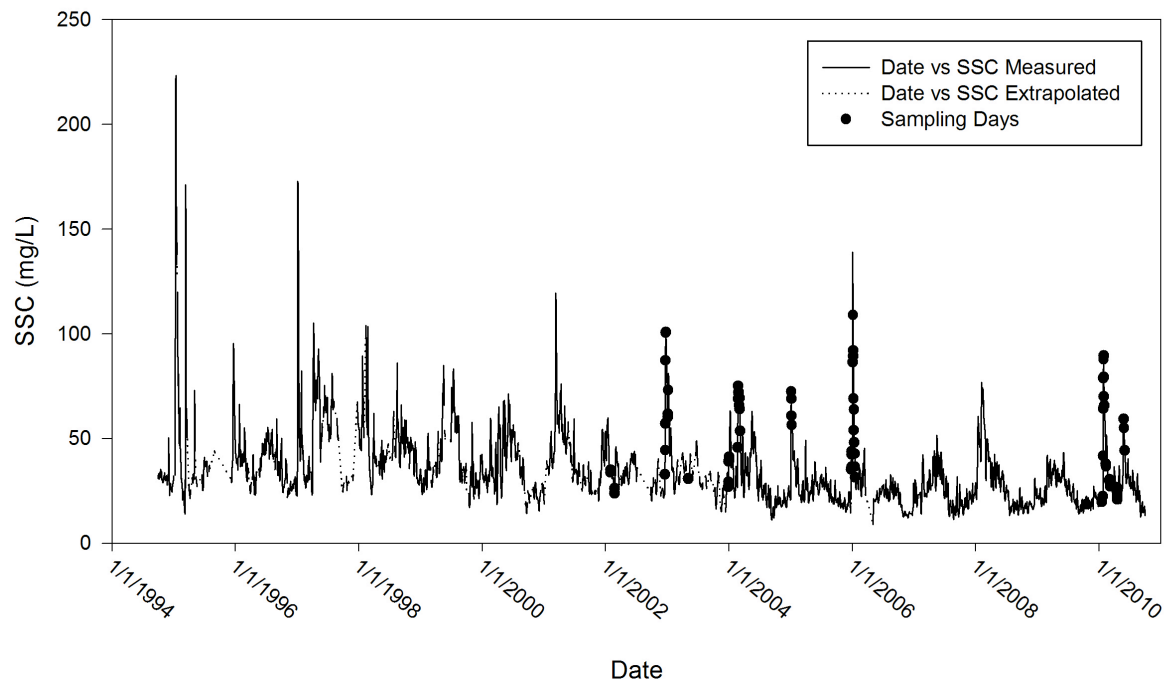


Figure 2. Daily average suspended sediment concentration at Mallard Island from water years 1995 to 2010. Sampling events for contaminants are marked with a dot.

To better show the dynamic of San Francisco Bay a comparison was made between the sediment/contaminant loads from the large river system during the wet season and the standing stock in water estimated for San Francisco Bay on an average summer day (Table 2). These summer masses were based on average concentrations from the Regional Monitoring Program (RMP) and the assumption that the volume of the Bay is approximately 5.5×10^{12} L (Oram et al. 2008). The masses in the water column of the Bay in the summer are only a fraction of the loads contributed from the Sacramento-San Joaquin River system during the winter.

4.2 Mercury

HgT concentrations

Unfiltered HgT concentrations in the Sacramento-San Joaquin River Delta varied from 4.1 to 25 ng/L during WY 2002-06, and WY 2010 with a FWMC of 12 ng/L. Two samples collected in January 2006 had much higher unfiltered HgT concentrations (42 and 75 ng/L, respectively). These samples were determined to be statistical outliers (Grubbs' outlier test) and were not included in the equation describing the regression. It was previously hypothesized (David et al. 2009) that the cause of the outliers could have been erosion or resuspension of exceptionally Hg-contaminated sediments, or that plant or invertebrate detritus could have been introduced into the sample. Review of the QA/QC samples for this analytical batch did not suggest anomalous laboratory error.

