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Understanding the Occurrence and Transport of Current-use Pesticides in the San Francisco Estuary Watershed

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Editor's Note: Dr. Robert Spies was originally commissioned by the Interim Science Advisory Board of the Ecosystem Restoration Program, CALFED, to assemble a series of papers on chemical contamination in the Bay-Delta. This important paper is the first of several submissions from that series that we hope to publish in SFEWS.

ABSTRACT

The occurrence and potential effects of current-use pesticides are of concern in the San Francisco Estuary watershed but our understanding of the spatial and temporal distribution of contamination is limited. This paper summarizes almost two decades of historical data and uses it to describe our current knowledge of the processes controlling the occurrence of current-use pesticides in the watershed. Monitoring studies analyze fewer than half of the pesticides applied in the watershed and most of our knowledge is about inputs of dissolved pesticides in the upper watershed. The four major seasonal patterns of riverine inputs of pesticides to the estuary can be identified by usage and transport mechanism. Dormant spray insecticides applied to orchards and herbicides applied to a variety of crops are transported by rainfall during the winter. Alfalfa pesticides are detected following rainfall and irrigation return flow in the spring, and rice pesticides are detected following release of rice field water in the summer. Irrigation return flows transport a variety of herbicides during the summer. In addition, pesticides applied on Delta islands can cause elevated pesticide concentrations in localized areas. Although not as well characterized, urban creeks appear to have their own patterns of insecticide concentrations causing toxicity throughout most of the year. Current-use pesticides have also been detected on suspended and bed sediments throughout the watershed but limited data make it difficult to determine occurrence patterns. Data gaps include the lack of analysis of many pesticides (or degradates), changing pesticide use, limited information on pesticide transport within the Delta, and an incomplete understanding of the transport and persistence of sediment-associated pesticides. Future monitoring programs should be designed to address these data gaps.

KEYWORDS

Pesticides, herbicides, insecticides, San Francisco Bay, Sacramento River, San Joaquin River, Sacramento-San Joaquin Delta, toxicity, sediment

SUGGESTED CITATION

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INTRODUCTION

Current-use pesticides pose a potential threat to aquatic organisms in the San Francisco Estuary watershed, an ecologically important habitat and a location for large-scale ecosystem restoration. It is critical to understand the effects of pesticides on the ecosystem; this requires a detailed knowledge of pesticide exposure throughout the watershed. Since 1988, studies conducted by the California Regional Water Quality Control Board (RWQCB) have used U.S. Environmental Protection Agency (USEPA) three-species bioassay protocols to identify frequent toxicity in the San Francisco Estuary; this toxicity is often linked to pesticides through toxicity identification evaluations (TIEs) (Cooke and Connor 1998). In addition, a number of monitoring programs have measured pesticides concentrations throughout the watershed at varying scales of time and space. Proposed water conveyance and restoration projects will likely cause changes in the distribution and bioavailability of pesticides; therefore, an understanding of the controlling processes is necessary to predict the resulting effects on the ecosystem.

In 2006, there were 161 pesticides applied in amounts of five hundred kilograms or more (active ingredient) within the San Francisco Estuary watershed (Table 1). As the name suggests, current-use pesticides are those pesticides currently in use as opposed to "historically-used" or legacy pesticides such as DDT which are still present on sediments in surface waters despite no longer being used in the United States. The

Table 1. Current-use pesticides applied in amounts greater than 500 kg, type of use and total kilograms (active ingredient) applied in San Francisco Estuary watershed in 2006 [California Department of Pesticide Regulation 2008]. Pesticides in red have never been monitored in the watershed.

Name	Types of Use[a]	Total Applied (kg)
Glyphosate	H	1,338,424
1,3-dichloropropene	fumigant	1,058,757
Propanil	H	679,108
Metam salts	F/H/I	667,607
Ziram	F	286,089
Maneb	F	199,142
Chlorpyrifos	I	198,495
Oryzalin	H	193,205
Diuron	H	175,289
Chloropicrin	fumigant	157,665
Chlorothalonil	F	154,382
Paraquat	H	147,729
Trifluralin	H	147,415
Thiobencarb	H	140,773
Propargite	I	133,522
Oxyfluorfen	H	111,798
2,4-D	H	108,942
Mancozeb	F	99,677
Captan	F	88,461
Metolachlor	H	77,068
Simazine	H	74,352
Pendimethalin	H	73,120
Ethephon	PGR	69,856
Molinate	H	64,085
Piperonyl butoxide	synergist	52,908
Triclopyr	H	43,231
Acrolein	A	41,898
Cypermethrin	I	40,250
MCPA	H	38,128
Malathion	I	37,372
Phosmet	I	37,122
Hexazinone	H	36,446

a A = algaecide; F = fungicide; H= herbicide; I = insecticide; IGR = insect growth regulator; PGR = plant growth regulator

Table 1. Current-use pesticides applied in amounts greater than 500 kg, type of use and total kilograms (active ingredient) applied in San Francisco Estuary watershed in 2006 [California Department of Pesticide Regulation 2008]. Pesticides in red have never been monitored in the watershed. (Continued)

Name	Types of Use[a]	Total Applied (kg)
Boscalid	F	35,935
Dimethoate	I	35,266
Iprodione	F	35,240
Permethrin	I	33,682
Diazinon	I	32,551
Clomazone	H	27,834
Methomyl	I	27,499
Azoxystrobin	F	26,795
Pyraclostrobin	F	22,930
Cyprodinil	F	22,461
Methyl parathion	I	21,708
Naled	I	21,133
Carbaryl	I	20,996
Bifenthrin	I	18,249
Cyfluthrin	I	17,720
Ethalfluralin	H	17,396
Dicofol	I	17,254
Methoxyfenozide	I	16,119
Trichloro-S-triazinetrione	microbiocide	15,247
Cyhalofop	H	14,888
2,4-DB	H	14,452
Norflurazon	H	14,077
Prodiamine	H	10,686
Flumioxazin	H	10,371
Aldicarb	I	10,222
Imazapyr	H	9,667
Methidathion	I	9,384
Imidacloprid	I	9,228
Acephate	I	9,094
Metribuzin	H	9,037
EPTC	H	8,553
Thiophanate-methyl	F	8,499
Azinphos-methyl	I	8,028
Bromacil	H	7,596
Myclobutanil	F	7,479
Ethoprop	I	7,256
Esfenvalerate	I	6,997
Bromoxynil	H	6,908
Diquat	H	6,641
Mefenoxam	F	6,590
Glufosinate	H	6,479
Fipronil	I	6,417
Pyrethrins	I	6,335
Lambda-cyhalothrin	I	5,797
Paclobutrazol	PGR	5,783
MSMA	H	5,650
Isoxaben	H	5,569
Diflubenzuron	I	5,354
Indoxacarb	I	5,315
Napropamide	H	5,113
Sethoxydim	H	4,874
Bifenazate	I	4,817
Tebuconazole	F	4,785
Bensulide	H	4,698
PCNB	F	4,675
Fenpropathrin	I	4,513
Pyrimethanil	F	4,471
Propiconazole	F	4,422
Trifloxystrobin	F	4,401
Carfentrazone-ethyl	H	4,266
Prometryn	H	4,165
Cycloate	H	4,125
Atrazine	H	3,875
Phorate	I	3,866
Fenamiphos	I	3,842
Clethodim	H	3,807
Disulfoton	I	3,633

