

Pesticides Associated with Suspended Sediments in the San Francisco Bay During the First Flush, December 1995

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ABSTRACT

The majority of suspended sediments are transported into estuaries by the “first flush” – runoff from the first major storm of the water year. Pesticides associated with these sediments may represent a significant fraction of pesticides transported to estuaries, where they have different environmental effects than dissolved pesticides.

Water and suspended sediment samples were collected at the head of the San Francisco Bay during a peak in suspended sediment concentration, following the first major storm. These samples were analyzed for a variety of pesticides that span a wide range of hydrophobicity. For the 19 compounds analyzed, an average of 10 was found on the samples. Few pesticides were found dissolved in concurrent water samples and at concentrations much lower than would be expected from equilibrium partitioning between the aqueous and sedimentary phases.

DDT and its metabolites were observed in all suspended sediment samples in concentrations ranging from 5.1 to 11.1 nanograms per gram dry sediment weight. Other compounds were sporadic in occurrence, but did occur at higher concentrations. For example, oxyfluorfen and endosulfan each exceeded 20 nanograms per gram in a single sample. However, there were no significant trends in the total or individual pesticide concentrations, or in the number of compounds observed as the peak in suspended sediment concentration passed the sampling site. Also, there were no significant relations between sediment-associated pesticide concentration and parameters such as K_{oc} of the pesticide, organic carbon content of the sediment, or amount of pesticide applied in the drainage basin, suggesting that observed sediment-associated pesticide concentrations may reflect disequilibrium between sedimentary and aqueous phases resulting from long equilibration times at locations where pesticides were applied, and relatively short transit times for reequilibration to occur.

INTRODUCTION

The majority of suspended sediments are transported into estuaries usually after the first major storm of the year, during the ensuing high flow (Meade, 1972; Goodwin and Denton, 1991). Onset of the winter storms causes runoff that transports sediment from upstream areas downstream to the estuary. In the estuary, these sediments represent an important food source for filter-feeding organisms such as clams (Canuel and others, 1995).

Equilibrium partitioning models (DeToro and others, 1991; Liljestrang and Lee, 1992) and field studies (for example, Pereira and others, 1996; Domagalski and Kuivila, 1993) indicate that some pesticides may be concentrated on suspended sediments. Because suspended sediment may carry appreciable amounts of associated pesticides, sediment transport may be an important mechanism for introduction of pesticides into the San Francisco Bay (for example, Domagalski and Kuivila, 1993; Bergamaschi, and others, 1997).

Pesticides associated with suspended sediments may have different environmental effects in estuaries than dissolved pesticides because suspended sediments are a primary source of nutrition for filter-feeding organisms such as clams. Also, sediments have a longer residence time in estuaries than does water (Meade, 1972; Schubel and Carter, 1984), and inputs of sediments occur in a pulse, typically once or a few times a year in response to precipitation events (Meade, 1972; Goodwin and Denton, 1991). This introduction by sediments may increase exposure times to pesticides or provide a mechanism for exposure during biologically sensitive times.

Many factors may control the concentration of pesticides on sediments. For example, the short transit times between areas of pesticide application and the estuary during winter storm runoff may mean that pesticides associated with suspended sediments do not have sufficient time to reach equilibrium (Domagalski and Kuivila, 1993; Jepsen and others, 1995; Lick and Rapaka, 1996). If

equilibrium is not achieved, higher concentrations of sediment-associated pesticides (SAPs) relative to aqueous concentrations may result. Thus, transport of suspended sediments from areas of pesticide use into estuaries may carry more pesticides than equilibrium models suggest.

Some of the possible factors that influence the distribution of pesticide concentrations, other than partitioning between the aqueous and sedimentary phases, are the timing and amount of pesticide applications, differences in the transit time between drainages and the Bay, variations in the time lag between pesticide application and onset of precipitation, the residence time of sediments within the drainage, and the effect of tidal cycles and river discharge on sediment transport and deposition (Schubel and Carter, 1984; Kratzer, in press).

We examine here the distribution of SAPs and dissolved pesticides following the first storm of the winter season at Mallard Island, a station near the head of the San Francisco Bay. The Sacramento and San Joaquin rivers drain California's Central Valley (fig. 1) through the Sacramento-San Joaquin Delta, and into San Francisco Bay. The Central Valley and Delta are areas of intense agricultural activity in which more than 500 different pesticides are applied (California Department of Pesticide Regulation, 1996).

The purpose of this study was to explore the variability in SAP concentrations in San Francisco Bay during the time suspended sediment concentrations are greatest, and the majority of sediment transport is expected to occur – during the “first flush,” the runoff of first major winter storm following the dry growing season (Goodwin and Denton, 1991, Schoellhamer, 1997). This report describes the pesticide content of suspended sediment samples collected at Mallard Island (fig. 1), near the head of the San Francisco Bay, following a storm on December 11-13, 1995 – the first major storm of the season, and during a period

of the highest recorded suspended sediment concentrations of the water year (Schoellhamer, 1997).

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EXPERIMENTAL

Samples were collected from a gage house on Mallard Island, California, located just south of the main shipping channel, 5 mi downstream of the confluence of the Sacramento and San Joaquin Rivers (fig. 1). A continuous record of optical backscatter data, stage height, and other ancillary parameters was maintained by the California Department of Water Resources and the U.S. Geological Survey during the study.