HgT loads

Daily loads of HgT varied from near 0 to 57 kg during WYs 1995-2010. Estimated annual HgT loads ranged from 38 kg in 2007 to 600 kg in 1995 with an average HgT load of 210 ± 75 kg (Table 2). Given the new data collected in WY 2010, the calculated annual average load is 20% less than that reported previously (David et al. 2009), not because of a trend, but simply due to a longer data set or possibly due to a decrease in SSC with no contaminant decrease in particle concentrations. The present, climatically adjusted mean annual HgT load is 189 kg. This annual average load meets the TMDL requirement and is below the HgT five-year average load allocation of 330 kg/yr for the Central Valley Watershed (Water Board, 2006). If normalized to watershed area, these mean loads are equivalent to $1.36 \mu\text{g}/\text{m}^2$. In this respect, the Sacramento River appears to be within the range of other large watersheds; for example the Minnesota River (0.97-1.4

$\mu\text{g}/\text{m}^2/\text{yr}$), the Headwater Mississippi (0.46-0.51 $\mu\text{g}/\text{m}^2/\text{yr}$) (Balogh et al. 1998), the Susquehanna River (1.35 $\mu\text{g}/\text{m}^2/\text{yr}$) (Lawson et al. 2001), the St Peter River (0.61-2.2 $\mu\text{g}/\text{m}^2/\text{yr}$), the Judson River (0.26-1.2 $\mu\text{g}/\text{m}^2/\text{yr}$), and the Anoka River (0.35-0.64 $\mu\text{g}/\text{m}^2/\text{yr}$) (Balogh et al. 2005). However, the Sacramento River loads are much smaller than observed in the Potomac River (8.5 $\mu\text{g}/\text{m}^2/\text{yr}$) (Lawson et al. 2001) and a San Francisco Bay urban watershed (5.3 $\mu\text{g}/\text{m}^2/\text{yr}$, Gilbreath et al., in review). Thus, despite its legacy of mercury and gold mining (David et al. 2009), the Sacramento- San Joaquin River system appears to transport relative high but dilute loads of HgT.

Table 2. Annual flows, suspended sediment and contaminant loads at Mallard Island, California, USA, from water years 1995 to 2010.

Water Year	Flow (10 ⁶ m ³)	Sediment (10 ⁶ t)	HgT (kg)	MeHgT (kg)	Se (kg)	Total PCB (kg)	Total PAH (kg)	Total PBDE (kg)	OCDD (kg)	OCDF (kg)	Sum DDT (kg)	Sum of Chlordanes (kg)	Sum of Dieldrin (kg)
Load Calculation		Regression	Regression	Regression	FWMC	FWMC	FWMC	FWMC	FWMC	FWMC	FWMC	FWMC	FWMC
1995	51,600	2.60	600										
1996	31,400	1.00	210										
1997	42,300	2.20	580										
1998	53,600	2.40	540										
1999	27,800	0.84	160										
2000	22,400	0.66	140										
2001	8,570	0.26	53										
2002	11,300	0.31	61			3.9	201				7.6	0.9	0.9
2003	17,300	0.55	100			9.9	259				11	1.6	2.9
2004	18,600	0.64	130			4.5	199				12	2.4	2.7
2005	18,600	0.42	86		11,100	5.8	271	13					
2006	50,000	2.00	470		21,400	19	1,030	8.7					
2007	7,770	0.13	38										
2008	8,230	0.22	59										
2009	8,280	0.16	45										
2010	12,800	0.32	78	1.5		3.0			0.15	0.014			
Average	24,400	0.92	210	1.5	16,300	7.7	392	11	0.15	0.014	9.9	1.6	2.2
Climatically-weighted mean loads		0.83	190			7.9	384						
Estimated summer standing stock in water for the Bay (RMP data)		0.17	28	0.2	550	1.7	295	1.2			1.4	0.2	0.3

Mercury Speciation

HgD concentrations were measured at Mallard Island in WYs 2002, 2003, and 2010. Concentrations ranged from 0.23 ng/L to 4.9 ng/L, with a FWMC calculated at 3.0 ng/L, representing between 8.0 and 65% of HgT (average of 27%). The average percentage in dissolved phase for the lower Sacramento River was slightly higher than described in other river studies, which reported HgD being closer to 20% of the total (e.g., Gill and Burland 1990) and studies conducted in San Francisco Bay (Conaway et al. 2003).

