Herbicide Concentrations in the Sacramento-San Joaquin Delta, California

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ABSTRACT

The Sacramento-San Joaquin Delta watershed in California encompasses agricultural areas that receive intense applications of various herbicides, including some designed to inhibit photosynthesis. This study is to determine whether herbicides impair phytoplankton primary productivity in the Sacramento-San Joaquin Delta. The sampling strategy contrasted conditions in May-June, a time of expected high herbicide concentrations, with conditions in October-November, a time of expected low herbicide concentrations. Water samples from May through November 1997 were analyzed for herbicide concentrations and phytoplankton primary production rates. Thirteen herbicides were detected in one or more water samples. Herbicide concentrations varied considerably spatially and temporally. Diuron, metolachlor, and diethatyl-ethyl had the highest concentrations in the study. Two sites, Paradise Cut at Paradise Road and French Camp Slough at McKinley Road, had the most frequent detections and highest concentrations of herbicides.

The highest concentrations of molinate and thiobencarb were detected at the site receiving input from the Sacramento River watershed, following application of these herbicides on rice in May. The highest use of EPTC is in the San Joaquin River watershed and the highest concentrations were detected at the site representing this watershed. In contrast, the source of the other herbicides could not be attributed to a single watershed. Diuron and metolachlor had widespread detections that can be explained by their relatively high use in all the watersheds, whereas diethatyl-ethyl primarily was detected at the one site near the highest application in the Delta. The distributions of 2,4-D and hexazinone were more complex, and the amounts and timing of application do not readily explain the pattern of occurrence.

The results of this part of the study illustrate the complexity of herbicide concentrations in the Sacramento-San Joaquin Delta. In particular, the occurrence of diuron and hexazinone needs to be studied in more detail to determine their influence on primary production and phytoplankton species composition.

INTRODUCTION

The Sacramento-San Joaquin Delta (Delta) is a complex system of tidally-influenced, interconnected sloughs and channels (Oltmann, 1994). The hydrologic complexity is increased further by freshwater inputs to the Delta from several rivers and various sloughs. One-half million pounds of over 30 different herbicides are applied annually on agricultural lands in the Delta, and an additional 5 million pounds are applied upstream in three other watersheds: the Sacramento River, San Joaquin River, and French Camp Slough (fig. 1) (California Department of Pesticide Regulation, 1996). Herbicides enter the Delta waters from these external (upstream) and from local (Delta) inputs.

Herbicides have different modes of action (table 1). Some herbicides are designed to kill plants by inhibiting photosynthesis and can directly affect phytoplankton primary productivity; these are atrazine, cyanazine, diuron, hexazinone, simazine, and thiobencarb. Although little is known about the concentrations and residence times of these herbicides in the Delta, field studies have detected atrazine, simazine, and thiobencarb during the spring and summer (cyanazine, diuron, and hexazinone were not measured) (K.M. Kuivila, U.S. Geological Survey, unpublished data, 1996).

This study was designed specifically to determine whether herbicides impair phytoplankton primary productivity in the Delta. This report presents the herbicide concentrations measured in the Sacramento-San Joaquin Delta and their possible sources. Potential effects of herbicides on phytoplankton primary production