Suspended sediment samples were collected at times of predicted slack current – either slack after ebb tide or slack after flood tide. This sampling was developed to provide a twice-a-day strategy for suspended solids concentrations that best reproduces the residual near-surface suspended solids concentrations (Jennings, and others, 1997). Due to mechanical and operational difficulties, it was not possible to collect every sample indicated by the strategy.

Water for suspended sediment analysis (approximately 100-200 L, depending on

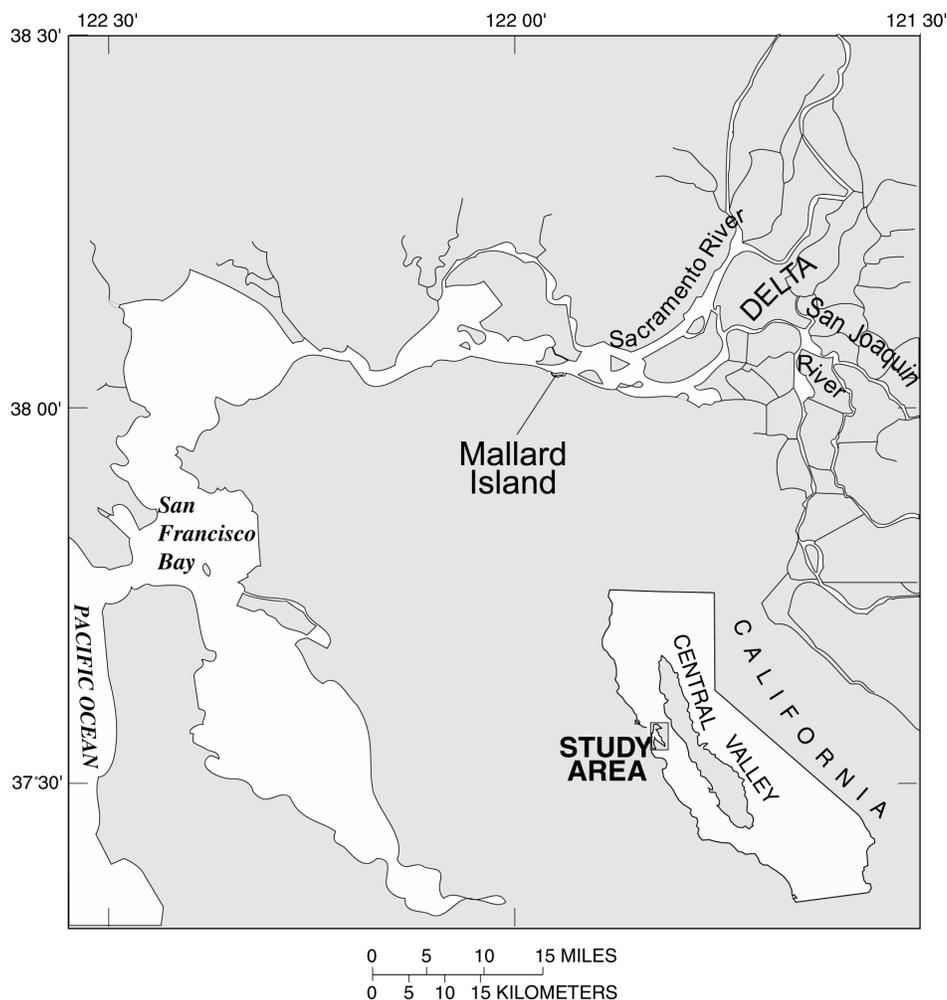


Figure 1. Location of sampling site in relation to San Francisco Bay, and the Sacramento and San Joaquin Rivers.

suspended sediment concentration) was collected by high volume peristaltic pump from 1 m below the surface into 37-L stainless steel containers, and transported to nearby facilities where sediments larger than 0.3 μm were isolated using a flow-through centrifuge into a 1 L slurry. Suspended-sediment slurries were dewatered on a high-speed centrifuge at 13,000 revolutions per minute in 50 mL Teflon centrifuge tubes, and frozen until analysis. (The use of brand names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.)

Suspended sediment samples were analyzed for pesticide content according to the method described by Bergamaschi and others (in press). Briefly, 1-10 grams (g) of wet sample were dried by grinding with Sodium Sulfate. Samples were extracted three times with fresh methylene chloride in 200-mL Teflon

bottles using an ultrasonic processor. The three extracts were composited and concentrated first by rotary evaporator, then under a stream of nitrogen to approximately 250 μL . Interfering coextracted compounds were removed by passing the sample through a 1 centimeter (cm) internal diameter (i.d.) 6 gram (g) column of 2 percent deactivated Florisil. The 250- μL sample extracts were loaded onto the cleanup column and eluted with 40 mL hexane:ethyl ether (4:1 by volume), then concentrated on a rotary evaporator and dried under nitrogen to a final volume of 1 mL. Finally, internal standards (deuterated acenaphthene, pyrene and phenanthrene) were added and the sample reduced to a final volume of 100 μL for chromatographic analysis.