In 2010, 18 samples were analyzed for MeHgT, MeHgD, and acid labile Hg in addition to HgT and HgD. MeHgT concentrations varied from below the 0.01 ng/L detection limit to 1.8 ng/L, with a FWMC of 0.22 ng/L. MeHgT accounted for 1 to 8% of the HgT (flow-weighted mean = 2%), which falls within the range reported for other large river systems (0.71-11% of HgT) (e.g., Balogh et al. 1998; Lawson et al. 2001; Balogh et al. 2005). The 2010 river annual MeHg load was calculated at 1.5 kg for this relatively low runoff year (53% of the WY 1971-2010 mean flow) (Table 2). The estimate from the present study is slightly lower than the mean MeHg input of 1.7 kg/yr into San Francisco Bay estimated by the Central Valley Regional Water Quality Control Board that was used for the development of the TMDL (Water Board 2008a). This difference may be due to the different study periods. Normalized to watershed area, the load for WY 2010 is equivalent to 0.019 $\mu\text{g}/\text{m}^2/\text{yr}$ and lower than other large river systems (0.033-0.090 $\mu\text{g}/\text{m}^2/\text{yr}$) (e.g. Balogh et al. 1998; Lawson et al., 2001; Balogh et al. 2005).

The dissolved fraction of MeHg represented between 4 and 81% of MeHgT and with a mean of 30% on a flow-weighted basis. The concentrations varied from below the 0.01 ng/L detection limit to 0.083 ng/L, with a mean of 0.064 ng/L on a flow-weighted basis. These measurements were lower than MeHgD concentrations reported in other studies (e.g., Apte et al. 2000) that ranged from 0.01 to 0.17 ng/L for 10 tributaries to Lake Murray, Papua New Guinea, accounting for, on average, 67% of MeHgT.

Only three of the 18 collected acid labile Hg samples at Mallard Island had measurable concentration, 0.9, 1.4, and 3.0 ng/L, respectively. The three samples represented 12, 18, and 52% of HgT, and the highest concentration was measured during the lowest flow period of the wet season. Predominantly, non-detects occurred during higher flow periods. Other studies have reported concentrations of reactive Hg in West Coast rivers ranging from 0.14 to 2.8 ng/L (Gill and Burland 1990) and characterized reactive Hg fractions at around 15% of total Hg (Dean and Mason 2007). At Mallard Island on the Sacramento River, the total bioavailable fraction (MeHgT and acid labile Hg), on average, accounted for 7.7% of HgT.

4.3 Selenium

Selenium concentrations were measured at Mallard Island in WYs 2005 and 2006 with concentrations ranging from 0.31 µg/L to 0.79 µg/L (flow-weighted mean was 0.42 µg/L). Se concentrations seem to be diluted during high flow at our study location (Figure 3). The FWMC was slightly but not statistically significantly lower in 2006 (0.4 µg/L), the much wetter year, than in 2005 (0.6 µg/L), consistent with the hypothesis that

the main sources of Se are groundwater and dry weather flows from agricultural irrigation return flows (Letey et al. 2003). The sampling scheme used in this study focused on high flows and Se concentration during low flow was not measured. Using the FWMC specific to each year, Se loads were calculated to be 11,100 kg in 2005 and 21,400 kg in 2006 (Table 2). These loads, derived from extreme flow conditions, are about 4-5 times greater than the annual average selenium load of 4,000 kg/yr derived by combining data collected routinely during average flow conditions from 1993 to 2006 by the Regional Monitoring Program for contaminants in San Francisco Bay (RMP) and reported in the preliminary Se TMDL report (Water Board 2011). The disparity between the two loading estimates suggests a need for an all season sampling scheme to estimate the Se load from this watershed with certainty; i.e., both flood and non flood flows and concentrations in wet season and dry season would fully illuminate seasonal and storm based concentration variations and ensure appropriate decisions on how to calculate loads with certainty. Even within wet and dry season, there may be differences in agricultural versus reservoir releases for any given flow, so awareness of crop cycles, irrigation, drainage of rice fields for example may need consideration. These possible processes will not likely affect total flow but might have significant influences on concentrations.

