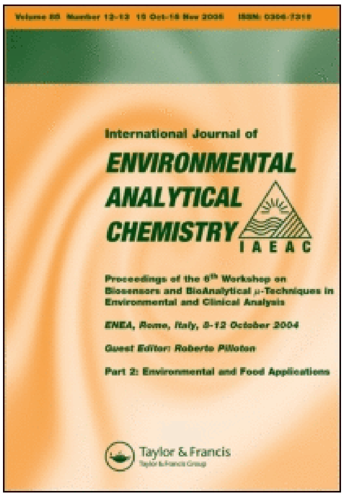

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Input, flux, and persistence of six select pesticides in San Francisco Bay

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Input, flux, and persistence of six select pesticides in San Francisco Bay

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Temporal patterns of pesticide inputs to San Francisco Bay were identified and correlated with timing of application and transport mechanism. Fluxes were calculated from measured concentrations and estimated flow. Persistence of the pesticides under typical riverine or estuarine conditions were estimated from laboratory experiments. Simazine was detected most frequently and had the highest flux into the Bay, which could be explained by its continuous use and long half-life. In comparison, diazinon was detected at lower concentrations and had a lower flux which corresponded to its lower use and shorter half-life. The order-of-magnitude lower fluxes of carbofuran and methidathion corresponded to their lower use and expected hydrolysis. Molinate was detected at the highest concentration but its flux was lower than expected, considering its very high use and persistence in the laboratory experiments. Additional loss of molinate is likely to occur from volatilization and photodegradation on the rice fields. Although thiobencarb had the second highest use, it had the lowest flux of the six pesticides, which can be attributed to its loss via hydrolysis, photodegradation, volatilization, and sorption to sediments. Fluxes into San Francisco Bay were equal to or greater than those reported for other estuaries, except for the Gulf of Mexico.

Keywords: Pesticides; San Francisco Bay; Degradation; Hydrolysis; Flux; California

1. Introduction

The Central Valley of California is a major agricultural region with more than 5% of all pesticide use in the USA [1]. A wide variety of crops are grown, resulting in a large number of different pesticides being applied throughout much of the year. These pesticides are transported into the Sacramento and San Joaquin Rivers which flow into San Francisco Bay (figure 1). This is the first study to measure the flux of current-use pesticides into San Francisco Bay, although many previous studies have measured pesticides in the two rivers and associated smaller streams (e.g. [2–6]). Pesticides are applied to crops during distinct seasons and are typically detected in the rivers within days to weeks after application.

This study focused on six pesticides: carbofuran, diazinon, methidathion, molinate, simazine, and thiobencarb. Used on a variety of crops in the watershed, these pesticides

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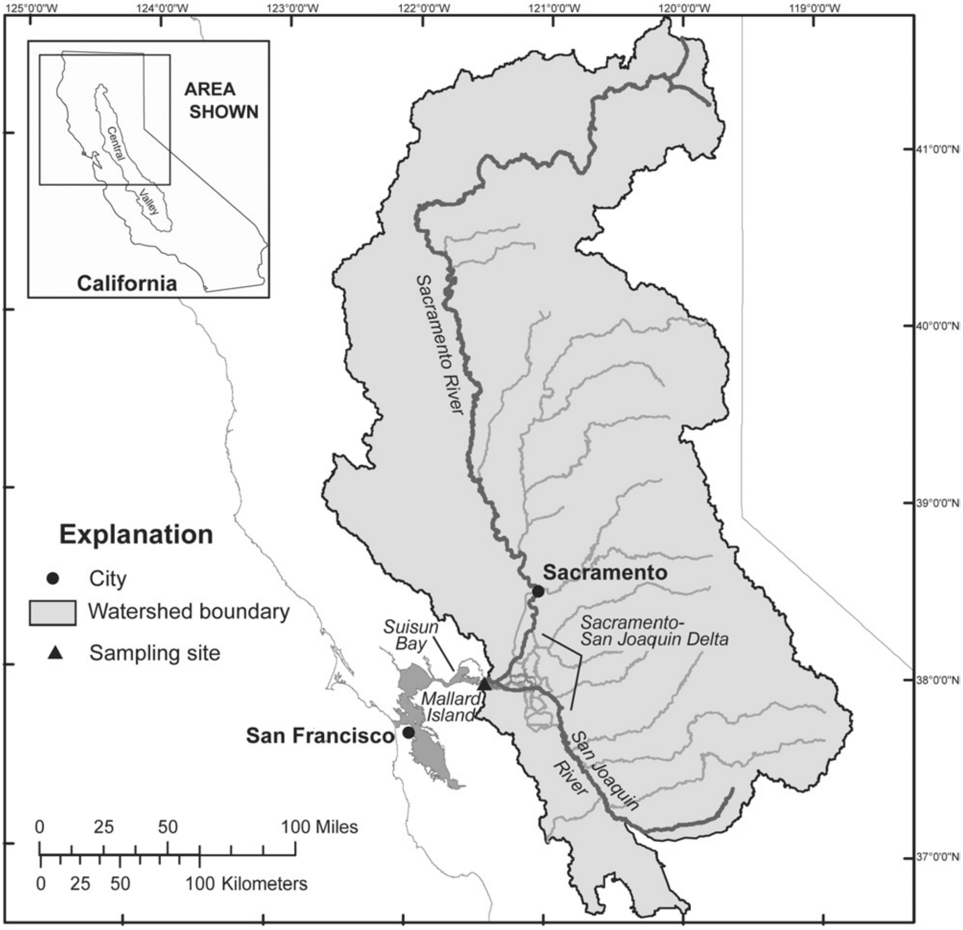