Water samples for dissolved pesticide analysis were collected using a peristaltic pump from 1 meter (m) below the surface, and

analyzed according to the method described in Crepeau and others (1994). Briefly, 1 liter (L) of sample was filtered through a 142 millimeter (mm) diameter precombusted, 0.7 micrometer, glass fiber filter, and then extracted onto a 3 cubic centimeter C-8 solid phase extraction cartridge. Cartridges were dried under a stream of carbon dioxide and frozen until analyzed. On the day of analysis, the cartridges were thawed and sample extracts were eluted with 6 milliliters (mL) of a 1:1 (by volume) mixture of hexane and diethyl ether. Eluates were concentrated under a stream of nitrogen to about 200 microliters (μL), where upon internal standards (deuterated acenaphthene, pyrene and phenanthrene) were added and the mixture concentrated to a final volume of 200 μL .

Chromatographic separations for dissolved pesticide samples and suspended sediment samples were accomplished using a gas chromatograph coupled to a ion-trap mass spectrometer, using a 30 m 5 percent-phenyl methylpolysiloxane bonded phase 0.25-mm i.d.-fused silica capillary column, and a oven temperature program providing full baseline separation of all analytes (Bergamaschi and others, in press). Samples were quantified by comparing the relative response of each analyte to the response of a known amount of the most closely eluting internal standard. The relative response of each analyte was calibrated daily by analyzing a suite of standards.

RESULTS

Hydrodynamics and suspended sediment concentrations

To evaluate the distribution of SAPs in the San Francisco Bay during the first flush, suspended sediment samples were collected at Mallard Island following the first major storm during the 1995-1996 water year.

Measurements of stage height at the Mallard Island site indicate it is strongly tidally influenced. The stage height ranged nearly 2 m during the sampling period, with an average inter-tidal range of 0.4 m, and associated spring-neap variability (fig. 2c). The suspended-sediment concentration (SSC) ranged from a high of 126 milligrams per liter (mg/L) to a low of 23 mg/L, over the course of the sampling period, and there was a large change in SSC between ebb and flood tides (fig. 2d). The inter-tidal change in suspended-sediment concentration ranged from a high of 70 mg/L to a low of 15 mg/L during the

sampling period, with an average inter-tidal change of approximately 30 mg/L (fig. 2d).

Peaks in Delta outflow and SSC were observed (fig. 2b, 2e) following heavy rainfall on December 11-13, 1995 (fig. 2a), the first storm of the winter season. Delta outflow is calculated on a daily basis, and represents the contribution of the tributaries of the Sacramento and San Joaquin Rivers as well as smaller and local inputs (California Department of Water Resources, 1986). Delta outflow began to rise from a level of 250 cubic meters per second (m^3/s) on December 11 and peaked at an outflow of 2,000 m^3/s . Following the increase in Delta outflow, the SSC increased (fig. 2d), and therefore the quantity of suspended sediment transported from California's Central Valley to the San Francisco Bay increased. Tidally averaged suspended sediment concentrations (Schoellhamer, 1996) in Delta outflow in the Sacramento River at Mallard Island increased to 97 mg/L following the storm (fig. 2e, 2f), from a base level of 30 mg/L.

Sediment Associated Pesticides

Total SAP concentrations ranged from 9.8 to 43.8 nanograms per gram (ng/g) dry weight sediment (table 1), which translates to 1-4 nanograms per liter (ng/L) SAP in whole water (unfiltered) samples. There was no apparent temporal variability in the total SAP concentrations associated with suspended sediments during the course of the peak in SSC following the December 11-13 storm. The observed lack of temporal variability stands in contrast to our previous study of sediments in the San Joaquin River (using the same methods) where total SAP concentrations were higher on the rising limb of the SSC peak than on the falling