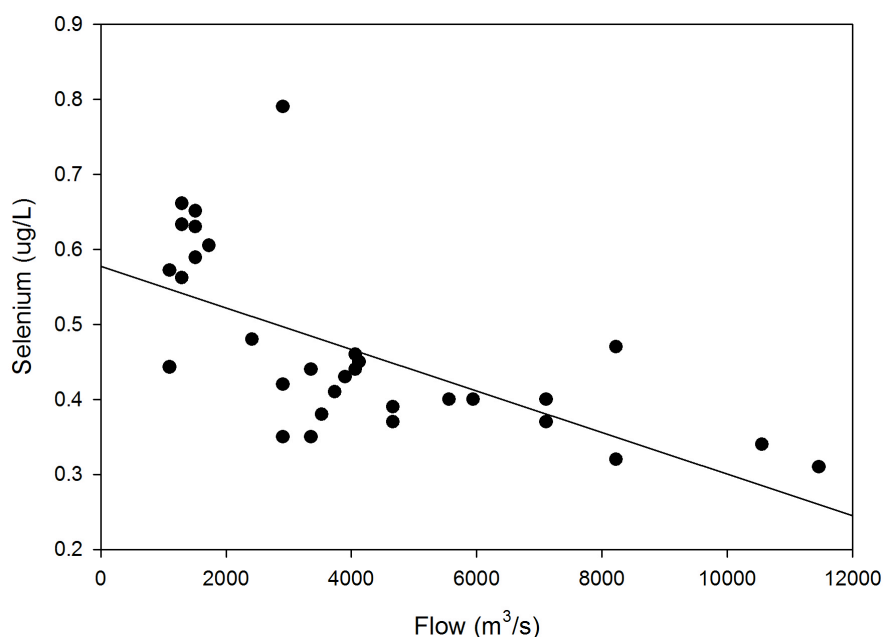


Figure 3. Selenium concentrations at Mallard Island in relation to flow (WY 2005 and 2006). Regression equation: $y = -0.00002.8x + 0.6$, $R^2 = 0.4$

San Francisco Bay is listed under Section 303(d) of the Clean Water Act as impaired for Se because concentrations may exceed levels that cause reproductive impairment in birds and fish (Water Board 2011). Bioaccumulation poses a threat to many estuarine organisms, and high Se concentrations for Suisun and Northern San Francisco Bay have been reported in bivalve tissue (Kleckner et al. 2010) and white sturgeon (Stewart et al. 2004). The concentrations measured in water in the present study were far below the chronic guideline for freshwater (4-day average) of 5 µg/L for San Francisco Bay and the Delta and below a water quality objective of 1 µg/L that US Fish and Wildlife Services support as a more protective guideline for aquatic life. When compared to the standing stock of Se in water in San Francisco Bay, the ratio of the upstream Se load contributed through this large river system to summertime mass in the Bay is four to seven times

greater than the ratios for other contaminants (Table 2). This is probably due to the predominant source of Se stemming from intensive agricultural land use around the San Joaquin River in the Central Valley of California while less Se is contributed from smaller watersheds in the Bay Area. However, during large Central Valley storms the Water Board finds no evidence of any Se related impact in the Bay. During large events, residence times in San Francisco Bay can be as short as two days and contaminants like Se in dissolved phase may be transported directly through the Bay to the Pacific Ocean.

4.4 Organic Contaminants

PCBs

Concentrations of 40 individual PCB congeners, including several co-eluting congeners, were routinely measured and summed to derive an estimate of total PCB (Σ PCB) concentrations in water samples. Σ PCB concentrations ranged from 120 to 6,700 pg/L and exhibited a FWMC of 340 pg/L (Table 3). These concentrations are over 1,000 times lower than PCB concentrations reported for other large river systems (e.g., Zhang et al. 2004). Σ PCB concentrations were significantly correlated to SSC ($p = 0.0001$) but the regression explained only 20% of the variance in the data. Thus loads were calculated by combining the FWMC with flows rather than by using a regression relationship with SSC. When the most abundant congener (PCB 153) was graphed against SSC it showed a slightly better relationship. Three results from samples collected in May 2003 had concentrations $>1,000$ pg/L; 10 times greater than the next largest concentration. A review of the QA data did not provide any explanation for these outlier concentrations. Perhaps they originated from an industrial PCB spill somewhere upstream just prior to or

during the May storm series that resulted in these higher concentrations but we have no supportive evidence to isolate the source. These data were only included in the May load, which was then added to the estimate of the remaining 11 months for that year.