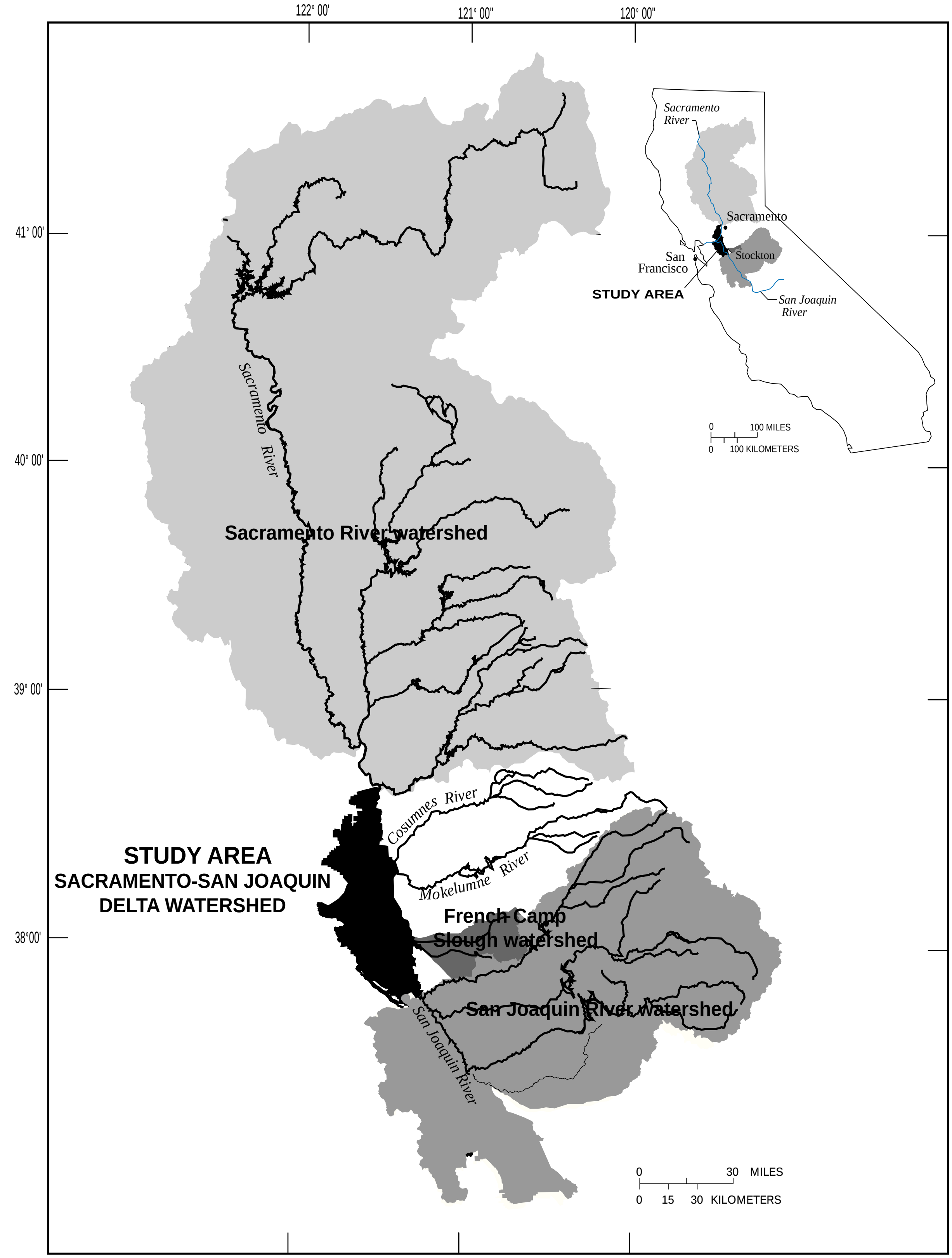

Figure 1. Location of the study area and the three adjoining watersheds, Sacramento-San Joaquin Delta, California.

Table 1. List of herbicides analyzed, mode of action, analytical method, method detection limit, and accuracy expressed as recovery from spiked water samples (in percent)

[Values in nanogram per liter; na, not available; HPLC, high-performance liquid-chromatography; GC/MS, gas-chromatography/mass spectrometry]

Herbicides	Mode of action	Method of analysis	Method detection limit	Recovery (percent)
2,4-D	Inhibits growth	HPLC	111	106
Atrazine	Inhibits photosynthesis	GC/MS	11	74
Cyanazine[1]	Inhibits photosynthesis	GC/MS	50	87
Dacthal	Inhibits germination	GC/MS	5	87
Diethatyl-ethyl	na	GC/MS	5	76
Diuron	Inhibits photosynthesis	HPLC	134	120
EPTC	Inhibits growth	GC/MS	25	72
Hexazinone	Inhibits photosynthesis	HPLC	45	71
MCPA	Inhibits growth	HPLC	28	103
Metolachlor	Inhibits germination	GC/MS	4	71
Molinate	Inhibits germination	GC/MS	24	113
Simazine	Inhibits photosynthesis	GC/MS	10	81
Thiobencarb	Inhibits photosynthesis	GC/MS	8	66

[1]Method detection limit and recovery data from Crepeau and others (1994).

are summarized by Edmunds and others (1999). This study is part of a larger project by the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program that is studying the fate and transport of pesticides in San Francisco Bay. Additional funding was received from the Interagency Ecological Program for the Sacramento-San Joaquin Estuary. The authors wish to acknowledge the efforts of Brian Cole and Richard Millette for assistance in sampling, and Lucian Baker III, Kathryn Crepeau, and Keith Starner for the herbicide analyses.