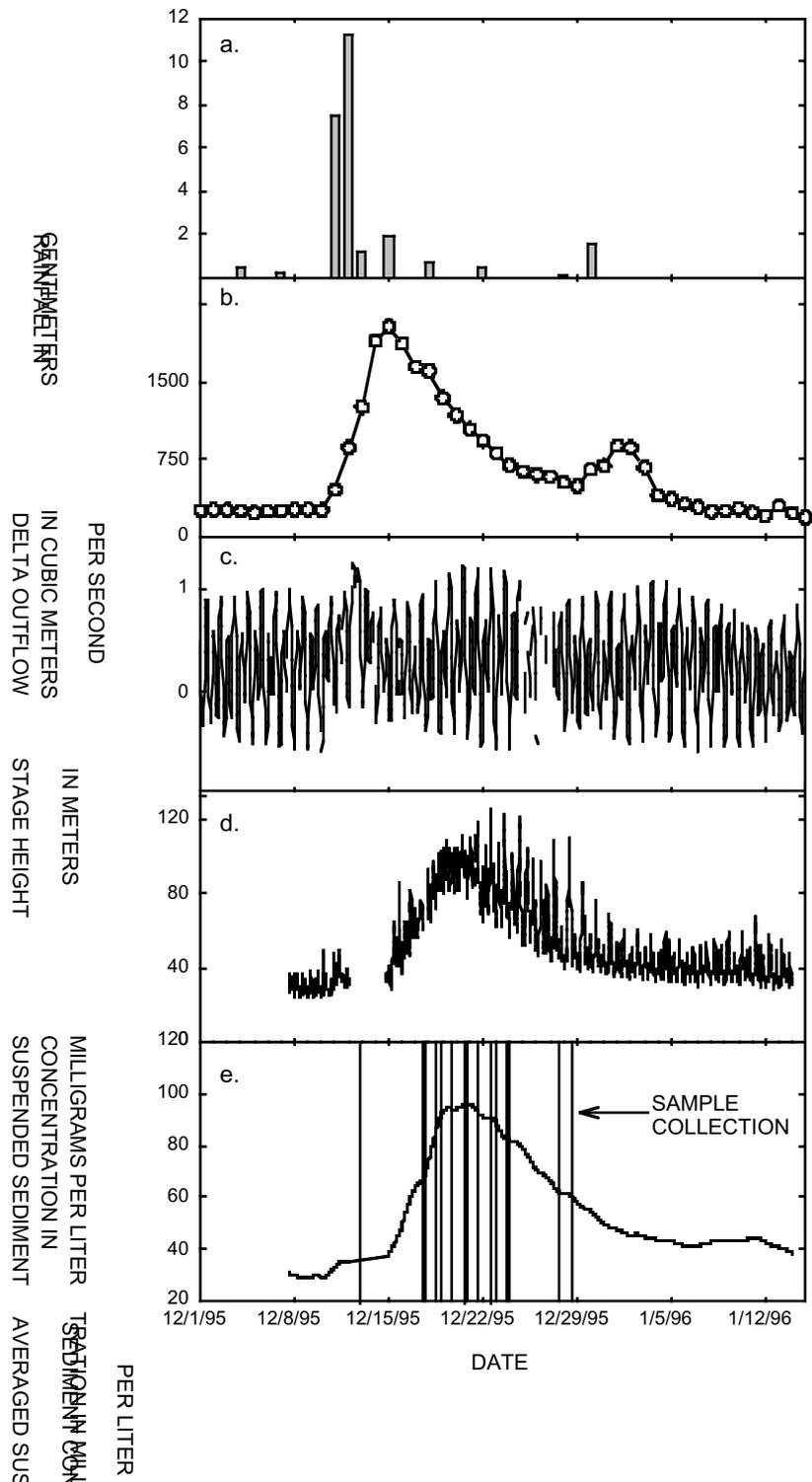


Figure 2. Graphs of Mallard Island local rainfall (a; Fairfield, California, National Oceanic and Atmospheric Administration, 1995), Daily calculated Delta outflow (b; California Department of Water Resources, 1986), stage height (c; California Data Exchange Center, 1998), suspended sediment concentration (d; Buchanan and Schoellhamer, 1998), and tidally-averaged suspended sediment concentrations calculated with a low-pass numerical filter (e; according to the method presented in Schoellhamer, 1996)

Table 1. Pesticide, organic carbon, total nitrogen, and suspended sediment concentrations in suspended sediment samples from Mallard Island study site, California, December, 1995

[Pesticide concentrations are in nanogram per gram dry weight of sediment. Endosulfan and chlordane values are the sum of all isomers. Organic carbon and total nitrogen concentrations are in weight percent. (C/N)_a, atomic ratio of organic carbon to total nitrogen; SSC, sediment concentration in milligrams per liter at time of sampling (Buchanan and Schoellhamer, 1998); Total, sum of observed pesticide values; na, not available; no, not observed; (), concentration below method detection limit. Suspended sediment samples also were analyzed for the following pesticides, but none were observed (method detection limit in parentheses): dieldrin(2.1), ethalfuralin(0.1), fonofos(0.9), and malathion(1.2)]

Sample date and time	% C	% N	(C/N) _a	SSC	Ala-chlor	Chlor-dane	Chlor-pyrifos	Dac-thal	DDD	DDE	DDT
12/12/95 19:00	2.59	0.19	15.9	na	no	(1.5)	1.7	(0.4)	2.1	2.6	(1.9)
12/17/95 12:10	2.63	0.17	18.0	61.2	no	(1.2)	no	(0.4)	3.3	6.9	(0.9)
12/17/95 19:00	2.17	0.16	15.8	na	(0.1)	(1.0)	0.6	(0.4)	1.5	3.5	(2.4)
12/18/95 12:50	2.33	0.16	17.0	75.5	(0.8)	(0.3)	no	no	1.5	3.7	(2.1)
12/18/95 20:20	2.09	0.15	16.2	89.2	no	(0.7)	(0.5)	(0.6)	1.6	3.9	(2.0)
12/19/95 14:05	2.42	0.17	16.6	87.2	no	(1.6)	(0.4)	(0.4)	1.1	2.6	(1.4)
12/20/95 14:30	2.03	0.14	16.9	88.7	no	(2.7)	1.0	(0.5)	2.0	4.2	(2.7)
12/20/95 21:40	2.37	0.17	16.3	89.3	no	no	1.7	(0.6)	2.1	5.1	(2.4)
12/21/95 15:20	2.30	0.16	16.8	93.3	no	(1.1)	0.7	(0.5)	1.6	3.8	(2.1)
12/22/95 16:00	2.23	0.17	15.3	101	no	(2.0)	1.3	(0.8)	1.9	5.2	(2.5)
12/22/95 23:10	2.20	0.16	16.0	64.5	no	(0.5)	1.4	(0.6)	2.1	6.3	(1.6)
12/23/95 16:50	2.04	0.14	17.0	107	no	(0.9)	(0.3)	(0.3)	1.0	3.0	(1.1)
12/23/95 23:50	2.23	0.15	17.3	58.9	no	no	2.1	(0.6)	2.4	4.5	4.4
12/27/95 14:50	2.25	0.17	15.4	46.9	no	(1.2)	1.0	(0.3)	1.0	3.3	(1.5)
12/28/95 15:30	2.59	0.20	15.1	48.0	no	(0.8)	0.8	(0.3)	1.3	3.9	(1.4)