Average annual loads for PCBs were estimated at 7.6 kg for the six years of monitoring (ranging from 3.0 kg in 2010 to 19 kg in 2006) (Table 2). The climatically adjusted mean annual load is 8 kg. This estimate is below the 10 kg/yr TMDL for PCBs loads to San Francisco Bay that was calculated for the California Regional Water Quality Control Board, San Francisco Bay Region (Water Board 2008b). When normalized to watershed size ($0.14 \mu\text{g}/\text{m}^2/\text{yr}$), it also is approximately 10-20 times lower than loads reported for other large river systems (Ko and Baker 2004; Foster et al. 2000) and similarly lower than a local urban small tributary systems ($2.9 \mu\text{g}/\text{m}^2/\text{yr}$, Gilbreath et al., in review). We propose that the Sacramento- San Joaquin River system, despite having patches of industrial legacy in Sacramento, Stockton and other larger cities in the Central Valley, is transmitting relatively low PCB concentrations diluted largely from a dominance of atmospheric sources, relatively low loads, and low particle concentrations.

In 2010, seven water samples were also analyzed for the expanded list of congeners (all 209) to determine whether the list of 40 congeners is representative of the bulk of total PCBs. A comparison of the results showed that the 40-congener list commonly monitored by the discharger community in the Bay Area represents only 67% of PCBs that are captured with a 208-congener list. PCB 11 was not included in the comparison because it does not originate from an Aroclor source (Hu and Hornbuckle 2010). PCB congener

patterns in 2010 indicated a generally consistent mix of Aroclors 1242, 1248, 1254, and 1260. Stronger contributions of Aroclor 1254 on April 15 and April 17, 2010, and Aroclor 1242 on April 18, 2010 suggest mobilization of different source areas during these storms.

PCB congener profiles observed over the six-year sampling period indicate a general mixture of Aroclor sources, dominated by Aroclor 1254 but with additional contributions by lower chlorinated mixtures (Aroclors 1016/1242 and 1248) and a more highly chlorinated mixture (Aroclor 1260) (Frame et al. 1996). The contributions of the lower chlorinated Aroclors were higher than is usually observed in ambient Bay samples further downstream. The congener profiles varied from year-to-year, suggesting mobilization of contaminated sediment from different source areas in response to spatially and temporally variable rainfall in the watershed. Also, reservoir releases often determine flow and thus mobilization of sediment.

PCB congener profiles also varied from storm to storm. For example, profiles observed in several samples collected in January and December 2002 indicated a relatively high contribution of Aroclor 1242 or 1016 (these two Aroclor mixtures have a similar congener composition). In December 2002, January 2003, and May 2003 a relatively high contribution of Aroclor 1248 was indicated. Relatively strong signals for Aroclor 1254 were observed in May 2003, December 2005, and April 2010. Aroclor 1242 and 1016 were commonly used in capacitors and transformers. Aroclor 1248 was used in heat transfer fluids, vacuum pumps, hydraulic fluids, and lubricants. Aroclor 1254 was used in

capacitors, Type D transformer fluids, and a variety of other products (heat transfer fluids, vacuum pumps, cutting oils, inks, adhesives, caulking compounds, insulation and other building materials, rubber, and wire and cable coatings) (Ericson and Kaley 2011). Therefore, we see nothing remarkable about the aroclor profiles that point us to a source during the May event, and generally each year and storm suggests most of the common Aroclor's are present in our samples at one time or another.

PAHs

To derive concentrations of total PAHs, 25 individual PAH congeners, spanning a range of molecular weight, were measured. Total PAH concentrations in the Sacramento-San Joaquin River Delta at Mallard Island ranged from 6,740 to 38,600 pg/L, with a FWMC of 19,000 pg/L (Table 3). Total PAHs were not significantly correlated to SSC ($p = 0.36$, t-test). Even concentrations of individual PAHs that are highly abundant and hydrophobic (e.g., benzo(a)pyrene) did not exhibit a significant relationship to SSC. Utilizing FWMCs for annual load estimations, total PAH loads ranged from 201 kg in 2002 and 2004 to 1,030 kg in 2006, with an average annual load of 392 kg (Table 2). The present, climatically adjusted mean annual load is 384 kg. When normalized to watershed area ($6.97 \mu\text{g}/\text{m}^2/\text{yr}$) these loads are approximately 35 times lower compared to PAH loads reported from other large river systems (e.g., Ko and Baker 2004; Foster et al. 2000).