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Table 1. Current-use pesticides applied in amounts greater than 500 kg, type of use and total kilograms (active ingredient) applied in San Francisco Estuary watershed in 2006 [California Department of Pesticide Regulation 2008]. Pesticides in red have never been monitored in the watershed. (Continued)

Name	Types of Use[a]	Total Applied (kg)
Spiromesifen	I	3,375
Oxytetracycline	F	3,227
Carbofuran	I	3,094
Fenhexamid	F	2,992
Dicamba	H	2,983
Spinosad	I	2,974
Methoprene	IGR	2,679
Sulfometuron methyl	H	2,455
Streptomycin	F	2,402
Clopyralid	H	2,358
Methamidophos	I	2,320
Hexythiazox	IGR	2,297
Endosulfan	I	2,246
Oxydemeton-methyl	I	2,180
Triflumizole	F	2,177
Mepiquat	PGR	2,013
Ethofumesate	H	2,009
Linuron	H	2,006
Dichlobenil	H	1,972
Dithiopyr	H	1,936
Oxamyl	I	1,904
Deltamethrin	I	1,887
Dimethomorph	F	1,879
Pyridaben	I	1,863
Buprofezin	IGR	1,839
Flutolanil	F	1,795
Dazomet	F	1,787
Kresoxim-methyl	F	1,784
Tebufenozide	I	1,757
Quinoxyfen	F	1,756
Thiamethoxam	F	1,689
DCPA	H	1,682
Oxadiazon	H	1,616
Thidiazuron	PGR	1,609
Thiram	F	1,605
Fluridone	H	1,602
Acequinocyl	I	1,506
Abamectin	I	1,357
Metaldehyde	molluscicide	1,353
Clofentezine	I	1,237
Butylate	H	1,202
Penoxsulam	H	1,188
Dicloran	F	1,184
Chloroneb	F	1,067
Imazethapyr	H	1,035
Chlorpropham	H	984
DDVP	I	884
Imazamox	H	868
Thiabendazole	F	821
Halosulfuron-methyl	H	787
Bispyribac	H	762
Chlorsulfuron	H	740
Fluazifop-butyl	H	712
Acetamiprid	I	690
Chlorfenapyr	I	643
Endothall	H	630
Propyzamide	H	613
Siduron	H	612
MCPP	H	601
Phenmedipham	H	590
Tebuthiuron	H	545
Rimsulfuron	H	501

a A = algaecide; F = fungicide; H= herbicide; I = insecticide; IGR = insect growth regulator; PGR = plant growth regulator

reason for emphasizing the difference is that many current-use pesticides are compounds with different physical-chemical properties and patterns of input than historically-used organochlorine pesticides. These differences in properties and input translate into differences in fate in the environment.

Our knowledge about the inputs, distribution, and persistence of current-use pesticides in the San Francisco Estuary watershed is limited. We have extensive knowledge about a few pesticides but relatively little about half of the highest-use pesticides applied in the watershed (Table 1). The purpose of this article is to describe the seasonal patterns of pesticide occurrence in the watershed and discuss our current understanding of how specific pesticide-use settings and transport mechanisms produce these patterns. This article is not intended to be a comprehensive review of pesticide concentrations in the San Francisco Estuary watershed. In addition, although toxicity tests are included when the results are used to identify specific pesticides, an analysis of the toxicological significance of the pesticide concentrations is beyond the scope of this paper. The pesticides selected for this review are all organic compounds; other compounds, such as inorganic fumigants and algaecides, are excluded from the discussion.

BACKGROUND

Pesticide Properties

Most of the current-use pesticides can be grouped into classes of similar structures and properties. The classes include carbamates, thio- and dithiocarbamates, chlorinated hydrocarbons (some are still being used), organophosphates, phenoxy and benzoic acid herbicides, pyrethroids, triazines, and ureas. Of course, some pesticides do not fit neatly into any of these classes.

The physical and chemical properties of each pesticide influence their fate in the aquatic environment. Most current-use pesticides are relatively hydrophilic with log K_{OC} values ranging from 1.3 to 3.9. Hydrophilic or high water solubility means that the pesticides are more likely to be in the dissolved phase and be transported via runoff, field water release, or ground water discharge into local streams or rivers. But one class of insecticides, the pyrethroids, are relatively hydrophobic with log K_{OC} values ranging from 4.3 to 5.5. Some current-use pesticides degrade quickly via hydrolysis or microbial degradation in the natural environment; the result is that they are less persistent. Degradation rates vary considerably and appear to be influenced by a variety of water quality parameters (such as temperature, pH, dissolved organic carbon, oxidation/reduction conditions, and the concentrations of some trace metals) (Walker 1976; Wolfe and others 1977; Noblet and others 1996; Smolen and Stone 1997).

Pesticide Use

The major sources of pesticides to the San Francisco Estuary are agricultural and urban use. Use of pesticides in agriculture typically involves application of more pesticides in larger quantities over a wider area than urban applications. Detailed reporting of registered use is recorded in the California Department of Pesticide Regulation (CDPR) Pesticide Use Report (PUR). Since 1990, full use reporting includes the date and location of the application and the kind and amount of pesticides used (CDPR 2008). Production agricultural reports cover application to crops, agricultural fields, forest and ornamental turf. Non-agricultural use includes post-harvest commodity treatments, rights-of-ways, landscapes, structural use, and other non-agricultural uses by commercial applicators. These data are less specific and reports include only the month and county of application.