Figure 1. San Francisco Bay watershed, key locations, and sampling site.

are applied in quantities greater than 40 000 kg [1]. With aqueous solubilities ranging from 5 to 880 mg/L (table 1 [7]), these pesticides are relatively hydrophilic and will be transported primarily in the dissolved phase. These six pesticides have been detected frequently in water samples from the Sacramento and San Joaquin Rivers.

The purpose of this study was to characterize the temporal inputs and calculate the fluxes of these six pesticides into San Francisco Bay. Laboratory studies were used to estimate the persistence of the pesticides once transported off-site into the rivers. Many factors influence the off-site transport and eventual flux of pesticides in aquatic environments, including climate, hydrology, geology, agronomic practices, and chemical–physical properties of the individual pesticides. By comparing the transport of multiple pesticides applied within the same watershed at the same time, many factors specific to the location or time period can be ignored For each pesticide, the relative flux was compared with the amount applied in the watershed and the persistence of the pesticide in the river and estuarine environment. The fluxes into San Francisco Bay were compared with those measured in other estuaries.

Table 1. Summary of pesticide solubility, method detection limit, detection frequency, and maximum concentration.

Pesticide	Aqueous solubility (mg/L)	Method detection limit (ng/L) [14]	Frequency of detection (%)	Maximum concentration (ng/L)
Simazine	5	8.5	83	149
Diazinon	40	5.0	50	52
Methidathion	240	6.0	19	79
Molinate	880	7.5	31	629
Thiobencarb	28	8.5	28	66
Carbofuran	520	10.5	36	50

2. Experimental

2.1 *Study area and sample collection*

San Francisco Bay comprises a series of embayments, with Suisun Bay being the most landward (figure 1). The major source of freshwater to San Francisco Bay enters at the eastern boundary of Suisun Bay [8]. This drainage area encompasses 99 587 km^2 and includes two major river systems, the Sacramento and the San Joaquin Rivers. The confluence of the two rivers forms the Sacramento–San Joaquin Delta (Delta), which consists of many interconnected sloughs and channels [9]. Two water projects also export water from the Delta to central and southern California for agriculture and drinking water, thus adding to the hydrodynamic complexity [9].

The sampling site at the eastern end of Suisun Bay, Mallard Island, is tidally influenced with salinities ranging from 0 to 13 practical salinity units (psu) over the year. Mallard Island is located just south of the main shipping channel, 8 km downstream of the confluence of the Sacramento and San Joaquin Rivers. During high flow periods, the majority of the water draining the watershed exits past Mallard Island into San Francisco Bay; however, during low flow periods, a significant fraction of the water is pumped directly from the Delta for export [9].

Traditional methods for measuring riverine discharge cannot be used at Mallard Island due to reversals of flow directions during the tidal cycle. The net daily flow into Suisun Bay is estimated using a computer program developed in 1978 called Dayflow [10]. This daily flow, called Net Delta Outflow, is an arithmetic summation of river inflows, precipitation, agricultural consumptive demand, and water project exports. None of the flows are routed to account for travel time, so all calculations are performed using data for the same day.

Water samples were collected daily or twice-daily from mid-January through mid-July 1996. Results from previous studies in San Francisco Bay [2] demonstrated that pesticides were transported in pulses lasting from days to weeks, so daily sampling was judged to be necessary for this study. In a 3-year monitoring study in the Sacramento and San Joaquin Rivers [3], few pesticides were detected in the late summer and autumn; therefore, our measurements represent the annual flux. Water was pumped from 1 m below the surface by autosampler at the gauge house at Mallard Island and stored on ice until use. Since the site is tidally influenced, samples were collected at slack after ebb to maintain consistency. A continuous record of optical backscatter data, stage height, and other ancillary parameters was maintained by the

California Department of Water Resources and the US Geological Survey during the study [11, 12].