When compared to the standing stock of contaminants in San Francisco Bay, PAHs are the only contaminant for which the mass in the Bay is higher than the load being contributed from the Sacramento- San Joaquin River system (Table 2). This is probably

due to larger sources of PAHs directly in the in the Bay Area that originate from combustion, vehicle emission and pavement brake down. The large river watershed in this case is likely not a major contributor of PAHs compared to smaller watersheds and direct urban runoff that create hotspots of PAHs predominantly in the northern and central sections of San Francisco Bay.

Four PAH isomer pair ratios were applied as diagnostic tracers to identify the possible sources that could contribute PAHs to the Sacramento- San Joaquin River: anthracene / anthracene + phenanthrene; benz[*a*]anthracene / benz[*a*]anthracene + chrysene; fluoranthene / fluoranthene + pyrene; and indenol[1,2,3-*c,d*]pyrene / indenol[1,2,3-*c,d*]pyrene + benzo[*g,h,i*]perylene. PAH isomer pair ratios determined from the Sacramento- San Joaquin River were then compared to PAH isomer pair ratios determined from several major PAH sources (environmental samples, petroleum, and single-source combustion) compiled previously by Yunker et al. (2002). Based on the PAH isomer measurements compiled by Yunker et al., the diagnostic tracers in the present study indicated petroleum combustion as the dominant sources for the measured PAHs. This interpretation also seems consistent with the diagnostic profiles reported in other studies (Li et al. 2003; Van Metre and Mahler 2010).

Table 3. Flow-weighted mean concentrations for all contaminants analyzed in water samples collected at Mallard Island.

Contaminant	min	max	FWMC	# of samples
HgT (ng/L)	4.1	75	12	135
HgD (ng/L)	0.23	4.9	3.0	47
MeHgT (ng/L)	<MDL	1.8	0.22	18
MeHgD (ng/L)	<MDL	0.083	0.064	18
Acid Labile Hg (ng/L)*	0.90	3.00	1.50	18
Se (µg/L)	0.31	0.79	0.42	35
PCBs (pg/L)**	120	6,700	340	135
PAHs (pg/L)	6,700	39,000	19,000	99
PBDEs (pg/L)	35	830	480	35
PBDE 47 (pg/L)	130	350	200	35
PBDE 209 (pg/L)***	110	400	190	35
OCDD (pg/L)	8.7	27	19	16
OCDF (pg/L)	0.68	2.3	1.5	16
DDT (pg/L)	240	1,600	610	64
Chlordanes (pg/L)	41	290	120	64
Dieldrin (pg/L)	60	250	150	64

*only 3 samples above MDL

** sum of 40 congeners

*** missing BDE 209 for 2006

PBDEs

Thirty-five samples were analyzed for PBDEs in WYs 2005 and 2006. However, because of blank contamination and recovery issues, BDE 209, which often represents a large proportion of the sum of PBDEs, could not be reported for many samples. Total PBDE concentrations varied from 35 pg/L to 830 pg/L with a FWMC of 480 pg/L (Table 3). Utilizing FWMCs, total PBDE loads of 13 and 8.7 kg were calculated for 2005 and 2006, respectively (Table 2). However, the 2006 loads were calculated without BDE 209 being reported for all samples. Loads made on that basis are likely to be lower bound estimates. Similar to Se, the FWMCs were diluted during wetter years; 670 and 270 pg/L for 2005 and 2006, respectively. This observation is consistent with a hypothesis that the main sources of PBDEs in the Sacramento- San Joaquin watershed was from urban areas that contribute proportionally more runoff during low flow years compared to higher flow years. Cleaner runoff from the Sierra Nevada Mountain Range likely dilutes

concentrations during high flows (Oram et al. 2008) and, if this is true, PBDE loads may be slightly underestimated because low flows were not sampled. BDEs 47 and 209 were the most dominant congeners in the PBDE mixture. BDE 47 concentrations ranged from 130 pg/L to 350 pg/L with an average of 190 pg/L and a FWMC of 200 pg/L. Due to blank contamination BDE 209 data were only available for WY 2005 and concentrations ranged from 110 pg/L to 400 pg/L with an average of 190 pg/L and a FWMC of 190 pg/L.