In contrast, there is not an official record of non-professional residential, institutional, and livestock applications. Although good data are not available on actual amounts used and timing of application, it is known which pesticides are registered for residential or home use. A report on annual urban pesticide sales focused on San Francisco Bay (TDC Environmental 2005) summarized information from pesticide sales data, retail shelf surveys, internet searches, pesticide use surveys, and interviews and discussed trends in urban pesticide use.

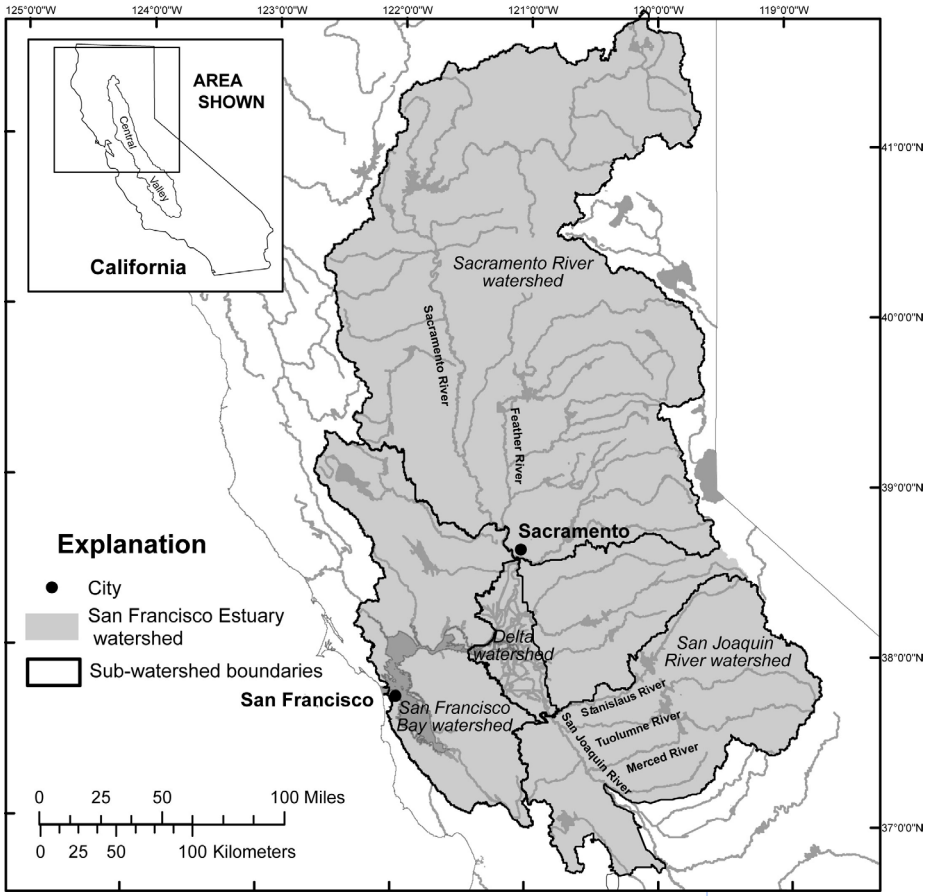

Figure 1. Location of San Francisco Bay watershed and key features

Pesticide Inputs

The San Francisco Estuary watershed encompasses nearly 11 million hectares and is drained by two major river systems, the Sacramento and the San Joaquin rivers (Figure 1). Over 2 million hectares (19%) within the watershed are devoted primarily to agriculture and produce a wide variety of crops, including alfalfa, grapes, orchards, rice, and tomatoes. The area also contains numerous urban centers of varying size with a combined area of almost 0.5 million hectares.

For the purpose of discussing pesticide inputs, the San Francisco Estuary watershed can be divided into four major sub-watersheds: Sacramento River, San Joaquin River, Sacramento-San Joaquin Delta (Delta), and San Francisco Bay (Figure 1). The Sacramento River watershed includes two major river systems (Sacramento and Feather) plus numerous smaller creeks and agricultural drains. Primary land use on the valley floor is agriculture but also has a large and rapidly expanding urban population of over 2.1 million people (U.S. Census Bureau 2000). The San Joaquin River watershed includes three major eastside tributaries (Merced, Tuolumne and Stanislaus rivers) plus a series of smaller westside creeks. The valley floor is primarily agricultural and involves a very complex water distribution system. Although the Delta watershed is a much smaller area, it is more complex hydrologically and is influenced by the tides. For this discussion, the Cosumnes and Mokelumne rivers and eastside creeks are included with the Delta proper (Figures 1 and 2). Sources of pesticides to the Delta include the external inputs from rivers and creeks and within-Delta inputs from applications on Delta islands. The San Francisco Bay watershed encompasses the Napa and Petaluma rivers, Sonoma Creek and all the smaller creeks that directly enter Suisun, San Pablo, Central and South bays (Figures 1 and 2).

The pesticide inputs to the Delta from the Sacramento and San Joaquin River watersheds are the best characterized (MacCoy and others 1995; Panshin and others 1998) with samples taken three to seven times per week over a continuous three-year period. Other studies have characterized the geographic sources of pesticides within these two watersheds (Ross and others 1996; Panshin and others 1998; Domagalski 2000). The occurrence and distribution of pesticides in the Delta and San Francisco Bay watersheds are less understood. The complicated hydrodynamics of the Delta make it difficult to choose appropriate sam-

pling sites to identify sources and transport of pesticides. Therefore, although pesticide samples have been collected in the Delta, little is known about local sources or extent of elevated concentrations (Foe and Sheipline 1993; Kuivila and others 1999; Werner and others 2000; Orlando and Kuivila 2006).

SEASONAL PATTERNS OF DISSOLVED PESTICIDES

Most pesticides are applied during a definitive "season" on specific crops or for a specific purpose, even in urban areas. Following application, transport to surface waters can occur via rainfall-runoff, irrigation, release of field water or atmospheric transport. The time interval between application and transport is important since degradation, volatilization, and sorption to soil occurs primarily on the field or application surface. These processes, in turn, will affect the amount and form of the pesticide (dissolved or sediment-associated) that is transported to surface water.

