WATER RESOURCES BULLETIN
VOL. 32, NO. 5 AMERICAN WATER RESOURCES ASSOCIATION OCTOBER 1996

PESTICIDES AND PESTICIDE DEGRADATION PRODUCTS IN STORMWATER RUNOFF: SACRAMENTO RIVER BASIN, CALIFORNIA[1]

Joseph Domagalski[2]

ABSTRACT: Pesticides in stormwater runoff, within the Sacramento River Basin, California, were assessed during a storm that occurred in January 1994. Two organophosphate insecticides (diazinon and methidathion), two carbamate pesticides (molinate and carbofuran), and one triazine herbicide (simazine) were detected. Organophosphate pesticide concentrations increased with the rising stage of the hydrographs; peak concentrations were measured near peak discharge. Diazinon oxon, a toxic degradation product of diazinon, made up approximately 1 to 3 percent of the diazinon load. The Feather River was the principal source of organophosphate pesticides to the Sacramento River during this storm. The concentrations of molinate and carbofuran, pesticides applied to rice fields during May and June, were relatively constant during and after the storm. Their presence in surface water was attributed to the flooding and subsequent drainage, as a management practice to degrade rice stubble prior to the next planting. A photodegradation product of molinate, 4-keto molinate, was in all samples where molinate was detected and made up approximately 50 percent of the total molinate load. Simazine, a herbicide used in orchards and to control weeds along the roadways, was detected in the storm runoff, but it was not possible to differentiate the two sources of that pesticide to the Sacramento River.
(KEY TERMS: agricultural hydrology; aquatic toxicology; nonpoint source pollution; drainage; water quality; stormwater management.)

INTRODUCTION

Organophosphate pesticides such as diazinon, methidathion, and chlorpyrifos are used in the Central Valley of California (Figure 1) on orchard crops including almonds, peaches, and prunes. The trees are treated with these pesticides during the dormant spray season from December through February. In 1993, over 45,000 kilograms of diazinon, 36,000 kilograms of methidathion, and 300 kilograms of chlorpyrifos were used during the dormant spray season. The spraying is intended to protect the trees and developing buds from insects that may have invaded the trees during the winter. Most of the spraying occurs in January. Organophosphate pesticides affect and disrupt nerve impulses in the target organisms by acetyl cholinesterase inhibition (Buchel, 1983). Some of these pesticides, such as diazinon at concentrations below 0.5 micrograms per liter, can also be toxic to aquatic organisms,especially zooplankton (Amato *et al.*, 1992). Organophosphate pesticides undergo transformation and/or degradation reactions after application in water or air, including hydrolysis, resulting in less toxic compounds, or conversion to oxon analogues. The oxon analogues are more toxic relative to the parent compounds (Buchel, 1983; Glotfelty *et al.*, 1987) and might result in increased acute toxicity to aquatic organisms if transported to the river systems by runoff or rainfall. However, the oxon analogues are known to undergo faster hydrolysis relative to the parent organophosphate pesticides (Buchel, 1983). Elevated concentrations of the oxon analogues of organophosphate pesticides have been measured in fog samples collected in the Central Valley of California (Glotfelty *et al.*, 1990; Seiber *et al.*, 1993), but to date no direct measurements of the oxon derivatives have been reported for river water of the Central Valley. It is possible that elevated concentrations of the oxon analogues might be transported to the Sacramento River by the rain, resulting in acutely toxic concentrations in the river water. Pesticide transport in rain has been discussed by Majewski and Capel (1995).

Orchards tend to be located on alluvial soils near river channels within the Sacramento Valley of California (Figure 1). The timing, December through

[1]Paper No. 95165 of the *Water Resources Bulletin*. **Discussions are open until April 1, 1997.**
[2]Supervisory Hydrologist, U.S. Geological Survey, 2800 Cottage Way, Sacramento, California 95825.