SAMPLING DESIGN

The difficulties of tracking water flow, let alone contaminants, led to sampling at times and locations of expected high concentrations of herbicides and contrasting them with times and locations of expected low concentrations. There was no intent to calculate herbicide loads or track herbicides through the waterways of the Delta.

Nine sites (fig. 2) were sampled during five periods in 1997: May 27-29, June 10-12, June 24-26, October 14-16, and November 11-13. Results from past sampling suggested that herbicide concentrations would be the highest in late spring/early summer and the lowest in the fall. The nine sampling sites were chosen to represent a range of inputs and flow conditions. French Camp Slough at McKinley Road (French Camp Slough) and San Joaquin River at Vernalis (Vernalis) are sites that characterize external inputs from the French Camp Slough and San Joaquin River watersheds, respectively (figs. 1 and 2). Sutter Slough at Courtland (Sutter Slough) is a site that, although not on the mainstem of the Sacramento River, is primarily Sacramento River water (Rick Oltmann, U.S. Geological Survey, oral commun., 1996). The Sacramento River watershed (fig. 1) is the source of herbicides detected at the Sutter Slough site, but the integrated load from the Sacramento River watershed is divided among Sutter Slough, Steamboat Slough, and the mainstem Sacramento River. The site at Mokelumne River at New Hope Bridge (Mokelumne River) was chosen as a control site because previous samplings have detected few, if any, herbicides. The Old River at Bacon Island (Old River) and Middle River at Bacon Island (Middle River) sampling sites are on the two major flow paths of Sacramento River water through the Delta to the pumping plants (Oltmann, 1994) and represent a mixture of external and local Delta inputs. Beaver Slough at Blossom Road (Beaver Slough) primarily receives local input. Paradise Cut at Paradise Road (Paradise Cut) and Werner Slough at Orwood Road (Werner Slough) are dead-end sloughs that generally have less flushing and longer residence times than the other sites, and they represent local inputs.

In addition, the site at Middle River was sampled biweekly from May 28 through November 12. The purpose of this more frequent sampling was to measure the changes in herbicide concentrations