2.2 *Pesticide analysis and flux calculations*

One-litre water samples were filtered through a baked, 0.7 μm glass-fibre filter within 48 h of sampling, spiked with a surrogate compound (terbuthylazine), and then extracted onto a C-8 solid-phase extraction cartridge. Cartridges were dried under a stream of carbon dioxide and frozen for up to 2 months until analysis. Cartridges were eluted with 6 mL of a 1 : 1 (by volume) mixture of hexane and diethyl ether. Eluates were concentrated under a stream of nitrogen to about 200 μL, internal standards (deuterated acenapthene, pyrene and phenanthrene) were added, and the mixture was concentrated to a final volume of 200 μL. The eluant was concentrated and analysed for pesticides using gas chromatography–mass spectrometry (GC/MS) with ion-trap detection. Method detection limits (MDLs) were determined as the minimum concentration that can be identified, measured, and reported with 99% confidence that the concentration is greater than zero [13] and are listed in table 1. Recoveries of the six pesticides spiked into San Francisco Bay water ranged from 78 to 100%. Details of the analytical method are described in the method report [14].

Quality-control data included field blanks, replicate samples, matrix spikes, interlaboratory samples, and surrogate recovery. No pesticides were detected in equipment blanks. Replicate and interlaboratory comparison samples agreed within method limits. Recovery of all compounds was verified using matrix spike samples, and recovery of the surrogate, terbuthylazine, was recorded to assess the efficiency of each extraction and ranged from 67% to 127% [14].

A daily flux was calculated for each of the six pesticides. For days with two pesticide samples, an average value was used for the daily pesticide concentration. On the days with no pesticide data, concentrations were estimated by interpolating between the surrounding days. The daily flux was calculated by multiplying the daily concentration by the estimated net Delta outflow. Pesticides can be identified at concentrations less than the MDL but with a lower confidence in the actual value; therefore, these estimated concentrations were also used in the flux calculations. For samples with non-detection of a pesticide, the concentration was set to zero. This method was chosen to calculate a conservative estimate of the flux.

2.3 *Hydrolysis experiments*

Laboratory experiments were conducted to estimate degradation rates for the six pesticides under typical conditions in the deepwater channels of the Sacramento River and San Francisco Bay (that is, in the dark with low suspended sediments) [8, 15, 16]. Water samples were collected from the San Francisco Bay watershed during April and August 1996. Each sample was centrifuged with a Westphalia continuous-flow centrifuge to reduce suspended sediments, stored in two 33-L stainless steel milk cans, and then spiked with the mixture of pesticides. The pesticides were combined in ethyl acetate in a glass bottle, and the mixture was evaporated to dryness with nitrogen to minimize the addition of solvent to the water sample. The bottle was rinsed several times with a centrifuged water sample, the rinsates were added to the milk can, and the entire sample was thoroughly mixed. Finally, approximately 20 L of the spiked sample was put into a clean Teflon bag that was collapsed to eliminate any headspace, sealed, and stored in the dark in an incubator. Final pesticide concentrations ranged from 300 to 500 ng/L. With this experimental design, the potential mechanisms of degradation are abiotic hydrolysis and possibly aerobic microbial degradation [17].

Separate experiments were done at 10 and 25°C, since the temperatures in the rivers and at the input to the Bay range from 6 to 28°C [8, 15]. Each water sample was mixed continuously with a motorized paddle stirrer throughout the experiment. Temperature, pH, and dissolved oxygen also were monitored with Campbell electrodes and a CR10 data logger. (The use of trade names in this report is for identification purposes only and does not constitute endorsement by the US Geological Survey.) Several days after spiking, and once the temperature had equilibrated, four 500-mL aliquots were pumped from each sample and analysed for the starting concentration of each pesticide. Subsequently, duplicate aliquots of 500 mL of water were collected for analysis at varying sampling intervals, ranging from 24 h initially to 7 days by the end of the 2-month experiment. As each sample was removed, the Teflon bag was further collapsed to eliminate headspace. The temperature and pH remained relatively constant, and the water samples remained aerobic throughout the experiments. Degradation rates were estimated from the measured decreases in concentrations with time [17].

Generally, the rate of hydrolysis for organic compounds in water is directly proportional to the concentration of the organic compound [18]. Assuming this relation, hydrolysis can be described using a first-order degradation curve:

$$C_t = C_0 e^{-kt}, \tag{1}$$

where C_t is the concentration of the pesticide at time t; C_0 is the initial concentration of the pesticide; and k is the rate constant [19].

A plot of $\ln(C_t/C_0)$ vs. time yields a straight line with slope equal to $-k$. The rate constant can then be used to derive the half-life, $t_{1/2}$:

$$t_{1/2} = (\ln 2)/k. \tag{2}$$

The slope of the line was calculated using linear regression analysis, and the half-life of each pesticide was calculated using equation (2). When the calculated half-life was shorter than the experiment, that value was reported. If the concentration of a pesticide decreased during the experiment, but the calculated half-life was longer than the experiment, the half-life was extrapolated and reported as an estimate. When no measurable decrease in concentration of a pesticide occurred during the experiment, the designation 'no degradation' was used.