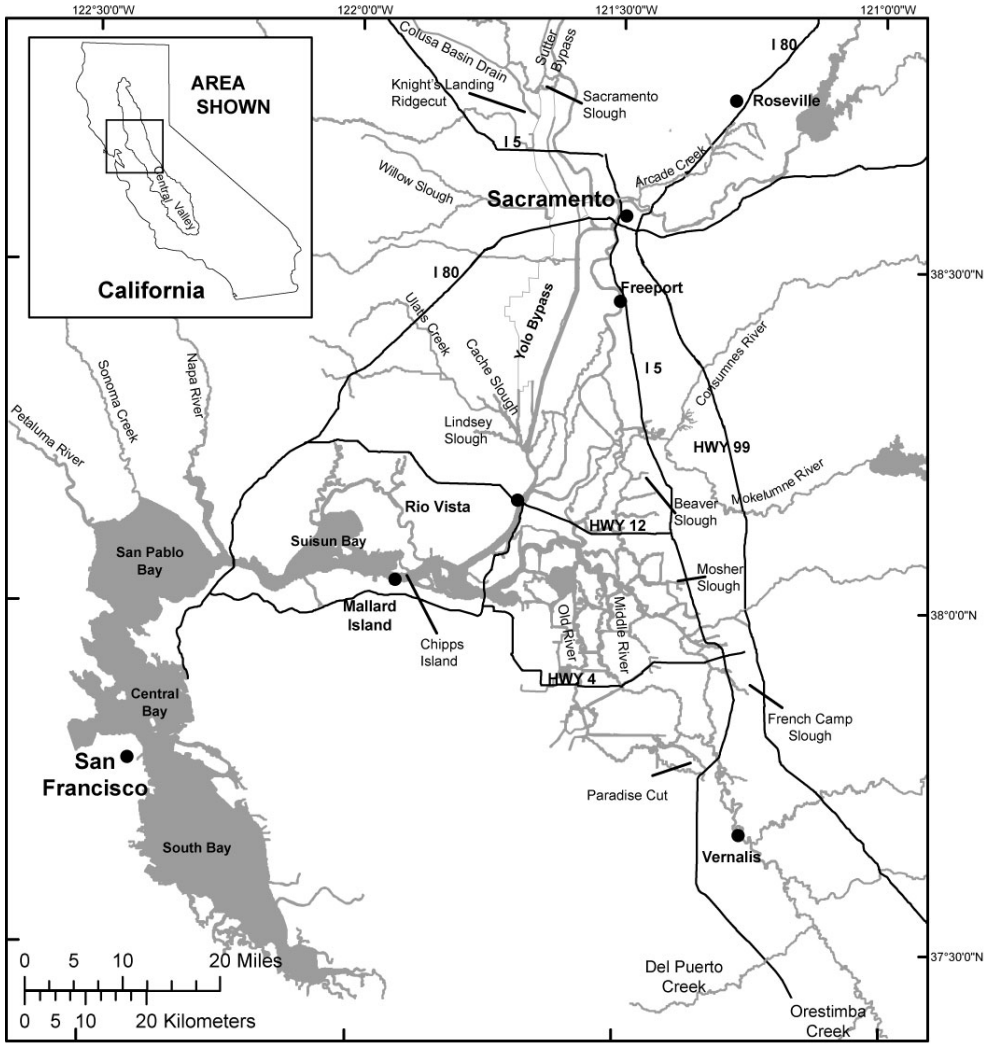

Figure 2. Sacramento–San Joaquin Delta and sampling locations in the cited studies

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. Some of the patterns are clearly defined as to source and transport mechanism but many patterns are not so clear-cut. Typical seasonal patterns characterized by transport mechanism include the first flush (the first large runoff event in the winter), spring late-rainfall runoff event or tailwater return (direct runoff of irrigation return water), rice-field water release, and summer tailwater return (Table 2). In addition, atmospheric transport of pesticides can occur during application (spray drift) or after application (volatilization or on dust particles).

First Flush of Dormant Spray Insecticides

Each year insecticides are applied to orchards in the Central Valley as dormant sprays, usually during December and January (Table 2). Chlorpyrifos, diazinon, and methidathion were the primary organophosphate insecticides used for many years and

Table 2. Overview of seasonal inputs of current-use pesticides with details of detection, transport, fate, and application

Description	Detection Season	Transport Processes	Major Pesticides of Concern	Persistence in Water	Major Commodities[a]	Timing of Application[a]
First flush of dormant-spray insecticides	Jan - Mar	rainfall-runoff atmospheric	diazinon methidathion chlorpyrifos	moderate[b,c]	orchards	Dec - Feb
First flush of herbicides	Jan - Mar	rainfall-runoff	simazine	stable[b]	orchards, grapes, rights-of-way, landscape	Nov - Feb
			hexazinone	stable[d]	alfalfa	Dec - Jan
			diuron	stable[c]	alfalfa, rights-of-way	Dec - Feb
			DCPA (dacthal)	stable[e]	onions, cole crops	Jan - Feb
Spring detection of insecticides	Mar - Apr	rainfall-runoff irrigation return flow	carbofuran chlorpyrifos malathion	variable[b] moderate[c] degrades[c]	alfalfa	Mar
Spring and summer detection of rice pesticides	May - Jul	release of rice field water (seepage)	molinate	stable[b]	rice	May - Jun
			carbofuran thiobencarb	variable[b]		
Summer detection of other pesticides	Jun - Aug	irrigation return flow	eptam	stable[c]	alfalfa, corn, safflower	May - Jul
			metolachlor	stable[c]	tomatoes	Apr - Jun
			chlorpyrifos diazinon	moderate[b,c]	almonds, walnuts	May - Aug
			malathion	degrades[c]		
Urban creeks	All year round	rainfall-runoff irrigation return flow	diazinon chlorpyrifos	moderate[b,c]	urban use	All year round
			carbaryl malathion	degrades[c]		

a CDPR 2008 (2006 data)
b Kuivila and Jennings 2007
c Panshin and others 1998
d Bouchard and others 1985
e Wettasinghe and Tinsley 1993

were found to be transported off site by subsequent rainfall-runoff events. This input of insecticides into the San Francisco Estuary in the winter has been the most studied seasonal pattern.