Sample date and time	Endo-sulfan	Eptam	Moli-nate	Oxy-fluorfen	Pebu-late	Sulfo-tep	Thio-bencarb	Triflur-alin	TOTAL
12/12/95 19:00	no	(0.5)	(1.1)	1.2	3.3	no	no	no	16.3
12/17/95 12:10	17.7	(1.1)	(1.4)	6.2	no	no	no	1.3	40.6
12/17/95 19:00	no	no	(0.8)	(0.5)	3.4	no	no	no	14.2
12/18/95 12:50	no	(0.2)	(0.2)	no	(1.0)	no	no	no	9.8
12/18/95 20:20	no	no	(1.2)	21.3	3.2	no	no	no	35.0
12/19/95 14:05	no	(0.6)	(0.9)	(0.8)	(1.2)	no	no	no	10.9
12/20/95 14:30	no	no	(1.0)	no	3.3	no	1.6	no	18.9
12/20/95 21:40	no	no	(1.4)	2.2	3.7	no	no	no	19.4
12/21/95 15:20	no	no	(1.4)	1.2	2.3	(0.3)	(1.4)	(0.5)	17.0
12/22/95 16:00	no	no	(2.0)	3.8	no	no	2.4	(0.6)	22.6
12/22/95 23:10	24.6	(1.1)	(1.6)	no	no	no	3.9	no	43.8
12/23/95 16:50	no	no	(0.8)	1.7	no	no	(1.3)	(0.2)	10.7
12/23/95 23:50	no	no	(1.5)	no	4.7	no	2.4	no	22.6
12/27/95 14:50	no	no	(1.3)	1.4	(1.7)	no	1.6	no	14.2
12/28/95 15:30	no	(0.7)	(1.2)	2.1	2.6	no	1.8	no	16.9

limb (Bergamaschi and others, 1997, Bergamaschi and others, in press). Detailed studies of the San Joaquin River and its tributaries indicated that temporal variations in SAP concentrations in the main stem of the river

were strongly influenced by the different travel times for water from various tributaries to the sampling site and differences in the SAP concentrations associated with sediment from each tributary (Kratzer and Biagtan, 1996;

Kratzer, in press). The lack of temporal variability in SAP concentrations at the Mallard Island site may be the result of inter-annual variability in sediment transport or the result of a more complex mixing of suspended sediments at the Mallard Island study site. Samples from the Mallard Island site integrate inputs from the Sacramento and San Joaquin Rivers and their tributaries, as well as local inputs in the Delta, and bay sediments moved landward by tidal currents.

Of the 19 pesticides analyzed, an average of 10 were observed in each of the 15 samples. This frequency is higher than the number detected previously in San Joaquin River suspended sediments using the same method (Bergamaschi and others, 1997). There were no inter-tidal variations apparent in the frequency of occurrence. Most samples contained chlordane, chlorpyrifos, dacthal, DDD, DDE, DDT, molinate, oxyfluorfen, pebulate, and thiobencarb. Alachlor, endosulfan, eptam, sulfotep, and trifluralin were intermittent in their occurrence (table 1). DDT together with its metabolites were generally the most abundant of the commonly occurring compounds, ranging from 5.1 to 11.1 ng/g. Oxyfluorfen concentrations exceeded 20 ng/g in one sample (December 18 20:20; table 1), but was generally much lower. Endosulfan occurred in concentrations greater than 17 ng/g in two samples (table 1), but was not observed in other samples. Of the compounds analyzed, only dieldrin, ethalfluralin, fonofos, and malathion were not found in any samples. Among the pesticides, only thiobencarb showed a temporal variation in occurrence; it was only found in samples collected after December 19 (table 1).

SAP concentrations of chlorpyrifos and DDE in the Mallard Island suspended sediment samples were similar to concentrations measured in other suspended sediments collected in San Francisco Bay after spring rains in 1991 (Domagalski and Kuivila, 1993), and similar to measurements of SAPs in Sacramento River (Bergamaschi, and others, 1997). Concentrations of organochlorine pesticides (DDD, DDE, DDT, chlordane) were much lower in the Mallard suspended sediments than in suspended sediments from the San Joaquin River and its tributaries in other years (Kratzer, in press; Bergamaschi, and others, 1997).

Dissolved pesticides

Water samples collected concurrently with the suspended sediment samples were analyzed for pesticide content. Although the analytical methods were considerably different, the 2

methods shared 11 analytes. In comparison to the suspended sediment samples, relatively few pesticides were found in the water samples; only three pesticides were observed. In part this lower frequency of pesticide occurrence may be the result of the higher concentrations required for observation in the much smaller water samples (1 L) in comparison to the suspended sediment samples (~200 L).