3. Results and discussion

3.1 *Pesticide occurrence*

Current-use pesticides are detected in seasonal patterns that depend on timing of application and transport mechanism. Often, a pesticide is applied in one season and transported to surface water in the same season, sometimes only a matter of days or weeks later. Typical seasonal patterns characterized by transport mechanism include the

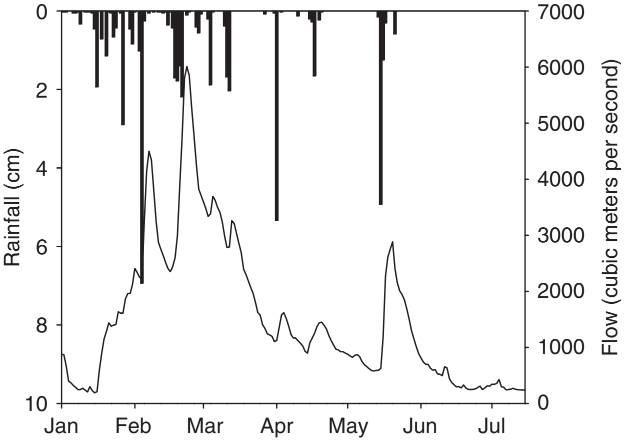

Figure 2. Rainfall at Nicolaus and flows at Mallard Island for January–July 1996.

first flush (the first large runoff event in the winter), spring late rainfall-runoff event or tailwater return (direct runoff of irrigation return water), and rice-field water release.

The total rainfall from January through July 1996 was 49.2 cm at Nicolaus, California. The first flush occurred during a series of storms from mid-January through early February with 17.6 cm of rain and a peak daily flow of 4498 m^3/s (figure 2). A second flush occurred in mid-February with 7.5 cm of rain and the highest flow of the sampling period (6008 m^3/s). A third flow peak in mid-May (2879 m^3/s) was due to a combination of rainfall-runoff and release of rice field water.

Simazine is a triazine herbicide applied throughout the year for agriculture and roadside maintenance [1, 6]. The highest simazine concentrations occurred during winter high flows with a maximum concentration of 149 ng/L following the first flush (figure 3a and table 1). Of the six pesticides measured, simazine was detected most frequently (83% of samples). Other studies of pesticide occurrence in the Sacramento and San Joaquin Rivers have also frequently detected simazine [3, 4, 20].

Diazinon and methidathion are organophosphate insecticides used primarily as orchard dormant sprays in January and February [1, 2, 21]. Both pesticides were detected in pulses following rainfall events after pesticide application (figures 3b and 3c). Diazinon was detected in 50% of the samples with a maximum concentration of 52 ng/L while methidathion was detected in only 19% of the samples with a maximum concentration of 79 ng/L (table 1). These two pesticides were typically detected each winter as pulses in the Sacramento and San Joaquin Rivers which were transported all the way through Suisun Bay [2]

Molinate and thiobencarb are thiocarbamate herbicides applied to rice in April and May [1, 22]. Water is held on the rice fields after pesticide application to allow for partial degradation of the pesticides [5, 23]. Molinate and thiobencarb were detected in a broad peak beginning in mid-May, following the release of rice-field water (figures 3d and 3e). The frequency of detection was similar for the two herbicides (31% and 28% for molinate and thiobencarb, respectively), but the maximum concentrations were very different. Molinate had a maximum concentration of 629 ng/L, while thiobencarb was only 66 ng/L (table 1). Changing management practices have reduced the