Diazinon and methidathion were typically detected each winter as pulses in the Sacramento and San Joaquin rivers with elevated concentrations lasting days to weeks (Kuivila and Foe 1995; MacCoy and others 1995). In 1993, Kuivila and Foe (1995) showed that these dormant spray insecticides were transported all the way through Suisun Bay. The duration of elevated concentrations appeared to be influenced by water residence time (rivers < Suisun Bay < Delta). Diazinon was the dormant spray insecticide detected most frequently and typically at the highest concentrations while methidathion was next frequently detected and typically at lower concentrations. Chlorpyrifos was detected intermittently and at much

lower concentrations in both rivers (Kuivila and Foe 1995; Panshin and others 1998; Domagalski 2000). In 1997, diazinon and methidathion were still detected in pulses following rainfall events at the input to Suisun Bay, but at lower concentrations than detected in 1993 (Kuivila and Jennings 2007). Atmospheric transport was also an important transport pathway, with detections of chlorpyrifos, diazinon, and methidathion in wet and dry deposition in the San Joaquin Valley (Turner and others 1989; Ross and others 1996; Vogel and others 2008).

In addition, bioassays have shown that surface water was often toxic to the cladoceran *Ceriodaphnia dubia*, a standard USEPA test species, during the winter (deVlaming and others 2000). Initial monitoring of the San Joaquin River (1988–1990) found that the 43–mile stretch between the confluence of the Merced and Stanislaus rivers was toxic to *C. dubia* in 40% to 50% of the samples, and diazinon, parathion, carbaryl, carbofuran were present at concentrations exceeding USEPA recommended criteria and literature toxicity values (Foe and Connor 1991). Subsequent monitoring in 1991–1992 showed similar results with half the samples in the San Joaquin River from January through March testing toxic and containing diazinon, chlorpyrifos, and parathion (Foe and Sheipline 1993). Kuivila and Foe (1995) showed that the pulses in 1993 were toxic to *C. dubia* in the Sacramento River at Rio Vista and San Joaquin River at Vernalis (Figure 2) and could explain the majority of the observed toxicity with diazinon concentrations. Diazinon was also the major cause of toxicity in a westside creek to the San Joaquin River (Orestimba Creek), main stem San Joaquin River, and Sacramento Slough in storm runoff in January and February of 1996 and 1997 (Foe and others 1998).

Use of organophosphate insecticides on orchards began decreasing in the mid–1990s as alternatives (*Bacillus thuringiensis*, pyrethroid insecticides, and oil) were promoted by various state agencies and programs (Epstein and others 2001; Zhang and others 2005). By the 1999–2000 dormant spray season, diazinon use in the Sacramento Valley was about 60% of the previous four–year average (Dileanis and others 2002) and in the San Joaquin River Basin was less than 21% of that applied in 1992–1994 (Kratzer and others 2002). Correspondingly, maximum concentrations of diazinon and methidathion in 2000–2002 were nearly an order of magnitude lower than in 1992–1994 (Kuivila and Orlando 2002). Total sales of diazinon within California have continued to decrease (TDC Environmental 2008a).

First Flush of Herbicides

Although the primary focus in the first flush has been on the dormant spray pesticides, rainfall-runoff transports a number of herbicides which are applied on crops and for roadside maintenance (Table 2). Although the timing of application varied by herbicide, the highest concentrations were detected following the first winter storm.

One triazine herbicide, simazine, is applied throughout the year on grapes, landscape maintenance, rights-of-way, and orchards. Simazine was frequently detected in the Sacramento River (MacCoy and others 1995; Guo and others 2007), the Yolo Bypass (Figure 2) (Smalling and others 2005; Smalling and others 2007) and the San Joaquin River (MacCoy and others 1995; Panshin and others 1998; Orlando and others 2004; Whitehead and others 2004). At Mallard Island (Figure 2), simazine was detected in 83% of samples collected daily from mid-January through mid-July in 1997 and had the highest flux of six current-use pesticides into San Francisco Bay (Kuivila and Jennings 2007). One factor is the relative persistence of simazine over a range of temperatures and environmental conditions (Noblet and others 1996; Kuivila and Jennings 2007). Also, simazine was detected in all rainfall samples collected in the San Joaquin Valley in 2003 and 2004 (Vogel and others 2008).

Hexazinone is another triazine herbicide applied primarily in the winter on alfalfa, but it has been monitored in relatively few studies. Some of the earliest measurements were in 2001 and 2002 when hexazinone was detected at a number of sites throughout the Sacramento River and San Joaquin River watersheds (Orlando and others 2003; Orlando and others 2004). During high-flow sampling in the winter of 2004, hexazinone was detected in all the inputs to Yolo Bypass with the highest concentrations

in Knight's Landing Ridgecut and Willow Slough (Smalling and others 2005; Smalling and others 2007). Elevated concentrations were also detected during a monitoring study of the Sacramento River main stem and tributaries in January and February 2005 (Guo and others 2007).

Diuron is a urea herbicide that is widely used on alfalfa, asparagus, grapes, rights-of-way, and walnuts. Despite being detected frequently (when measured) and implicated often in algal toxicity, diuron has not been routinely measured in monitoring programs. This is probably because it requires analysis by liquid chromatography (LC), as opposed to gas chromatography (GC) which is the more common analytical method. The highest concentrations of diuron were detected in the winter in the San Joaquin River at Vernalis (Panshin and others 1998), tributaries and main stem of the Sacramento River (Guo and others 2007), and an eastside Delta slough, French Camp Slough (Kuivila and others 1999). TIE results demonstrated that diuron was the cause of algal toxicity in the Delta (Miller and others 2005).

DCPA (also called dacthal or chlorthal-dimethyl) is a phthalic acid herbicide applied to onions and cole crops in winter. Although typically detected at lower concentrations than other herbicides, DCPA was frequently detected in the San Joaquin River (MacCoy and others 1995; Panshin and others 1998; Orlando and others 2003; Orlando and others 2004). Atmospheric transport was also important with frequent detections at low concentrations in San Joaquin Valley rainfall samples (Vogel and others 2008). Although DCPA has a relatively low use (Table 1), its frequent occurrence can be explained by its persistence in water, soil, and the atmosphere (Ross and others 1990; Wettasinghe and Tinsley 1993).

Spring Detection of Insecticides

Three insecticides (carbofuran, chlorpyrifos, and malathion) are applied to alfalfa in March and April (Table 2). Carbofuran, a thiocarbamate insecticide, was detected in the spring in several studies. In 1993, carbofuran was detected in the San Joaquin River watershed immediately after application on alfalfa (Panshin and others 1998). Water from Paradise Cut (Figure 2) in the Delta caused toxicity to *C. dubia* in a bioassay on April 27, 1994; the measured carbofuran concentration of 4,800 ng L^{-1} could account for the observed toxicity (Werner and others 2000). In April 1995, a synoptic sampling of the Delta detected elevated concentrations of carbofuran throughout the Delta. The highest concentration (990 ng L^{-1}) was detected at Beaver Slough (Figure 2) (Orlando and Kuivila 2006). Carbofuran was detected in almost half the water samples collected in Delta smelt spawning and larval habitat in the spring of 1998 through 2000 (Kuivila and Moon 2004).