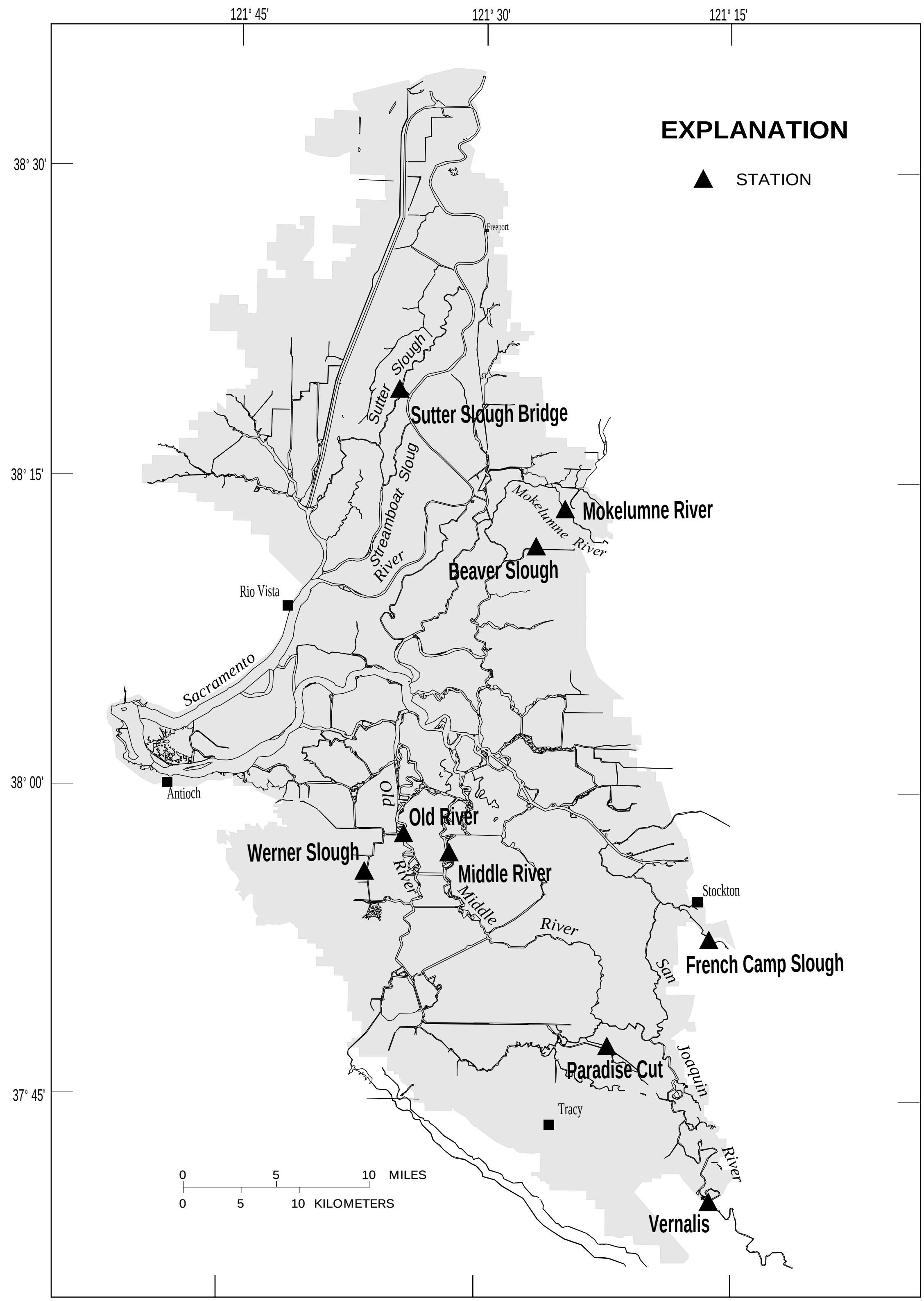

Figure 2. Locations of sampling sites in the study area, Sacramento-San Joaquin Delta, California. Table 2 gives full and abbreviated forms of site names.

throughout the entire sampling period and to determine the timing of the highest concentrations. Middle River was chosen as a site representative of the central Delta.

ANALYTICAL METHODS

Water samples were collected 1 meter (m) below the water surface using a 2.5-liter (L) Teflon-lined Niskin[1] bottle deployed horizontally. Water samples (8-10 L) were composited in a stainless-steel milk can and then split into aliquots using a Teflon cone-splitter (Shelton, 1994). Different aliquots were analyzed for herbicide concentrations, phytoplankton biomass, species composition, phytoplankton primary-production rates, and basic water-quality constituents. Two 1-L aliquots for herbicide analyses were filtered and analyzed by gas chromatography/mass spectrometry (GC/MS) with ion-trap detection and by high-performance liquid chromatography (HPLC) with photodiode-array detection at the organic-chemistry laboratory at the California District Office of the USGS.

For analysis by GC/MS, the filtered water sample was extracted onto a C-8 solid-phase extraction (SPE) cartridge. Complete details of the method, analysis, and quality assurance are given in Crepeau and others (1994). New method detection limits and recoveries from spiked water samples were determined in November 1995 using the same method as in Crepeau and others (1994) (table 1), except that eluates were concentrated to 100 microliters (μL), rather than to 200 μL. For analysis by HPLC, the filtered water sample was extracted onto a Carbopak-B SPE cartridge. More details of this method, analysis, and quality assurance are given in Werner and others (1996). One method change was the use of a longer HPLC gradient than listed in Werner and others (1996) to enable the separation of additional herbicides. Method detection limits and recoveries from spiked water samples are given in table 1.

[1]The use of trade names in this report is for identification purposes only and does not constitute endorsement by the USGS.

RESULTS AND DISCUSSION

Thirteen herbicides were detected in one or more water samples. Concentrations varied considerably by site and with time (table 2). Three herbicides (diuron, hexazinone, and thiobencarb) that inhibit photosynthesis and five herbicides (2,4-D, diethatyl-ethyl, EPTC, metolachlor, and molinate) with different modes of action occurred frequently and at elevated concentrations. The other three herbicides (atrazine, cyanazine, and simazine) that inhibit photosynthesis and two other herbicides (dacthal and MCPA) occurred less frequently or at much lower concentrations and will not be discussed in this report.