C—035249

C-035249

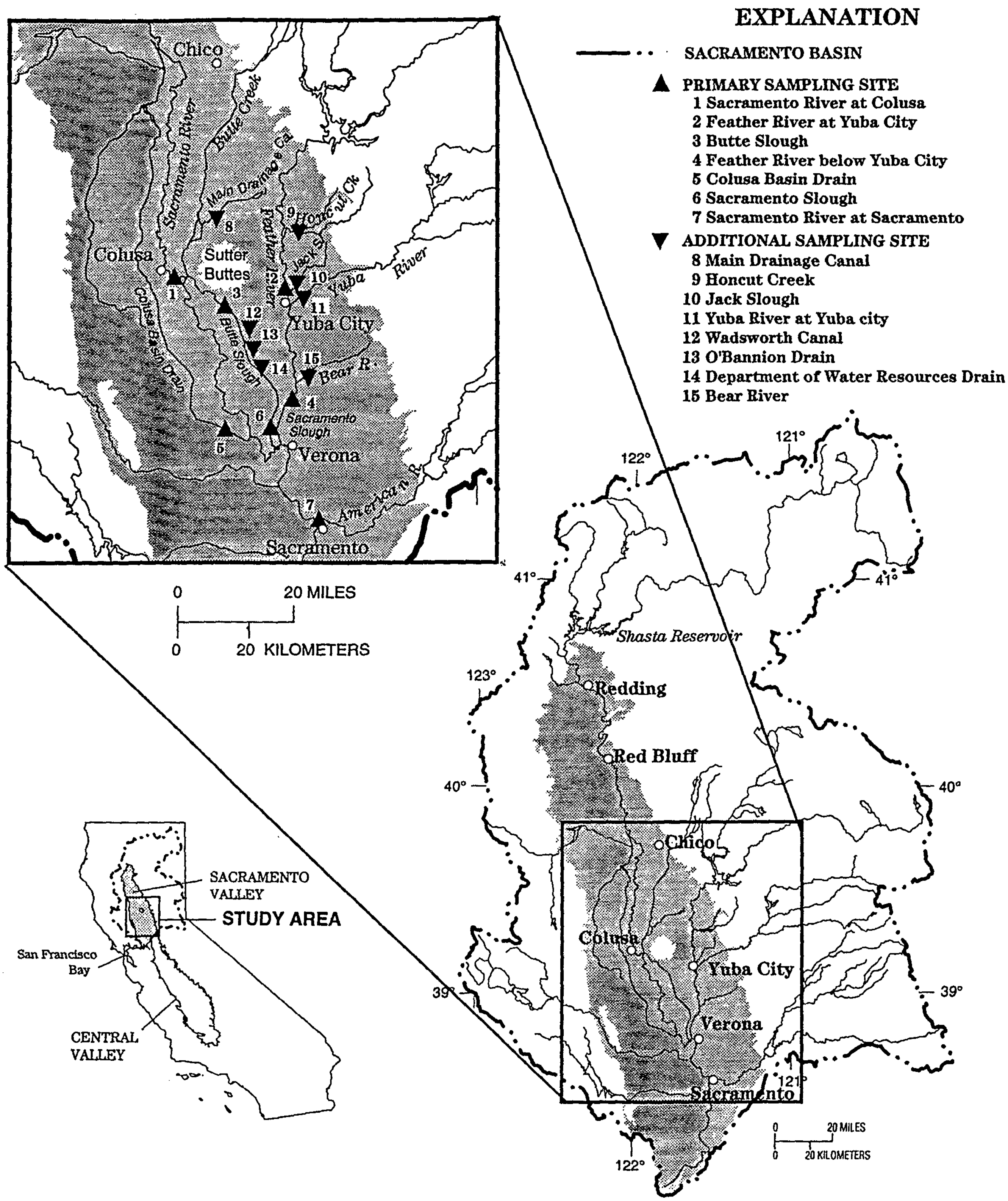

Figure 1. Study Area, Sacramento Basin, California.

C-035250

C-035250

February, of the organophosphate pesticide applications on these orchards coincides with the period when most of the rainfall occurs in this region. As a result of runoff from the orchards following rainfall, the potential exists for the transport of these pesticides to the rivers. It is of critical importance to understand the transport and concentrations of these pesticides in surface waters so that effective control strategies can be implemented. Previous studies on organophosphate pesticide occurrence in California have been restricted to the southern half of the Central Valley, San Francisco Bay, and one downstream site on the Sacramento River (Domagalski, 1995; Domagalski and Kuivila, 1993; Kuivila and Foe, 1995; MacCoy *et al.*, 1995). Accordingly, a study was implemented to determine the principal locations of sources of organophosphate pesticides to the Sacramento River. The study was conducted during January and February of 1994 and had two goals. The first was to measure the concentrations of organophosphate pesticides and other pesticides, not specifically from orchard crops but in the tributaries and in the mainstem of the Sacramento River and, thus, to determine which streams contribute the principal loading to the Sacramento River. The second goal was to measure the ratio of the oxon analogues of organophosphate pesticides and the degradation products of other pesticides to the parent pesticides. The purpose of this paper is to present the results and interpretation of that sampling, to determine the major sources of pesticides to the Sacramento River, and to suggest some suitable locations for future pesticide sampling and monitoring activities.