Chlorpyrifos and malathion are both organophosphate insecticides. In the San Joaquin Basin, chlorpyrifos was detected in 85 of 190 samples in a monitoring study between April and June in 1991 and 1992 (Foe 1995). In 43 of those samples, the concentrations were at a level toxic to *C. dubia*. In another study from 1993–1995, water samples were toxic to *C. dubia* 13 times in backwater sloughs (Werner and others 2000) and toxicity identification evaluations were used to attribute the observed toxicity to chlorpyrifos. Chlorpyrifos was still detected in 1998 through 2000 in the Delta (Kuivila and Moon 2004). In contrast, malathion is only infrequently detected (Panshin and others 1998), despite being applied in larger quantities than carbofuran or chlorpyrifos. Malathion degrades rapidly in the environment (Panshin and others 1998).

Spring and Summer Detection of Rice Pesticides

Rice is a pesticide-intensive crop with the application of thiocarbamate herbicides (molinate and thiobencarb), a carbamate insecticide (carbofuran), and organophosphate insecticides (methyl parathion and malathion) either directly to the soil prior to planting and flooding of the fields, or a few weeks after flooding (Table 2). In the 1980s, rice pesticides were identified as causing fish kills in the Sacramento River (due to molinate), taste problems in drinking water (due to thiobencarb), and toxicity to invertebrates in the Colusa Basin Drain and Sacramento River (due to carbofuran, methyl parathion, and malathion). Central Valley RWQCB and CDPR established performance goals for these five pesticides in 1990. The subse-

quent management practice of holding water on the rice fields after pesticide application allowed time for degradation and resulted in significant decreases in pesticide concentrations in adjoining surface waters (Cooke and Connor 1998). Additional increases in mandated holding times made little difference in surface water concentrations of molinate, thiobencarb, and carbofuran. From 1990 through 1993, pesticide concentrations and loads in the Sacramento River at Sacramento were best explained by the acreage of emergency releases of rice field water, rather than mandated holding times (Crepeau and Kuivila 2000). Early releases of only 1% to 6% of the fields (up to 10,000 hectares) treated with molinate appeared to be minimizing the benefit of the mandated holding times. Since the majority of rice pesticides are applied by air, aerial drift was originally a problem. By the mid–1990s, management practices such as buffer zones, nozzle specifications and wind speed limits were instituted to control pesticide drift.

Molinate concentrations exceeded the performance goal in Colusa Basin Drain for several weeks to months in almost every year from 1990–1997 and less frequently in Butte Slough. During this time, molinate was detected throughout the Delta (Kuivila and Moon 2004; Orlando and Kuivila 2006) and at Mallard Island (Kuivila and Jennings 2007). More recently, concentrations of molinate continued to exceed the performance goals in several drains in 2002–2003, although less frequently (Orlando and Kuivila 2004). Storm-event emergency discharges continued to contribute to peak concentrations of molinate, such as in 2002. The use of molinate has being cancelled by USEPA with no more sales or distributions after June 30, 2008.

Similarly, thiobencarb concentrations were elevated throughout the 1990s and often exceeded the performance goals, even through 2002 (Crepeau and Kuivila 2000; Kuivila and Moon 2004; Orlando and Kuivila 2006). A combination of increasing thiobencarb use through 2002 and uncontrolled seepage from rice fields was the likely cause of these levels. Since then, requirements were instituted for growers to compact levees and for county agricultural commissioners to conduct seepage inspections. These regulations plus a trend of decreasing thiobencarb use has resulted in much lower concentrations (Central Valley RWQCB 2007). Carbofuran was typically detected with molinate and thiobencarb but at lower concentrations. Its use on rice was banned in 2000 by the USEPA.

Summer Detection of Other Pesticides

A variety of pesticides is applied in the summer on truck crops (e.g. tomatoes and vegetables) and transported off-target via tailwater return (Table 2). Several studies detected elevated concentrations of pesticides from June to August in the San Joaquin River and within the Delta. The duration of these elevated pesticide concentrations typically ranged from weeks to months.

Two herbicides, eptam and metolachlor, are typically applied in April through June and were detected in the San Joaquin River and within the Delta in the summer (MacCoy and others 1995; Panshin and others 1998; Kuivila and others 1999; Domagalski and Munday 2003; Kuivila and Moon 2004; Starner and others 2005; Orlando and Kuivila 2006). Eptam is a thiocarbamate herbicide used on alfalfa, corn, and safflower. Concentrations of eptam within the Delta tend to be "spikey" and localized with the highest measured values typically detected in the central Delta (Kuivila and Moon 2004; Orlando and Kuivila 2006). In contrast, the concentrations of metolachlor, a chloroacetanilide herbicide, were generally highest in the southern Delta (MacCoy and others 1995; Orlando and Kuivila 2006). In 1992–1994, the duration of elevated concentrations of both herbicides in the San Joaquin River ranged from two to three months (MacCoy and others 1995). Other herbicides detected in the summer in the San Joaquin River included alachlor, azinphos-methyl, butylate, dimethoate, diuron, fonofos, propargite, and simazine (Panshin and others 1998; Domagalski and Munday 2003; Starner and others 2005).

Three organophosphate insecticides are also applied during the late spring and summer. Diazinon and malathion are applied to walnuts while chlorpyrifos is applied to both almonds and walnuts. Diazinon and chlorpyrifos were detected frequently but at low concentrations in the San Joaquin River and its tributaries (Panshin and others 1998; Domagalski and

Munday 2003; Starner and others 2005). In weekly sampling of 12 sites from April to August in 2001, only 25% of all samples had diazinon concentrations greater than 20 ng L^{-1} and chlorpyrifos concentrations greater than 30 ng L^{-1} (Domagalski and Munday 2003). In July 1993, toxicity at Paradise Cut was attributed to chlorpyrifos, and in September 1994, toxicity in a Delta eastside slough (French Camp Slough; Figure 2) was attributed to chlorpyrifos and malathion (Werner and others 2000). The infrequent detection of malathion (MacCoy and others 1995; Panshin and others 1998; Starner and others 2005) can be attributed to its rapid degradation in surface waters.