Reported herbicide application in each watershed—Sacramento River, San Joaquin River, French Camp Slough, and the Delta—is listed in table 3. The application data is primarily agricultural use, most of the urban use is not included. Data from 1997 were not available at this time so data from 1995 were used as an approximation; application amounts may vary from year to year but are not expected to change radically. The areas of these four watersheds vary by two orders of magnitude so the applied amounts must be evaluated in relation to the scale of each watershed.

Molinate and Thiobencarb

Elevated concentrations of molinate and thiobencarb progressed over time from Sutter Slough through the Delta (fig. 3; table 2). The highest concentrations of molinate and thiobencarb were measured at Sutter Slough on May 29, 861 nanograms per liter (ng/L) and 313 ng/L, respectively. In subsequent samples, the concentrations of these herbicides were considerably lower. The molinate concentrations at Werner Slough, and Old and Middle Rivers peaked on June 25 at levels of 160, 267, and 290 ng/L, respectively. Concentrations of thiobencarb followed a similar pattern, but at much lower levels. The biweekly sampling at Middle River confirmed that the concentrations of molinate and thiobencarb decreased after June 25. The highest concentration of molinate (152 ng/L) at French Camp Slough was measured on May 27.

Table 2. Total agricultural herbicide application in 1995 in each watershed: Sacramento River, San Joaquin River, French Camp Slough, and Sacramento-San Joaquin Delta, California. (California Department of Pesticide Regulation, 1996)

[lbs. a.i., pounds per active ingredient. Shaded values indicate highest application of the 13 herbicides in watershed shown. Figure 1 shows watershed locations]

Herbicides	Sacramento River (1,000 lbs. a.i.)	San Joaquin River (1,000 lbs. a.i.)	French Camp Slough (1,000 lbs. a.i.)	Sacramento-San Joaquin Delta (1,000 lbs. a.i.)
2,4-D	200	60	21	61
Atrazine	6	0	<1	7
Cyanazine	13	56	1.7	6
Dacthal	<1	<1	1.5	<1
Diethatyl-ethyl	1	<1	<1	2
Diuron	35	33	11	35
EPTC	68	78	17	55
Hexazinone	16	20	3	6
MCPA	172	19	7	11
Metolachlor	58	25	11	29
Molinate	1,400	20	9	1
Simazine	36	48	15	13
Thiobencarb	570	5	4	<1
Total watershed acres, in thousands	17,161	4,683	258	679

The concentrations of molinate and thiobencarb were much lower at all the other sites. These herbicides are applied only to rice in the Sacramento River watershed in April through June (table 3). A much smaller quantity (two orders of magnitude) of the two herbicides are applied to rice in the French Camp Slough watershed (table 3). Sutter Slough receives drainage from rice fields in the Sacramento River watershed via the Sacramento River; rice-field water typically is released at the end of May.

EPTC

The highest concentrations of EPTC were detected at Vernalis on October 14 (387 ng/L) and June 24 (222 ng/L). Elevated concentrations also were measured on June 24 at French Camp Slough

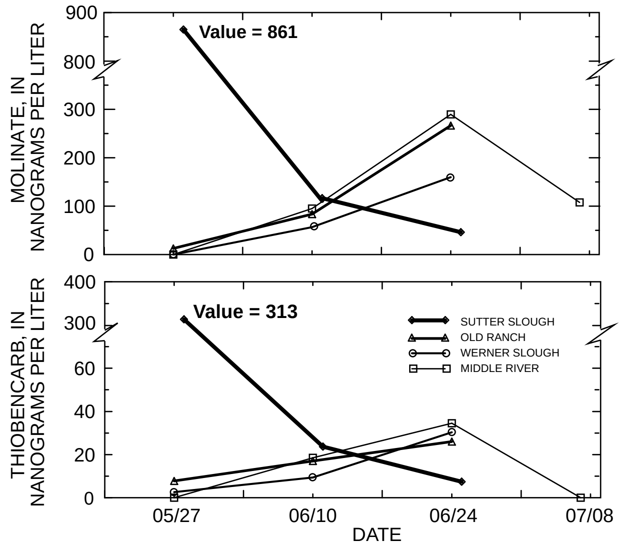

Figure 3. Concentrations of molinate and thiobencarb at the sampling sites Sutter Slough, Old River, Werner Slough, and Middle River detected biweekly between May 27-July 8, 1997, Sacramento-San Joaquin Delta, California. Table 2 gives full and abbreviated forms of site names.