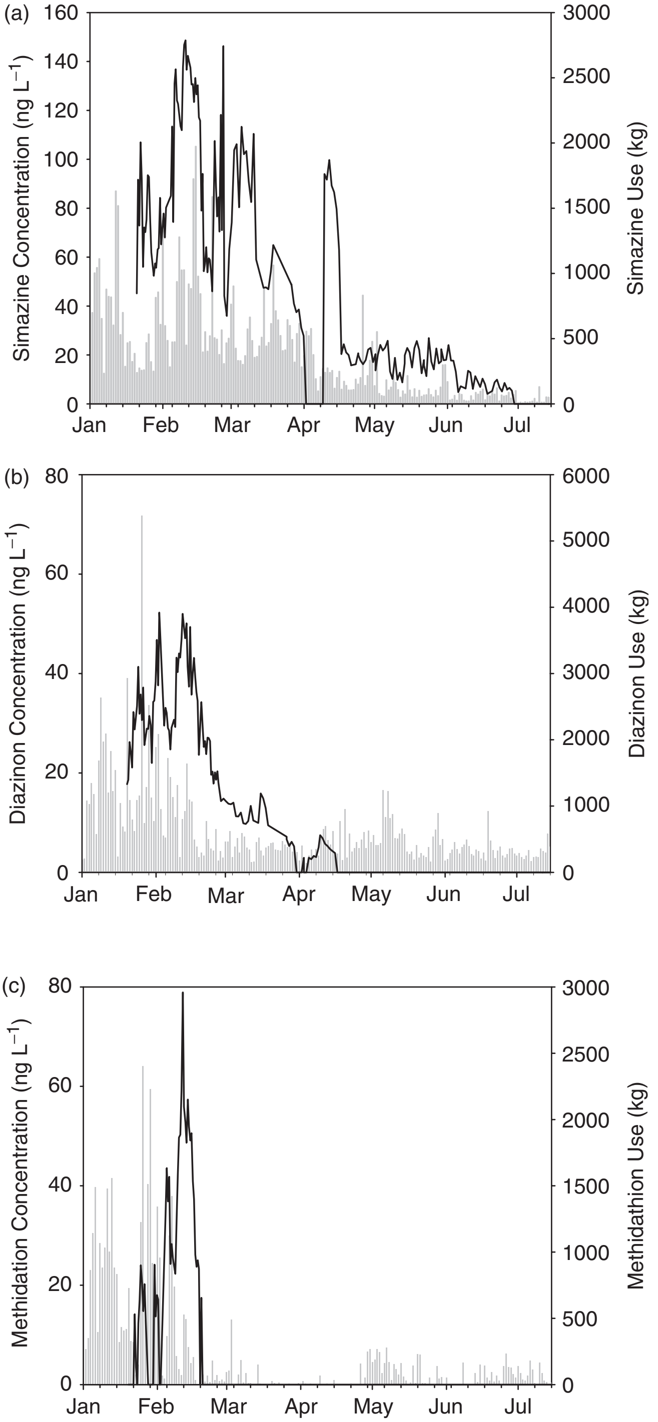

Figure 3. Dissolved pesticide concentrations at Mallard Island (solid line) and use in watershed (bars) for: (a) simazine, (b) diazinon, (c) methidathion, (d) molinate, (e) thiobencarb, and (f) carbofuran for 1996.

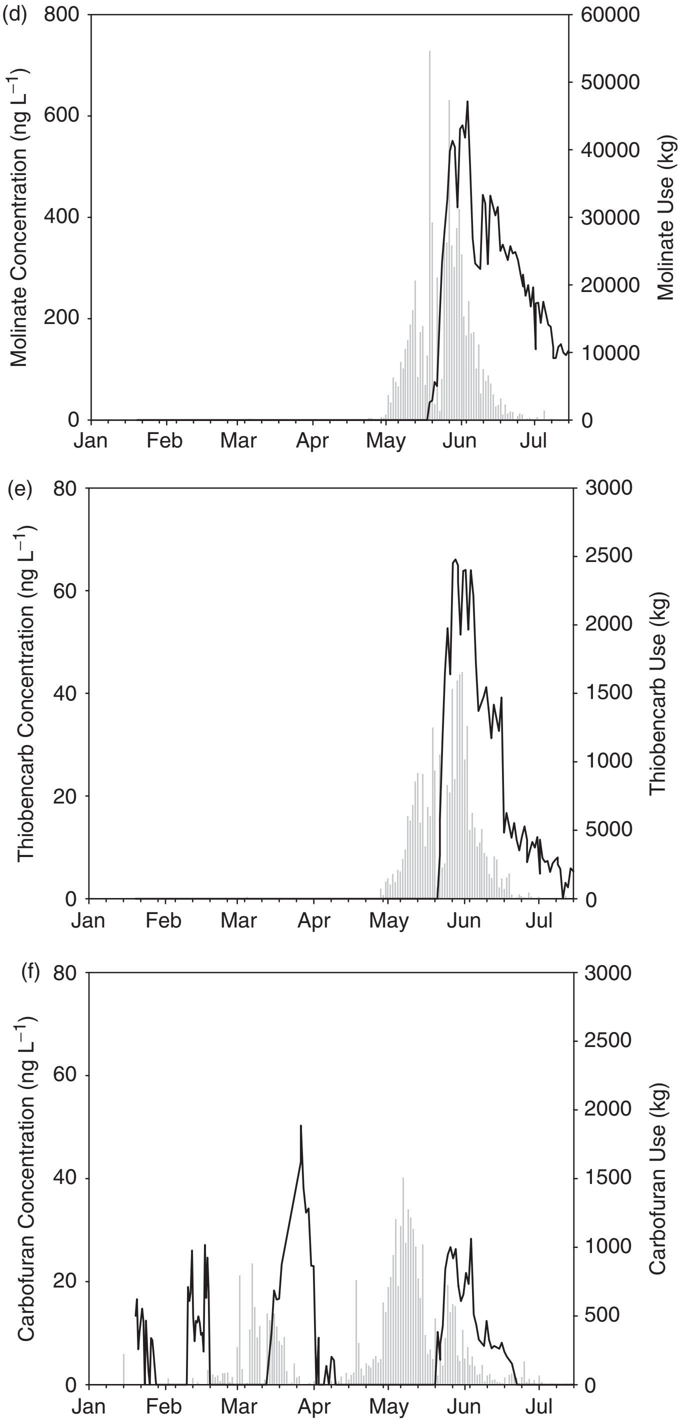

Figure 3. Continued.