A monitoring study of the San Joaquin River and it tributaries included analysis for dicofol (Domagalski 1996). To the best of my knowledge, these are the only measurements of dicofol in surface waters of the Central Valley. Elevated concentrations were detected for two to three months at all sites with the peak in late June and early July. The highest concentrations were measured in a San Joaquin River westside creek (Orestimba Creek) at 2,500 ng L^{-1}. Although these concentrations are one to two orders of magnitude below acute toxicity levels, dicofol has been implicated as a potential endocrine disruptor (Colborn and Clement 1992).

Insecticides in Urban Creeks

Urban creeks have a different pattern of pesticide occurrence and toxicity compared to agricultural sites (Table 2). Toxicity has been found in urban creeks almost all year round and typically attributed to diazinon and chlorpyrifos (Bailey and others 2000; Werner and others 2000). Urban use of these two pesticides has been as dormant sprays on fruit trees, landscape applications, and structural pest control for termites and ants.

Pesticides were analyzed in an urban creek in Sacramento (Arcade Creek) from December 1996 through April 1998 (Domagalski 2000). Two insecticides, diazinon and carbaryl, were detected in every sample, while chlorpyrifos and malathion were detected in 53% to 73% of the samples. All of the diazinon concentrations exceeded California Department of Fish and Game (CDFG) acute Water Quality Criteria for diazinon of 80 ng L^{-1} (Domagalski 2000). Monitoring in Sacramento and Stockton urban streams, primarily during runoff events (Bailey and others 2000), found that 74% of the water samples (out of 231 samples) exceeded CDFG acute Water Quality Criteria for diazinon and 80% (out of 90 samples) exceeded the criteria for chlorpyrifos (20 ng L^{-1}). Bioassays with Ceriodaphnia dubia resulted in total mortality within 72 hours in 77% of the tested samples (out of 47 samples), and TIEs confirmed that toxicity was due diazinon and chlorpyrifos. In another study (Werner and others 2000), Mosher Slough was sampled monthly from December 1994 through June 1995 and tested toxic to *C. dubia* four times with diazinon and chlorpyrifos accounting for the observed toxicity.

Under an agreement between the USEPA and registrants, residential use of diazinon was phased out with all retail sales ending by December 31, 2004 (USEPA 2004). Analyses of Bay area creeks during 2004–2005 documents fewer detections and lower concentrations of diazinon compared to the 1990s as the residential use was phased out (Ruby 2005). The majority of creek samples analyzed did not contain detectable diazinon with only one sample containing concentrations greater than the Bay Area urban creek TMDL target (100 ng L^{-1}). Correspondingly, fewer samples tested acutely toxic to *C. dubia* in the more recent study compared to the 1990s (Ruby 2005).

SEDIMENT-ASSOCIATED PESTICIDES

Until recently there have been relatively little data on current-use pesticides associated with sediments in the San Francisco Bay watershed. Traditionally, sediment studies were focused on the more hydrophobic, organochlorine pesticides; however, even moderately hydrophilic pesticides are partially sorbed onto soils. These soils are transported into surface waters during rainfall runoff events and carry their associated pesticides along with them.

Suspended Sediments

Current-use pesticides have been detected on suspended sediments in the San Francisco Bay watershed

at concentrations higher than predicted from equilibrium partitioning (Domagalski and Kuivila 1993; Bergamaschi and others 1999; Bergamaschi and others 2001; Smalling and others 2005; Smalling and others 2007). Diazinon and chlorpyrifos were detected on suspended sediments in Suisun Bay as early as 1991 (Domagalski and Kuivila 1993). Suspended sediments collected at San Joaquin River at Vernalis in 1992 contained elevated concentrations of chlorpyrifos, DCPA, eptam, oxyfluorfen, and trifluralin (Bergamaschi and others 1999) A similar study was conducted during the first flush of suspended sediments into Suisun Bay at Mallard Island in December 1995 (Bergamaschi and others 2001). Most of the twice-daily samples during the two-week event contained elevated concentrations of chlordane, chlorpyrifos, DCPA, molinate, and oxyfluorfen. A few samples contained elevated concentrations of endosulfan, eptam, pebulate, thiobencarb, and trifluralin. Once again, concentrations of the sediment-associated pesticides were significantly higher than predictions from equilibrium models, suggesting non-equilibrium conditions.

Bifenthrin, a pyrethroid insecticide, was detected during a high-flow event at Mallard Island in 1997 (Hladik and Kuivila 2008). To our knowledge, this is the earliest known detection of a pyrethroid in California surface waters. Although at low concentrations (0.3 to 1.1 µg kg^{-1}, dry weight), bifenthrin was detected in 6 of 30 samples collected during January. The highest bifenthrin concentration co-occurred with the maximum suspended sediment concentration and maximum concentrations of chlorpyrifos, thiobencarb and trifluralin.

A modified analytical method was used to analyze 38 current-use pesticides on suspended sediments in a study of pesticide inputs to Yolo Bypass in 2004 and 2005 (Smalling and others 2005; Smalling and others 2007). Some of the same pesticides were detected as in the previous studies: chlorpyrifos, molinate, oxyfluorfen, thiobencarb, and trifluralin. In addition, two pyrethroid insecticides were detected: bifenthrin and tau-fluvalinate.

Bed Sediments

Current-use pesticides have also been detected on bed sediments but typically at lower concentrations than suspended sediments. In a study of the San Joaquin River and its tributaries (Pereira and others 1996), chlorpyrifos, DCPA, and dicofol were detected. More pesticides were detected in a study of bed sediments at six input sites to Yolo Bypass (Smalling and others 2005; Smalling and others 2007), including carbaryl, chlorpyrifos, DCPA, metolachlor, molinate, napropamide, oxyfluorfen, thiobencarb, and trifluralin.