(101 ng/L) and Paradise Cut (110 ng/L). EPTC was not detected above the method detection limit at any of the other sites. This is in agreement with previous studies where elevated concentrations of EPTC were detected at Vernalis in the summer but were not detected at the Sacramento River at Sacramento (MacCoy and others, 1995; Panshin and others, 1998). In the San Joaquin River watershed, EPTC had the highest use of the 13 herbicides detected [78 thousand pounds (table 3)]. In the French Camp Slough and Sacramento-San Joaquin Delta watersheds, EPTC is the second most commonly used herbicide and is used near Paradise Cut.

Diuron, Metolachlor, and Diethatyl-ethyl

The highest concentrations of diuron and metolachlor were detected at Paradise Cut and French Camp Slough. In comparison, diethatyl-ethyl also had the highest concentrations at Paradise Cut, but was not detected at French Camp Slough in all the samples.

The highest concentration of diuron (2,141 ng/L) was measured at French Camp Slough on November 11, the day following rainfall. The next highest concentration (1,012 ng/L) of diuron was measured at Paradise Cut on May 27. At both French Camp Slough and Paradise Cut, concentrations of diuron were above the detection limit in all the samples (table 2). Concentrations of diuron above the method detection limit also were measured at Vernalis, Old River, Middle River, and Werner Slough. Other studies (California Regional Water Quality Control Board, 1995; Panshin and others, 1998) have detected high concentrations of diuron in the Sacramento and San Joaquin River watersheds in the winter following application and rainfall. Diuron is applied primarily on rights-of-way in the winter. In the Delta, diuron also is applied on alfalfa and asparagus in December-March near Paradise Cut.

The highest concentrations of metolachlor were measured at Paradise Cut; 916 ng/L on May 27, 1,019 ng/L on June 10, and 1,107 ng/L on June 24 (table 2). The site with the next highest concentrations was French Camp Slough (106-502 ng/L). Metolachlor concentrations at Vernalis were less than 100 ng/L and are in agreement with previous studies (MacCoy and others, 1995; Panshin and others, 1998). Detectable concentrations were measured at all other sites except Mokelumne River. Use of metolachlor primarily is on corn and beans during April-June. Within the Delta, metolachlor is applied in the vicinity of Paradise Cut.

Four of the five samples at Paradise Cut contained detectable concentrations of diethatyl-ethyl; the highest concentration was on October 14 (1,041 ng/L). The only other site with concentrations above the method detection limit was Old River on October 15 (65 ng/L). The use of diethatyl-ethyl is low in all the watersheds and within the Delta (table 3), but diethatyl-ethyl is applied directly to sugar beets adjacent to Paradise Cut. The application is in May but the highest concentration was detected in October.

The variable spatial distribution of diuron and metolachlor could be the result of the relatively high use in all the watersheds. But, for diuron, the timing of detection is not easily explained from the timing of application. In contrast, metolachlor was detected shortly after application. Diethatyl-ethyl was detected almost entirely at the site closest to application in the Delta, Paradise Cut; however, the timing of detection (October) was much different than application (May).

2,4-D and Hexazinone

The distribution of both 2,4-D and hexazinone varied considerably temporally and spatially. The highest concentrations of 2,4-D were measured during November 11-12 at French Camp Slough (495 ng/L) and at three sites receiving local inputs: Werner Slough (840 ng/L), Paradise Cut (356 ng/L), and Old River (190 ng/L). The next highest concentrations were measured on June 24-25 at the same three local-input sites but not at French Camp Slough. Only limited measurements of 2,4-D have been reported in previous studies; concentrations at Vernalis were not detected in samples from March to December 1993 (Panshin and others, 1998). The herbicide 2,4-D is commonly used in all the watersheds and is applied to a variety of crops several different times of the year. Applications are in February on wheat, almonds, and barley, and in May-July on corn and asparagus. In the Sacramento Valley, the predominant use of 2,4-D is on rice, but the application is in June and July, after the release of the rice field water.