Table 2. Pesticide concentrations measured in water samples from the Mallard Island study site, California, December 1995

[Values are in nanograms per liter. no, not observed; (), concentration below method detection limit (Crepeau and others, 1994). Water samples also were analyzed for the following pesticides, but none were detected (method detection limit shown in parentheses): alachlor(22), atrazine(28), butylate (19), carbaryl(31), carbofuran(28), chlorpyrifos(35), cyanazine(50), dacthal(63), eptam(129), ethalfluralin (31), fonofos(25), malathion(44), methidathion(28), molinate(53), napropamide(28), pebulate(44), thiobencarb(60), trifluralin(60)]

Sample date and time	Diazinon	Metolachlor	Simazine
12/12/95 13:30	no	no	(23)
12/12/95 13:30	no	(1)	(33)
12/17/95 12:10	no	no	64
12/17/95 12:10	(2)	no	(55)
12/17/95 19:00	(6)	no	(38)
12/18/95 12:50	(9)	(4)	69
12/18/95 12:50	(5)	(2)	(57)
12/18/95 20:20	no	no	(25)
12/19/95 14:05	(2)	(5)	68
12/19/95 20:50	(2)	(3)	(32)
12/20/95 14:30	(7)	(4)	76
12/20/95 21:40	no	(4)	(53)
12/21/95 15:20	no	(6)	(59)
12/22/95 16:00	no	(4)	(47)
12/22/95 23:10	no	(3)	(15)
12/22/95 23:10	no	(4)	(29)
12/23/95 16:50	no	(6)	(48)
12/23/95 23:50	no	(5)	(34)
12/27/95 14:50	no	(4)	(28)
12/28/95 15:30	no	(5)	(24)

The only dissolved pesticides detected in the water sampled between December 12-28 were diazinon, metolachlor, and simazine (table 2). The following pesticides were not detected in the dissolved phase in any of the samples: alachlor, atrazine, carbaryl, carbofuran, chlorpyrifos, cyanazine, dacthal, diazinon-oxon, diethatylethyl, eptam, fonofos, malathion, methidation, molinate, napropamide, pebulate, sulfotep, thiobencarb, and trifluralin. Simazine

concentrations ranged from 15 to 76 ng/L and were highest during the peak of suspended sediment concentrations (table 2).

DISCUSSION

The distribution of pesticides between water and suspended sediment at equilibrium commonly is described by the aqueous phase-sedimentary organic carbon partition coefficient, K_{OC} , which is defined as the concentration in a system at equilibrium of sorbed pesticide in ng/g of sedimentary organic carbon divided by the concentration of dissolved pesticide in nanograms per milliliter. Log K_{OC} values for pesticides in this study vary from 1.97 milliliters per gram (mL/g; molinate) to 5.38 mL/g (DDD and DDT) (table 3), indicating a wide range in expected equilibrium behavior for the suite of compounds analyzed.

K_{OC} values may be used to calculate equilibrium dissolved pesticide concentrations from SAP concentrations (for example, Domagalski and Kuivila, 1993; Kratzer, in press). Calculated dissolved pesticide concentrations for waters in equilibrium with the Mallard Island suspended sediment samples (table 4) were very different from measured dissolved pesticide concentrations (table 2). Calculated concentrations of alachlor, eptam, molinate, pebulate, and thiobencarb were well above the dissolved pesticide method detection limits, yet none of these compounds were observed in the Mallard Island water samples. Also, there is no significant positive correlation between individual SAP concentrations and K_{OC} in this study. Nor are there significant relations between SAP concentrations and sediment organic carbon content or the sediment carbon quality as indicated by C/N (table 1). Taken together, these observations indicate that pesticides are not in

Table 3. Pesticide log K_{OC} and usage data for the regions of the Delta and the Sacramento and San Joaquin drainages that drain into the Delta

[Log K_{OC} values are in milliliters per gram. Usage values are integrated amounts applied during registered activities for the portion of the Sacramento and San Joaquin River drainages, and the Delta that ultimately drain into the San Francisco Bay at Mallard Island for 1995. Usage values are in kilograms active ingredient applied]

Pesticide	Log K_{OC}	⁷ Usage
Alachlor ^{1,2}	2.28	12,521
Chlordane ²	5.15	53
Chlorpyrifos ^{1,3}	3.93	380,113
Dacthal ⁴	3.70	8,968
DDD ⁵	5.38	—
DDE ⁵	5.29	—
DDT ^{1,2,6}	5.38	—
Dieldrin ^{3,5,6}	4.08	—
Endosulfan ⁵	3.37	16,842
Eptam ^{1,5}	2.38	100,309
Ethafluralin ⁴	3.60	15,069
Fonofos ⁴	2.94	18,584
Malathion ³	3.10	87,851
Molinate ⁵	1.97	647,312
Oxyfluorfen ⁴	5.00	70,632
Pebulate ¹	2.66	91,243
Sulfotep ⁵	2.82	32
Thiobencarb ⁴	2.95	260,624
Trifluralin ¹	3.96	230,712

¹Kenega (1980)

²Environmental Protection Agency (1994)

³Howard (1991)

⁴Wauchope and others (1991)

⁵Montgomery (1993)

⁶Jury and others (1987)

⁷California Department of Pesticide Regulation (1996)

equilibrium between water and sediments, in agreement with what has been observed previously (Domagalski and Kuivila, 1993; Pereira and others, 1996; Brown, 1997; Kratzer, in press), and suggest that equilibration was not a determining factor for SAP concentrations.