Dioxins/Furans

Octa-chlorinated dibenzo dioxin (OCDD) was the most abundant dioxin in water samples from the Sacramento-San Joaquin River. The most toxic tetrachlorinated dioxins were not detected; had they been detected we would have expected to see them at very low concentrations only. In only four out of the 16 samples PeCDD, 1,2,3,7,8- (a toxic pentachlorinated dioxin) was detected (flow-weighted average 0.085 pg/L). Similarly, the relatively toxic PeCDF, 2,3,4,7,8- (a pentachlorinated furan) was only detected in four samples with an average of 0.073 pg/L. The also toxic tetrachlorinated furan TCDF, 2,3,7,8- was detected in six samples that ranged from 0.07 pg/L to 0.12 pg/L (average 0.10 pg/L) (Table 4). As an index for dioxin presence in water samples, OCDD concentrations ranged from 8.7 pg/L to 27 pg/L, with a FWMC of 19 pg/L.

Octachlorinated dibenzofuran (OCDF) was the most abundant furan in water samples, ranging from 0.68 pg/L to 2.3 pg/L (FWMC was 1.5 pg/L). These concentrations were much lower than dioxin and furan congener concentrations reported for other mixed land use watersheds (Okumura et al. 2008). OCDD and OCDF showed statistically significant

relationships with SSC ($p = 0.002$ and 0.006 , respectively, t -test). For 2010, a total river load of 0.15 kg for OCDD and 0.014 kg for OCDF was calculated (Table 2). Normalized to watershed size, these loads are 10 times lower than loads reported from other watersheds with known point sources such as a pulp and paper mill discharge (e.g., Gobas et al. 1998).

Dioxin and furan data can also be presented as toxic equivalents (TEQs); the relative toxicity of a dioxin- or furan-like compound compared to dioxin/furan (toxic equivalency factors, or TEF) is multiplied by the measured concentration or load of the chemical to derive a dioxin/furan TEQ (WHO, 2005). For example, 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is one-tenth as potent as dioxin and has a TEF of 0.1 . If the load for 2,3,7,8-TCDF is 1.3 g the furan TEQ load attributable to 2,3,7,8-TCDF is only 0.13 g. Dioxin/furan TEQs for measured dioxin- and furan-like compounds with established TEFs were added to calculate the total dioxin TEQs loads, although this likely underestimates the contribution of 2,3,7,8- TCDD due to the lack of detected results, which may not be zero.

Table 4. Toxic equivalency factors for the results of 14 dioxins and furans samples collected on the Sacramento- San Joaquin River at Mallard Island.

Analyte	WHO 2005 TEF	Number of Detection	Average pg/L	FWMC pg/L	Load g	TEQ Loads
TCDD, 2,3,7,8-	1	ND	-	-	-	-
PeCDD, 1,2,3,7,8-	1	4	0.09	0.09	1.1	1.11
HxCDD, 1,2,3,4,7,8-	0.1	10	0.13	0.12	1.5	0.15
HxCDD, 1,2,3,6,7,8-	0.1	13	0.19	0.20	2.6	0.26
HxCDD, 1,2,3,7,8,9-	0.1	13	0.19	0.20	2.5	0.25
HpCDD, 1,2,3,4,6,7,8-	0.01	14	2.2	2.5	33	0.33
OCDD, 1,2,3,4,6,7,8,9-	0.0003	14	16	19	250	0.08
TCDF, 2,3,7,8-	0.1	6	0.10	0.10	1.3	0.13
PeCDF, 2,3,4,7,8-	0.3	9	0.08	0.08	1.1	0.32
PeCDF, 1,2,3,7,8-	0.03	4	0.07	0.07	0.91	0.03
HxCDF, 1,2,3,4,7,8-	0.1	13	0.12	0.12	1.6	0.16
HxCDF, 1,2,3,6,7,8-	0.1	9	0.10	0.10	1.3	0.13
HxCDF, 1,2,3,7,8,9-	0.1	4	0.13	0.13	1.7	0.17
HxCDF, 2,3,4,6,7,8-	0.1	8	0.12	0.11	1.5	0.15
HpCDF, 1,2,3,4,6,7,8-	0.01	14	0.62	0.70	9.2	0.09
HpCDF, 1,2,3,4,7,8,9-	0.01	7	0.14	0.13	1.6	0.02
OCDF, 1,2,3,4,6,7,8,9-	0.0003	14	1.4	1.5	20	0.01