The pattern of hexazinone concentrations is even more complex. High concentrations were measured during three different times in different areas of the Delta. During May 27-29, the highest concentrations were detected at Paradise Cut (669 ng/L), French Camp Slough (275 ng/L), and Sutter Slough (217 ng/L). At Middle River, the site sampled biweekly, hexazinone concentrations were elevated from June-September (fig. 4) with the maximum concentration on August 5 (342 ng/L). Finally, on October 16, the highest concentration was measured at Beaver Slough (305 ng/L). The use

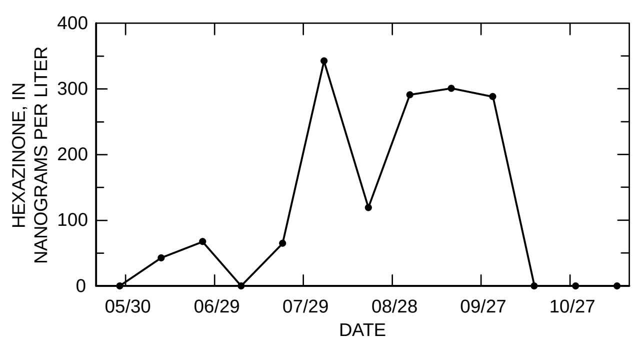

Figure 4. Concentrations of hexazinone at Middle River at Bacon Island, May 27-November 11, 1997, Sacramento-San Joaquin Delta, California. Table 2 gives full and abbreviated forms of site name.

of hexazinone is relatively low in all four watersheds, with applications in October-February on alfalfa and forests. The pulse of hexazinone observed at Middle River cannot be explained with this data set or application patterns.

Both 2,4-D and hexazinone had complex patterns of concentration. There are few previous measurements of 2,4-D in the Delta and adjoining watersheds, and no other reported measurements of hexazinone. The limited data in this study and other studies make it difficult to determine the sources and transport of these herbicides.

CONCLUSIONS AND POSSIBLE EFFECTS ON PHYTOPLANKTON

The measured concentrations of 13 herbicides in the Sacramento-San Joaquin Delta varied considerably temporally and spatially. The most frequent detections and some of the highest concentrations were measured in May and June. Some samples in November also had unexpectedly high concentrations; this could be due to rainfall near the time of our sampling. Paradise Cut and French Camp Slough were the sites with the most frequent detections and highest concentrations. For some herbicides, elevated concentrations could be attributed to one of the watersheds as a source. Molinate and thiobencarb could be attributed to use on rice in the Sacramento River watershed; elevated concentrations were detected at Sutter Slough in late May, and then at central Delta sites in late June. The primary source of EPTC was the San Joaquin River watershed in the summer, with the highest concentrations detected at Vernalis. In contrast, explaining the distribution of other herbicides was not so simple. Diuron concentrations were highest at Paradise Cut and French Camp Slough, but diuron was detected at a variety of sites at different times. The ubiquitous nature of diuron applications on rights-of-way could explain the widespread detection. Metolachlor was measured at concentrations above the method detection limit at all sites except Mokelumne River, and the highest concentrations occurred shortly after application. Diethatyl-ethyl was detected at the site closest to its Delta application (Paradise Cut), but the timing of detection cannot be explained by the timing of application. The pattern of 2,4-D and hexazinone concentrations was complex, and cannot readily be explained by times or locations of application.

In the 53 samples collected for this study, Edmunds and others (1999) found little correlation between the concentrations of the six herbicides that inhibit photosynthesis and the maximum rate of phytoplankton primary production (Pmax). But the one sample with the highest diuron concentration (2,141 ng/L at French Camp Slough on November 11) had the lowest Pmax (0.9 milligrams carbon per milligram chlorophyll per hour). Edmunds and others (1999) concluded that there is no indication of system level impairment of primary production in the Delta, but caution that there are localized events when production is impaired.

Of the six herbicides that inhibit photosynthesis, diuron and hexazinone had the highest concentrations and most frequent detections and therefore, are the herbicides most likely to impair primary production in localized events. More sampling is needed to understand the source(s) of these two herbicides and to predict the location and timing of the highest concentrations in the Delta. Species composition also was measured in this study; this data will be analyzed to assess any effect of herbicide concentration on the phytoplankton community structure.

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