Another possible determining factor for SAP concentrations was mixing of sediments from varying inputs. The absence of temporal trends may be the result of tidal mixing of riverine suspended sediments before they reach the bay, or mixing with estuary sediments. Mixing would result from episodes of deposition and resuspension during transport, or shear effects in the flow. Mixing would obscure any temporal riverine signal. If tidal mixing obscured changing inputs, the expected result

would be a gradual change in the amount and identity of SAPs. However, early SAP occurrences and concentrations (Dec. 12, table 1) were not different from later samples, suggesting that although mixing probably did occur, mixing of sediments from various inputs did not cause the observed distribution during the sampling period.

SAP concentrations also may have been influenced by the amount of pesticide applied in the drainage basin. However, there is no apparent relation between the amount applied in the Central Valley (fig. 1, table 3) and the SAP concentration (table 1).

What then controls the SAP concentration and distribution? The occurrence of molinate and thiobencarb may provide some insight. Molinate and thiobencarb are herbicides used in the cultivation of rice. They were applied in large amounts (table 3) to rice fields in April-June (California Department of Pesticide Regulation, 1996). In comparison with the other pesticide analytes, molinate has the lowest log K_{oc} (1.97), and thiobencarb has an intermediate value (2.95, table 3). Nevertheless, they are observed 6 months later on suspended

sediments, suggesting that long equilibration times (in relation to transit times) may be an important factor.

One additional consideration is whether the observed SAP concentrations will have any effect on the health of the ecosystem. EPA chronic water quality criteria for protection of freshwater aquatic life contaminant chronic exposure levels have been established for four of the pesticides found in this study (chlordane, DDT, endosulfan, and chlorpyrifos; Environmental Protection Agency, 1996). Of these four pesticides, only the SAP concentrations of Σ DDT approached the criteria of 1 ng/L. The observed Σ DDT ranged from 0.4 – 1.0 ng/L.

Despite the low concentrations of SAP, the SAP may still affect the estuary. Filter-feeding organisms have been shown to accumulate pesticides to levels far in excess of the associated sediment concentrations (for example, Pereira and others, 1996; Brown, 1997). Thus, annual flux of sediments with low concentrations of pesticides into the Bay may cause chronic exposure effects because of the long residence time of sediments.

Table 4. Calculated dissolved pesticide concentrations in water samples from the Mallard Island study site, California, December 1995

[Calculated from pesticide concentrations on suspended sediments using K_{oc} values in table 3. Values are given only for pesticides analyzed both in the dissolved and particulate phases. Values are in nanograms per liter. no, not observed associated with sediment; (), concentration below method detection limit (Crepeau and others, 1994)]

Sample date and time	Alachlor	Chlorpyrifos	Dacthal	Eptam	Molinate	Pebulate	Thiobencarb	Trifluralin
12/12/95 19:00	no	(9)	(4)	96	531	322	no	no
12/17/95 12:10	no	no	(3)	173	574	no	no	(6)
12/17/95 19:00	36	(3)	(4)	no	400	341	no	no
12/18/95 12:50	181	no	no	(37)	90	97	no	no
12/18/95 20:20	no	(3)	(6)	no	631	332	no	no
12/19/95 14:05	no	(2)	(3)	103	437	117	no	no
12/20/95 14:30	no	(6)	(4)	no	507	353	88	no
12/20/95 21:40	no	(8)	(5)	no	641	345	no	no
12/21/95 15:20	no	(4)	(5)	no	685	222	71	(3)
12/22/95 16:00	no	(7)	(8)	no	972	no	122	(3)
12/22/95 23:10	no	(7)	(6)	214	762	no	198	no
12/23/95 16:50	no	(2)	(3)	no	430	no	69	(1)
12/23/95 23:50	no	(11)	(5)	no	700	464	123	no
12/27/95 14:50	no	(5)	(3)	no	613	163	81	no
12/28/95 15:30	no	(4)	(3)	127	563	256	89	no

CONCLUSIONS

A large number of pesticides were found associated with suspended sediments entering

the San Francisco Bay during the first storm of the 1995-1996 water year. The total amounts of pesticides associated with the sediments were similar to those measured previously in

Sacramento River suspended sediment, but much lower than those previously measured in San Joaquin River suspended sediment. Few pesticides were found in concurrent water samples and their concentrations were much lower than may be expected from equilibrium partitioning between the aqueous and sedimentary phases.

There were no significant trends in the concentration or occurrence of pesticides found as the peak in suspended sediment concentration passed the sampling site. Nor were there significant relations between pesticide content and such parameters as K_{oc} of the pesticide, organic carbon content of the sediment, or amount of pesticide applied annually in the Central Valley. This finding suggests that observed sediment-associated pesticide concentrations may reflect disequilibrium between sedimentary and aqueous phases resulting from long equilibration times at locations where pesticides were applied, and relatively short transit times for reequilibration to occur