This study was completed as part of the National Water Quality Assessment (NAWQA) program of the U.S. Geological Survey. The goals of the NAWQA program are to describe the status of, and trends in, the nation's water quality with respect to natural features of the environment and human activities or land use. These goals are described more fully by Hirsch *et al.* (1988). A number of monitoring and research activities are designed to accomplish those goals, including the sampling of surface waters for general water-quality parameters and for specific contaminant groups such as pesticides. The design of the monitoring networks for these samplings is based on land use and basin physiography. Sampling sites are chosen in relatively small drainages with fairly homogeneous land use and physiography and also on larger rivers, which potentially receive contaminants from a variety of sources. The relative importance of various land uses in specific physiographic zones and the input of contaminants to the major rivers are examined. Most of the sampling is temporal, and measurements are taken at pre-planned times. In addition to this temporal sampling, extreme hydrologic events, such as rainfall-induced runoff, are targeted for sampling to determine their importance for contaminant transport.

DESCRIPTION OF STUDY AREA

The size of the Sacramento River Basin is approximately 70,000 square kilometers. The study area includes the Sacramento Valley (Figure 1) and the adjacent forested uplands. The Sacramento Valley is a major agricultural region and also has a growing urban population. Average annual rainfall in the valley ranges from 33 to 66 centimeters (Bertoldi *et al.*, 1991). Most of the rain occurs during the winter months, and agricultural production is dependent on the availability of irrigation water. Water derived from rain or snow is stored in upstream reservoirs for use in the spring and summer. More than 8,000 square kilometers are irrigated. Major crops include rice, fruits and nuts, tomatoes, sugar beets, corn, alfalfa, and wheat. Dairy products also are an important agricultural commodity. The principal water-use and population centers are in the Sacramento Valley, and that part of the study area will be given the highest priority for the Sacramento River Basin studies of the National Water Quality Assessment Program.

The length of the Sacramento River is 525 kilometers. Its average annual runoff is more than 27 thousand million cubic meters, approximately one-third of the total runoff in the state. The Feather and American Rivers are the major tributaries to the Sacramento River, and the Sacramento River is vital to the state's economy. It is a major source of drinking water for residents of northern and southern California, is a principal source of irrigation water for Central Valley farmers, and is the principal source of fresh water to San Francisco Bay. The flows of the Sacramento River are controlled mainly by dams, including those on the upper Sacramento River and to a lesser extent those on the Feather, Yuba, and American Rivers. A part of the runoff from winter rains and spring snowmelt is stored in reservoirs and is released during the normally dry summer months.

SELECTION OF SAMPLING SITES

The primary consideration for selection of sampling sites was proximity to the orchards. Almond, prune, and peach orchards are mainly located in proximity to river channels in order to take advantage of well-drained alluvial soil, or in other locations of well-drained soil. The principal orchard areas are located

C-035251

C-035251

along the Sacramento, Feather, and Yuba Rivers, between the Sacramento and Feather Rivers, near the city of Chico, in a portion of the area served by the Colusa Basin Drain, and in portions of the northern valley, principally between Chico and Red Bluff. Areas that are not suitable for orchard production are planted with other crops, especially rice, or may be used for pasture.

The primary sampling sites were chosen on the mainstem of the Sacramento River (at Colusa, site 1; at Sacramento, site 7), on a major tributary (Feather River, sites 2 and 4), and on sites whose drainage is largely runoff from agricultural land (Butte Slough, site 3; Colusa Basin Drain, site 5; Sacramento Slough, site 6). Site locations are shown in Figure 1.