OC Pesticides

Total DDT concentrations accounted for concentrations of o,p' and p,p'-isomers of DDD, DDE, and DDT. Total DDT concentrations varied from 240 to 1,600 pg/L with a FWMC of 610 pg/L (Table 3). These concentrations are about 50 times lower than reported by Kratzer (1999) for low flow conditions on the San Joaquin River at Vernalis. Total DDT (the sum of six isomers) showed a significant linear regression in the first three years of the present study with an R^2 of 0.34 ($p = 0.00002$). However, since much of the variability could not be explained by this regression, annual FWMCs were combined with annual flows to calculate loads. The average annual DDT load for WYs 2002-2004 was 9.9 kg (Table 2). Peak “instantaneous” loads were measured on February 27, 2004 (370 g/d). These were about 10 times smaller than reported by Kratzer (1999) for a winter storm (4,500 g/d in January 1995) and about four times greater than reported by Hladik et al. (2009) for the San Joaquin River near Vernalis (11 and 97 g/day for two high flow days in January 2008) and consistent with the ratio of flow between the San Joaquin and Sacramento Rivers. The relative abundance of DDT isomers provided information on

potential sources. High proportions of the p,p'- isomer occurring in samples collected at Mallard Island suggest increasingly fresher inputs of DDT during incrementally higher flows. The normalized loads ($0.014 \mu\text{g}/\text{m}^2/\text{yr}$) appear to be much smaller than observed in other larger river systems (Foster et al. 2000a; Foster et al. 2000b) despite of the long history of agriculture in the Central Valley.

Total chlordane concentrations were comprised of alpha-, gamma-, and oxy-chlordane, cis- and trans-nonachlor, heptachlor, and heptachlor epoxide. Total chlordane concentrations (the sum of five compounds) ranged from 41 to 190 pg/L with a FWMC of 120 pg/L (Table 3). Similar to total DDT, total chlordane exhibited a correlation with SSC. The observed correlation was statistically significant ($p = 0.01$) but weak ($R^2 = 0.13$). The average load derived from FWMCs for total chlordane was 1.6 kg. Dieldrin concentrations varied from 60 to 250 pg/L with a FWMC of 150 pg/L (Table 3). Total dieldrin concentrations were significantly correlated to SSC ($R^2 = 0.43$ and $p = 0.0000006$). The average annual dieldrin load was 2.2 kg for the three years of monitoring. Concentrations of these OC pesticides in Bay fish are currently below the threshold of concerns, consequently the reported loads are not considered to be problematic (Davis et al. 2011). These loads when normalized also appear to be smaller than loads from other larger river systems.

5. Conclusion

The Sacramento-San Joaquin River system supplies large loads of dilute concentrations of almost all contaminants that were measured. The exceptions seem to be MeHg and Se.

Concentrations for Se in incoming loads, for example, are higher than average ambient concentrations in North San Francisco Bay for the wet season. Efforts by the Central Valley Regional Board to reduce Se and MeHg loads in these watersheds will help reduce exposure and risk from these contaminants in Bay Area wildlife and human consumers. Combined with information on other significant transport pathways, the results from the present study have characterized loads to the Bay with high certainty. Data collected during WYs 2002-2006 and WY 2010 have resulted in significantly lower calculated loads to San Francisco Bay than previously estimated, except for Se. As explained above, we cannot at this time reconcile the apparent disparity between upstream concentrations and loads of Se and loads at Mallard Island. Resolving this issue has local regulatory importance.

The more accurate characterization of contaminant loads to San Francisco Bay from the Sacramento- San Joaquin River basin has provided information that is essential to management decisions. This new information helped to focus on load reduction efforts on other significant pathways such as runoff from smaller local watersheds in the highly urbanized nine-county Bay Area. Markedly higher contaminant concentrations and area normalized loads have been observed through RMP studies in urban storm water from these smaller local watersheds.

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