Table 2. Calculated half-lives of pesticides in water (days) and ancillary water chemistry (R^2 value from linear regression analysis of plot of $\ln(C_t/C_0)$ as a function of time is shown in parentheses).

	April 1996		August 1996	
Pesticide	10°C	25°C	10°C	25°C
Simazine	No[a]	No	No	No
Diazinon	9 (0.95)	16 (0.92)	Est.[b] 134 (0.40)	Est. 103 (0.82)
Methidathion	33 (0.94)	21 (0.94)	No	18 (0.99)
Molinate	No	No	No	No
Thiobencarb	15 (0.91)	13 (0.94)	Est. 158 (0.64)	Est. 92 (0.85)
Carbofuran	Est. 108 (0.66)	6 (0.97)	48 (0.85)	3 (0.95)
pH	7.9 ± 0.1		7.6 ± 0.2	
Specific conductance	110 μS/cm		155 μS/cm	
Dissolved organic carbon	2.71 mg/L		1.70 mg/L	

[a] No: no degradation where there was no measurable decrease in concentration. [b] Est.: estimated degradation where the half-life exceeded the length of experiment.

concentrations of these two pesticides in the Sacramento River since the 1980s, but concentrations continue to exceed performance goals in the upper watershed [22].

Carbofuran is a carbamate insecticide applied on various crops including alfalfa in the early spring and rice in late spring [1]. Carbofuran was detected in multiple peaks that corresponded to transport by high flows (similar to simazine, diazinon, and methidathion), application to alfalfa in March, and release of rice field water in late May and June (similar to molinate and thiobencarb) (figure 3f). Although detected in 36% of the samples, carbofuran concentrations were the lowest of the six pesticides with a maximum of only 50 ng/L. Carbofuran has been detected previously at a number of sites in the watershed [6].

3.2 *Hydrolysis rates*

The half-lives of pesticides in this experiment varied greatly (table 2), ranging from 3 days to no observable change in concentration. The hydrolysis rate of some pesticides varied primarily with temperature (10°C vs. 25°C) or between the samples from April and August. The pH values for the samples collected in April ranged from 7.8 to 8.0, and those for the samples collected in August ranged from 7.4 to 7.8. Other water-quality parameters varied between the two samples, such as specific conductance and dissolved organic carbon (table 2).

Simazine and molinate did not degrade measurably in either water sample or at either temperature (table 2). Simazine was stable under all the experimental conditions. As reported in the literature, hydrolysis of simazine is not significant at pH values from 4 to 10 [24] or at temperatures as high as 40°C [25]. Similarly, molinate concentrations did not change during the 2 months of the laboratory experiment (data not shown). These results agree with the conservative transport of molinate along the Sacramento River observed during a Langrangian sampling study [26]. In addition, published results from other studies suggest that molinate does not readily undergo hydrolysis in rice fields [27, 28].

Both carbofuran and methidathion degraded during the experiment, and their half-lives were influenced by temperature (table 2). The hydrolysis of carbofuran was highly

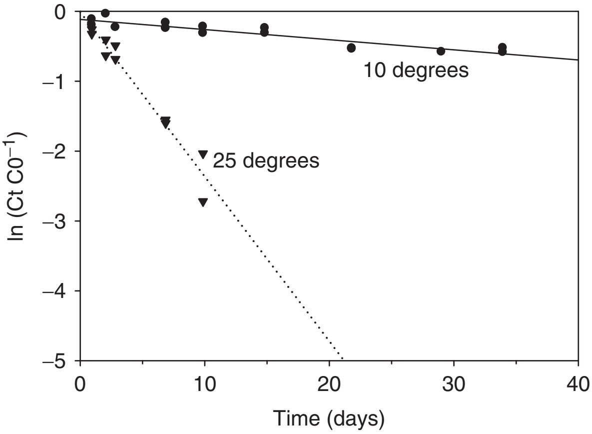

Figure 4. Carbofuran degradation at 10°C and 25°C in the water sample collected in April 1996.

temperature-dependent, with a half-life ranging from months at 10°C but less than 1 week at 25°C in both water samples (April data shown in figure 4). Studies using rice field water in the dark yielded similar hydrolysis rates with a half-life of 10 days at 27°C and pH 7 [29]. The hydrolysis of methidathion was also influenced by temperature but with some variability between the two water samples. Methidathion half-lives at 10°C ranged from 1 month (April) to more than 2 months (August) and decreased to 2–3 weeks at 25°C. In a study of methidathion in river water [30], hydrolysis half-lives were estimated to be 139 days at 4°C and 20 days at 21°C.