The Sacramento River site at Colusa provided information on the potential for pesticide transport from the northern part of the valley. Any pesticides detected at that location would have been applied north of the confluence of the Sacramento and Feather Rivers, Colusa Basin Drain, and Sacramento Slough. The Sacramento River site at Sacramento provided additional information on drainage from the Colusa Basin Drain, the Feather River drainage, and the Sacramento Slough as potential sources of pesticides. Sampling both of the sites on the Sacramento River allowed for the differentiation of pesticide inputs from two major parts of the Sacramento Valley. Two sites were chosen on the Feather river: one above most of the orchard areas and one downstream of Yuba City. Three other sites were the Colusa Basin Drain, the Sacramento Slough, and the Butte Slough. The Colusa Basin Drain was sampled to determine if the western Sacramento Valley was a potential source of pesticides to the Sacramento River. The Sacramento Slough is the terminus of a complex series of integrated drains that originate in the area near Chico. The orchards that drain into this system include those near Chico and those located between the Sacramento and Feather Rivers. The Butte Slough site was chosen in order to distinguish the relative contributions from drainage originating near Chico and that originating below the Sutter Buttes. These sites were sampled once prior to a rainfall event and daily for five days following a rainfall. One final sampling was completed ten days after the rainfall event to determine if concentrations had decreased compared to those measured prior to the runoff.

An additional set of sites was selected in smaller drainages. These sites were sampled only once, shortly after the rainfall event. These sites were the Main Drainage Canal, Honcut Creek, Jack Slough, the Yuba River at Yuba City, the Wadsworth Canal, the O'Bannion Drain, the Department of Water Resources Drain, and the Bear River. Contaminant concentrations were expected to be highest in the smaller drainages shortly after the rainfall and were expected to decrease rapidly. It has previously been shown (Domagalski, 1995) that organophosphate pesticide concentrations increase rapidly in small agricultural drains in response to runoff and that peak concentrations occur prior to peak discharge. The initial rise in concentration was attributed to runoff from adjacent fields, and the decrease in concentration was attributed to dilution. Accordingly, the smaller drainages were only sampled once during the initial period of runoff.

METHODS

Water samples were collected near the center of river flow, or by bank-sampling if suitable bridge access was not available. The samples were collected in clean glass bottles, which were immediately placed on ice. Shortly after collection, the water samples were passed through glass fiber filters (GF/F grade) in an aluminum filter support. A Teflon diaphragm pump was used to pump the water. A surrogate compound, terbuthylazine, was added at a concentration of 100 nanograms per liter, and one liter of water was passed through a cartridge containing 500 milligrams of C18 packing material. Recovery of the surrogate compound provided information on the overall efficiency of the extraction. The cartridges were partially dried by centrifugation and then were placed in a desiccator for final drying. Completion of drying was indicated by comparing the weight of the cartridge prior to and after the extraction and desiccation steps. Pesticides were eluted by passing three aliquots of a 1:1 solution of hexane and ether. Each aliquot consisted of 2 milliliters of solvent. Internal standards – deuterated anthracene, phenanthrene, and pyrene – were added, and the solvent was concentrated to a final volume near 200 microliters. Instrumental analysis was done by gas chromatography-ion trap detector (Varian Model 3400 gas chromatograph, Finnigan Model 800 ion trap detector). The chromatography column was a 30 meter capillary with a 5 percent phenyl methylpolysiloxane stationary phase. The internal diameter of the column was 0.25 millimeters and the film thickness was 0.25 micrometers. Complete details of this analytical method have been published elsewhere (Crepeau *et al.*, 1994). The pesticides analyzed, detection limits, and recoveries are listed in Table 1. The analytical method described is an adaptation of that given by Zaugg *et al.* (1995). The method was specifically designed to be applicable to waters of the Central Valley of California. Therefore, detection limits and recoveries were determined using water from the Sacramento River or other rivers of

C–035252

C-035252

the Central Valley. That water was collected when pesticide concentrations were sufficiently low as to not interfere with the analyses.

TABLE 1. Detection Limits, Mean Recoveries, and Relative Standard Deviation from Seven Determinations of Pesticides Spiked to a Concentration of 100 Nanograms Per Liter Into Sacramento River Water (concentrations reported below the detection limit are estimates).

Pesticide	Detection Limit (nanogram per liter)	Mean Recovery (percent)	Relative Standard Deviation (percent)
Alachlor	35	91	12
Atrazine	47	95	16
Butylate	44	76	19
Carbaryl	50	103	16
Carbofuran	44	101	14
Chlorpyrifos	44	89	16
Cyanazine	50	87	18
Dacthal	44	111	13
Diazinon	38	85	14
Fonofos	28	86	10
Malathion	35	92	12
Methidathion	31	85	12
Metolachlor	35	104	11
Molinate	110	95	26
Napropamide	47	104	14
Pebulate	50	70	23
Simazine	60	83	23
Terbuthylazine	50	94	8
Thiobencarb	41	99	13