REFERENCES

- Bergamaschi, B.A., Baston, D.S., Crepeau, K.L., and Kuivila, K.M., in press, Determination of pesticides associated with suspended sediments in the San Joaquin River, California, USA, using gas chromatography-ion trap mass spectrometry: Toxicological and Environmental Chemistry.
- Bergamaschi, B.A., Crepeau, K.L., and Kuivila, K.M., 1997, Pesticides associated with suspended sediments in the San Francisco Bay Estuary, California: U.S. Geological Survey Open-File Report 97-24, 12 p.
- Brown, L.R., 1997, Concentrations of chlorinated organic compounds in biota and bed sediment in streams of the lower San Joaquin River drainage, California: U.S. Geological Survey Open-File Report 98-171, 22 p.
- Buchanan, P.A., and Schoellhamer, D.H., 1998, Summary of suspended-solids concentration data, San Francisco Bay, water year 1996: U.S. Geological Survey Open-File Report 98-175, 59 p.
- California Data Exchange Center, 1998, Data: California Department of Water Resources, <http://cdec.water.ca.gov/>.
- California Department of Pesticide Regulation, 1996, Pesticide use data for 1995 [digital data]: Sacramento, California Department of Pesticide Regulation.
- California Department of Water Resources, 1986, DAYFLOW program documentation, Dayflow data summary users guide: variously paged.
- Canuel, E.A., Cloern, J.E., Ringleberg, D.B., Guckbert, J.B., and Rau, G.H., 1995, Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San Francisco Bay: *Limnology and Oceanography*, v. 40, no. 1, p. 67-81.
- Crepeau, K.L., Domalgalski, J.L., and Kuivila, K.M., 1994, Methods of analysis and quality-assurance practices of the U.S. Geological Survey Organic Laboratory, Sacramento, California—Determination of pesticides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Open File Report 94-362, 17 p.
- DeToro, D.D., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Nelson, T.A., and Paquin, P.R., 1991, Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning: *Environmental Toxicology and Chemistry*, v. 10, p. 1541-1583.
- Domagalski, J.L. and Kuivila, K.M., 1993, Distributions of pesticides and organic contaminants between water and suspended sediment, San Francisco Bay, California: *Estuaries*, v. 16(3A), p. 416-426.
- Environmental Protection Agency, 1994, Environmental Protection Agency Online Database.
- , 1996, Drinking water regulations and health advisories: Environmental Protection Agency 822-B-96-002.
- Goodwin, P., and Denton, R., 1991, Seasonal influences on the sediment transport of the Sacramento River, California: *Proceedings of the Institute of Civil Engineers*, Part 2, v. 91, 163-172.
- Howard, P.H., 1991, Handbook of environmental fate and exposure data for organic chemicals: Vol. III, Pesticides: Michigan, Lewis.
- Jennings, B., Schoellhamer, D., and Kuivila, K., 1997, Optimum sampling strategy for sediment-associated pesticides in Suisun Bay: *Newsletter of the Interagency Ecological Program for the Sacramento-San Joaquin Estuary*, v. 10, no. 4, p. 16-20.
- Jepsen, R., Borglin S., Lick, W., and Swackhamer, D.L., 1995, Parameters affecting the adsorption of Hexachlorobenzene to natural sediments: *Environmental Toxicology and Chemistry*, v. 14, no. 9, p. 1487-1497.

- Jury, W.A., Focht, D.D., Farmer, W.J., 1987, Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation: *Journal of Environmental Quality*, v. 16, p. 422-428.
- Kenega, E.E., 1980, Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals: *Ecotoxicology and Environmental Safety*, v. 4, p. 26-38.
- Kratzer, C.R., and Biagtan, R.N., 1996, Determination of travel times in the lower San Joaquin River basin, California, from dye-tracer studies during 1994-1995: U.S. Geological Survey, Water-Resources Investigations Report 97-4018, 20 p.
- Kratzer, C.R., In Press, Transport of sediment-bound organochlorine pesticides to the San Joaquin River, California: *Journal of the American Water Resources Association*.
- Lick, W. and Rapaka, V., 1996, A quantitative analysis of the dynamics of the sorption of hydrophobic organic chemicals to suspended sediments: *Environmental Toxicology and Chemistry*, v. 15, no. 7, p. 1038-1048.
- Liljestrand, H.M. and Lee, Y.D., 1992, The distribution of organic pollutants onto suspended sediments, humic materials and fulvic materials in the transverse mixing zone: *Water Science and Technology*, v. 25, no. 11, p. 49-56.
- Meade R.H. (1972) Transport and deposition of sediments in estuaries: *Geological Society of America*, v. 133, p. 91-120.
- Montgomery, J.H., 1993, Agrochemicals desk reference—Environmental data: Chelsea, Mich., Lewis.
- National Oceanic and Atmospheric Administration, 1995, Climatological data. California, December 1995: ISSN 0145-0069, v. 099, no. 12. p. 14-15.
- Pereira, W.E., Domagalski, J.L., Hostettler, F.D., Brown, L.R., and Rapp J.B., 1996, Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin River and Tributaries, California: *Environmental Toxicology and Chemistry*, v. 15, no. 2, p. 172-180.
- Schoellhamer, D.H., 1996, Factors affecting suspended-solids concentrations in South San Francisco Bay, California: *Journal of Geophysical Research*, v. 101, no. C5, p. 12087-12096.
- , 1997, Time series of suspended-solids concentration, salinity, temperature, and total mercury concentration in San Francisco Bay during water year 1996: *San Francisco Estuary Institute 1996 Annual Report of the Regional Monitoring Program for Trace Substances*, p. 65-77.
- Schubel, J.R. and Carter, H.H., 1984, The estuary as a filter for fine-grained suspended sediment *in* Kennedy, V. S., ed., *The estuary as a filter*: New York, N.Y., Academic, p. 81-105.
- Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Deckers, P.W.M., and Burt, J.P., 1991, The SCS/ARS/CES pesticide properties database for environmental decision-making: *Reviews of Environmental Contamination and Toxicology*, v. 123, p. 1-164.

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