Diazinon and thiobencarb behaved similarly. The two pesticides degraded more quickly in the water sample collected in the spring than in the summer with little temperature influence (table 2). Half-lives for diazinon and thiobencarb ranged from 1 to 2 weeks in the April sample to more than 2 months in the August sample (thiobencarb data at 10°C shown in figure 5). The results suggest that differences in chemistry between the water collected in April and August were much more important than temperature in controlling the hydrolysis rate. Some of the difference for diazinon can be explained by pH, since hydrolysis increases from neutral to basic pH [31]. Published studies also suggest that hydrolysis of pesticides in aqueous solution can be catalysed by divalent metal ions such as copper(II) [32] or influenced by dissolved organic carbon [33]. In a study focused on thiobencarb hydrolysis, rates were shown to vary considerably in different waters, but the controlling factors were not identified [34]. The longer half-life of thiobencarb measured in the August water sample corresponds with the conservative transport observed during June in the Sacramento River Lagrangian sampling study [26].

3.3 *Comparison of flux to use and persistence*

The maximum concentration, frequency of detection, and flux into the Bay of each pesticide can be compared with the amounts applied in the watershed and the persistence of the pesticide in the environment. The flux for each pesticide was calculated for the January through July sampling period (table 3). In California,

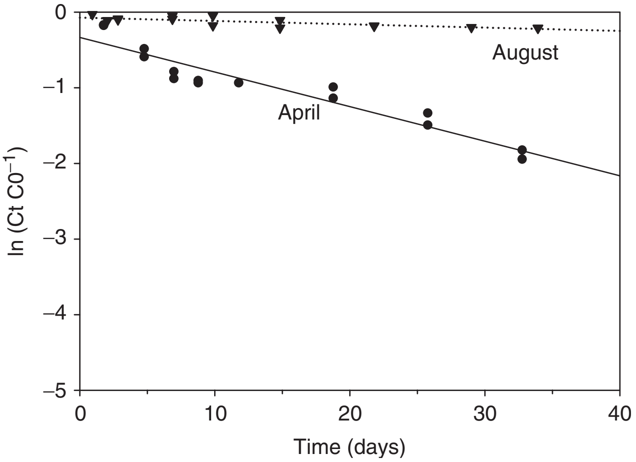

Figure 5. Thiobencarb degradation at 10°C in the water samples collected in April and August 1996.

Table 3. Calculated flux for January–July 1996, application amount for November 1995 to July 1996, flux as a percentage of the amount applied, and major factors controlling the flux.

Pesticide	Calculated flux (kg)	Application amount (kg)	Flux as a percentage of the amount applied	Factors controlling flux
Simazine	1617	102 018	1.58	Moderate use and persistent
Diazinon	407	135 458	0.30	Moderate use but degrades
Methidathion	172	46 988	0.37	Low use and degrades
Molinate	1067	653 861	0.16	Highest use and persistent under hydrolysis (lab) but volatilizes in rice field
Thiobencarb	108	289 134	0.06	High use but degrades under hydrolysis (lab) and in rice field
Carbofuran	170	39 419	0.27	Low use and degrades

detailed reporting of registered pesticide use is recorded in the Department of Pesticide Regulation pesticide use report and includes the date and location of the application and the kind and amount of pesticides used [1]. The total amount of each pesticide applied in the watershed was estimated using GIS to delineate the watershed boundaries (table 3). The application amount was summed from November 1995 through July 1996 for comparison with the measured flux.

In a comparison of the six pesticides, simazine was detected in the most samples, with the second highest maximum concentration, and had the highest flux (1617 kg). This can be explained by its continuous use over many months and persistence in the environment as demonstrated in the laboratory experiments. Molinate was detected only after the release of the rice-field water but at the highest concentrations and the second highest flux (1067 kg). Molinate was applied in quantities more than five times that of simazine and was persistent in our laboratory study; therefore, if hydrolysis was the only loss mechanism, this would suggest that molinate should have the highest flux of the six pesticides. But a significant fraction of the molinate volatilizes from the rice fields or photodegrades before it can be transported to the rivers, resulting in the lower-than-expected flux of molinate [23, 27, 28, 35, 36].

Diazinon was detected at lower concentrations and had a lower flux (407 kg) than did simazine and molinate. This corresponds to its lesser application amount than molinate and shorter half-life than simazine. Carbofuran, methidathion, and thiobencarb all had lower maximum concentrations and lower fluxes (table 3). The application amounts of carbofuran and methidathion were lower than the other pesticides, and both pesticides degraded during the lab study. In contrast, thiobencarb had the second highest use, lower than molinate but twice that of simazine and diazinon, but still had the lowest flux (108 kg) of all six pesticides. Besides degrading via hydrolysis as demonstrated in the laboratory study, thiobencarb sorbs to soils, volatilizes, and photodegrades in the rice fields [23, 36–38]. The combination of all of these loss mechanisms can explain the low thiobencarb flux.