More recently, a series of studies has focused on pyrethroid insecticides on bed sediments and corresponding sediment toxicity to the amphipod *Hyalella azteca* (Weston and others 2004; Weston and others 2005). In bed sediments of agricultural creeks in the San Francisco Bay watershed, bifenthrin, esfenvalerate, lambda-cyhalothrin, and permethrin were detected with maximum concentrations of 21, 30, 2.6, and 55.4 µg kg^{-1} dry weight, respectively (Weston and others 2004). Some of these samples caused significant mortality to either *Hyalella azteca* or *Chironomus tetans* in ten-day sediment toxicity tests. A study of a small, westside creek (Del Puerto Creek) in the San Joaquin River watershed detected bifenthrin in bed sediments at 24 µg kg^{-1} dry weight (Bacey and others 2005). Pyrethroid concentrations were much higher in bed sediments in urban creeks near Roseville (Weston and others 2005), where bifenthrin, cyfluthrin, cypermethrin, and permethrin were detected at maximum concentrations of 437, 169, 736, and 335 µg kg^{-1} dry weight, respectively. Deltamethrin, esfenvalerate, and lambda-cyhalothrin were also detected but at much lower concentrations. Sediment toxicity to *H. azteca* observed in the majority of these samples and in sediment samples from various urban creeks in Sacramento and East Bay was attributed primarily to bifenthrin (Weston and others 2005; Amweg and others 2006).

DATA GAPS AND UNCERTAINTIES

Despite a thorough knowledge of the occurrence and transport of some pesticides in certain use-settings (e.g. organophosphate insecticides used as dormant

sprays), there are still important data gaps. Many pesticides are not being monitored and very few degradation products are analyzed. In addition, pesticide use is continually changing and monitoring studies are slow to add new analytes. Geographically, little is known about the spatial and temporal distributions of pesticides in the Delta, especially in delta smelt spawning and nursery habitats. Data for sediment-associated pyrethroids are limited to recent studies done in agricultural drains or small streams (Werner and Oram 2008) and information on occurrence and transport of other current-use pesticides on sediments is also scarce. This knowledge is crucial for understanding how water management changes can affect pesticide transport, fate and effects in the San Francisco Estuary watershed.

Monitoring studies analyze fewer than half of the pesticides applied in the watershed (Table 1). Analytical laboratories generally take one of two approaches for developing methods: (1) a small number of the same pesticide type are analyzed by each individual method (e.g. organophosphate, carbamate, or pyrethroid insecticides), or (2) a single, multi-residue method is developed with large suites of pesticides from different classes but limited to analytes that respond similarly. Either way, compounds requiring different extraction, cleanup or analysis techniques are not included in these methods. Sometimes analytical lists are driven by high use throughout the U.S. with the result that pesticides used almost entirely in California are overlooked (e.g. methidathion). In other cases, a lack of information about fate or toxicity results in an absence of a driving factor to develop analytical methods. For example, fungicides have always been under-represented in monitoring studies; only 2 of the 33 fungicides applied in the San Francisco Estuary watershed have been analyzed (Table 1). Similarly, only a few pesticide degradates are routinely monitored, usually when the metabolite is pesticidally active (e.g. diazinon oxon). But other degradates may be of concern. Although propanil has been the highest-use herbicide on rice in the Sacramento Valley since 2000 (CDPR 2008) and it degrades readily to 3,4-dichloroaniline (Santos and others 1998), it is not routinely monitored. During the reregistration of propanil, additional information on the toxicity and fate of this major degradate was requested (USEPA 2006).

Pesticide use is not static—it changes with time. Pesticide use changes over time as older pesticides are withdrawn, new pesticides or new uses for pesticides are registered, and new pests become a problem. Over the past decade, a major change has been the switch from organophosphate insecticides to pyrethroid insecticides for both agricultural and home use (CDPR 2008; TDC Environmental 2005; TDC Environmental 2008a). In response, analytical methods were developed, toxicity testing was done in the laboratory, and these compounds were added to a number of monitoring studies. But the majority of analytical methods are not sensitive enough to measure pyrethroids at concentrations below their toxicity levels (Werner and Oram 2008). Other substitutes for the organophosphate insecticides are fipronil and imidicloprid; these have not been added to very many monitoring programs. Other changes in pesticide use are occurring but receiving less attention. The older fungicides (chlorothalonil and ziram) have decreased in use while newer fungicides (strobilurins and conazoles) have increased. On rice, the use of new herbicides (e.g. bispyric-sodium, cyhalofop-butyl, and clomazone) is expected to continue to rise as molinate is phased out. Although changes in registered use can be readily tracked through the CDPR PUR, changes in residential use can be much more difficult to recognize. As part of the Urban Pesticide Pollution Prevention (UP3) Project, a series of annual reports are published which analyze urban pesticide use patterns, with an emphasis on insecticides and related toxicity (TDC Environmental 2008a). Monitoring programs need to be aware of changing use patterns and utilize smaller-scale, focused sampling to identify when new analytes need to be added to analysis lists. Although some of our current knowledge is transferable to the new pesticides, different properties such as hydrophobicity and persistence can result in major differences in pesticide fate. Modes of action and environmental toxicity can also vary widely between pesticides.

Most of our knowledge is about inputs of dissolved pesticides in the upper watershed. The majority of monitoring sites are on small creeks with unidirectional

flows and well-defined banks. In contrast, the Delta consists of many interconnected sloughs and channels with flows complicated by tides, barriers, and water diversions. Sources of pesticides are multiple external rivers and internal agricultural and urban discharges. A significant effort would be required to sample sufficiently in time and space to characterize pesticide distributions in the Delta. The sampling that has been done highlights the importance of within-Delta inputs and the patchy nature of elevated concentrations, especially in back sloughs. In urban creeks, the focus has been on insecticides and little is known about herbicides and fungicides in these environments. Current-use pesticides have also been detected on suspended and bed sediments throughout the watershed but limited data make it difficult to detect occurrence patterns. As a result, our understanding of the transport, persistence, and fate of sediment-associated, current-use pesticides is incomplete (and much less than for the dissolved phase).

Currently, there is not a comprehensive long-term monitoring program which measures current-use pesticides. Our understanding of the occurrence and transport of current-use pesticides in the San Francisco Estuary watershed is primarily based on 10 to 15 year old monitoring data. Often reactive, pesticide monitoring should strive to be proactive (TDC Environmental 2008b). Analytical methods should include large numbers of pesticides and degradates and need to be constantly modified to include new or changing pesticides. A variety of environmental compartments should be analyzed, including surface water, suspended and bed sediments, rainfall, and biological tissue when appropriate. A well-designed sampling program with sufficient temporal and spatial coverage is critical for understanding complex environments, such as the Delta. The recent UP3 project report (TDC Environmental 2008b) states that "pesticide monitoring program planning is often short term and sometimes ad-hoc." A long-term, comprehensive monitoring program is critical to understand the input and transport of pesticides and assess the resulting impacts on the ecosystem.

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