One way of accounting for the variation in application is to calculate the pesticide flux as a percentage of the amount applied in the watershed. Since some of the water and associated pesticides exiting the watershed are exported by the water projects instead of flowing past Mallard Island, and this fraction varies during the year, there is some uncertainty with this calculation; however, the order-of-magnitude difference between the pesticides is significant (table 3). The calculated flux as a percentage of the amount applied is similar for carbofuran, diazinon, methidathion, and molinate (0.16–0.37%) but significantly higher for simazine (1.58%) and significantly lower for thiobencarb (0.06%). For most pesticides, the runoff loss (the measured flux in this case) is typically 0.5% or less of the amount applied [39]. The higher value for simazine is likely due to a combination of formulation type, timing of rainfall relative to application and environmental persistence. In contrast, the very low thiobencarb percentage is likely due to processes occurring in the rice fields.

The fluxes estimated in this study can be compared with fluxes in other estuaries (table 4). Only four of the six pesticides measured in this study were monitored in the other studies. Fluxes into San Francisco Bay were equal to or greater than the other estuaries except for the Gulf of Mexico [40], which has a much larger drainage area and potentially higher use. In the six other studies [41–45], simazine fluxes were relatively similar (i.e. within a factor of four) with the exception of the Amvrakikos Gulf in Greece, which has a much smaller drainage area. But in a comparison of the simazine flux calculated as a percentage of total amount applied, San Francisco Bay (1.58%) and Amvrakikos Gulf (1.72%) were very similar. Diazinon fluxes in San Francisco Bay were one to two orders of magnitude higher than in Chesapeake Bay, Columbia River or Ebro River [40–42]. The carbofuran flux was similar to that in the Columbia River [40], but molinate flux was more than an order of magnitude greater than in the Ebro River [41]. It is interesting to note that the molinate flux in San Francisco Bay was within a factor of two of the Yazoo River flux [44] during the same year, 1996. But in 1997, the flux in the Yazoo River was five times greater. The molinate flux as a percentage of application amount was much lower for San Francisco Bay (0.16%) than for the Yazoo River (2.1 and 9.9%); this difference is primarily due to loss of molinate when the water is held for a period of time on the California rice fields.

Table 4. Comparison of pesticide fluxes measured in this study with published values for other estuaries and rivers.

Water body	Drainage area (km^2)	Flux (kg/yr)				Ref.
		Carbofuran	Diazinon	Molinate	Simazine	
San Francisco Bay, USA	99 587	170	407	1067	1617	This study
Chesapeake Bay, USA	71 200	–[a]	34	–	820	[42]
Columbia River, USA	258 800	100–400	n.d.[b]–2	–	1000–1800	[40]
Gulf of Mexico, USA[c]	2 914 000	612–4500	1560–2290	1367–10 410	21 030–48 700	[40]
Yazoo River, USA[d]	34 590	–	–	2160–10 050	682–744	[44]
Amvrakikos Gulf, Greece	5200	–	–	–	43	[43]
Ebro River, Spain	84 000	–	6	62	367	[41]
Scheldt Estuary, Netherlands	21 000	–	–	–	750	[45]

[a] –: not analysed. [b] n.d.: not detected. [c] Fluxes were measured 1996–2000. [d] Fluxes were measured 1996–1997.

4. Conclusions

This study documents the input of six current-use pesticides into San Francisco Bay from January through July 1996 at the freshwater input to the bay. The frequency of detection of the pesticides ranged from 19% for methidathion to 83% for simazine, and molinate was detected at the highest concentration (629 ng/L). The occurrence of each pesticide followed the application of that pesticide in distinct seasonal patterns. The primary transport mechanism was rainfall-runoff, but release of rice field water was also important for carbofuran, molinate, and thiobencarb. The pesticide persistence in laboratory studies varied from a half-life of 3 days to no measurable change in concentration over 2 months. Temperature, pH, and other water chemistry influenced the hydrolysis rates.

Calculated pesticide fluxes ranged from 108 kg for thiobencarb to 1617 kg of simazine over the sampling period. The amount applied and environmental persistence could explain the differences in fluxes for four of the pesticides. But for molinate and thiobencarb, it was important to consider also the loss occurring on the rice fields where the water was held after pesticide application. Loss due to volatilization, photodegradation, and sorption to soil resulted in lower-than-expected fluxes. In comparison with measured fluxes into other estuaries in the US and Europe, diazinon fluxes were significantly higher in San Francisco Bay, while the fluxes of carbofuran, molinate, and simazine were equal or slightly higher.

This study was conducted during a single year, so the effect of different hydrologic conditions is not known. Pesticide use continues to change over time, with pesticides being phased out and new pesticides taking their place. Monitoring studies need to adapt and include analysis of new pesticides as needed. In addition, measurement of pesticide degradates and other environmental compartments such as sediment should be considered when evaluating the transport of pesticides into San Francisco Bay.

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