The detection limits shown in Table 1 are defined as the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the compound concentration is greater than zero. The detection limits were calculated according to the method of Eichelberger *et al.* (1988). Pesticides can be positively identified by the mass spectrometer at concentrations below the detection limit. The structures of the pesticides and pesticide degradation products detected in this study are shown in Figure 2. Concentrations reported below the detection limit are estimates, however. The estimated concentrations reported were calculated using a calibration routine. Blank extractions consisted of passing organic-free water through all of the sampling equipment and then analyzing the sample in the same manner as any other sample. Neither pesticides nor pesticide degradation products were detected in these blanks. Other quality assurance practices included the collection and analysis of replicates. The replicate analyses consisted of 15 percent of the total number of analyses. The concentrations were checked to determine if they were within the relative standard deviation of the method. The mass spectra of each detected pesticide was verified by checking that of the sample with that of an authentic standard.

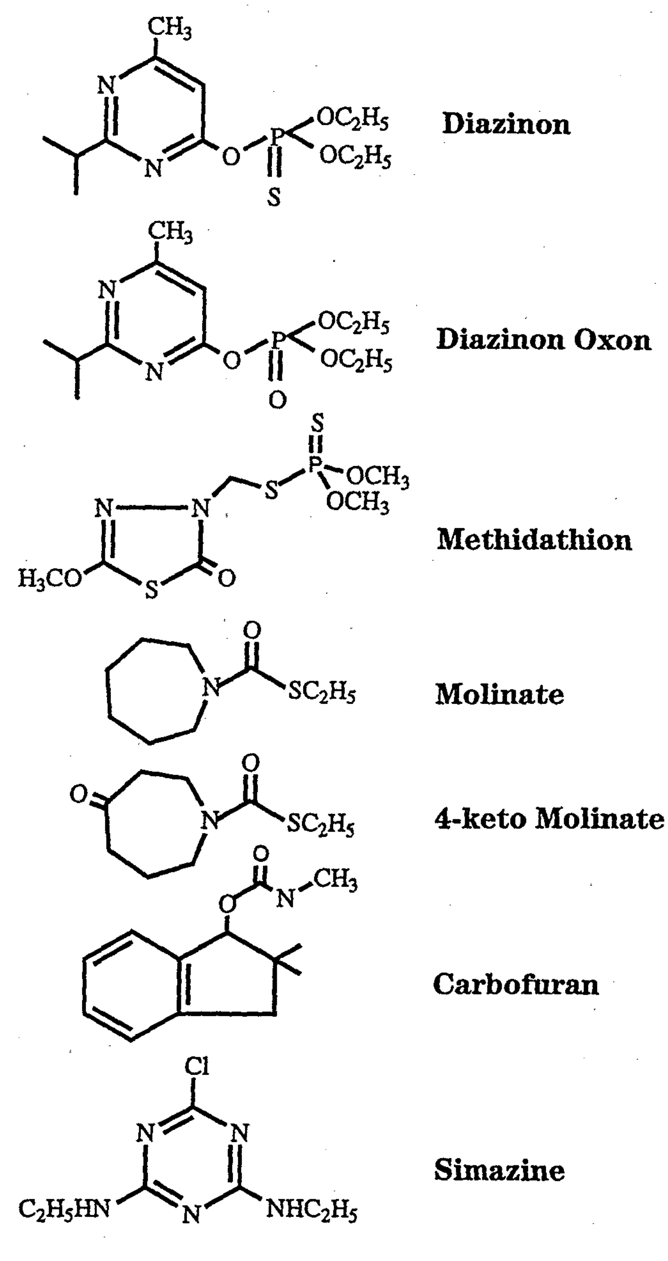

Figure 2. Structures of Pesticides and Pesticide Degradation Products Detected in This Study.

C—035253

C-035253

RESULTS AND DISCUSSION

The pre-rainfall sampling was done on January 12, 1994. The results are given in Table 2. Of the 20 pesticides analyzed, diazinon was detected most frequently and was detected at all sampling stations. It was expected that diazinon, methidathion, and simazine would be detected because of their use during the winter months. Molinate and carbofuran were detected, although their presence was not expected because they are applied on rice during May and June. An interpretation of their occurrence in these samples will be discussed later in this article

The rainfall record for the storm event at Colusa, California, is shown in Figure 3. Rainfall of 4.3 cm was recorded at Colusa between January 22 and 26. Flow hydrographs for the Sacramento River at Colusa and Verona are shown in Figure 3. These hydrographs are from continuous monitors, which measure and record discharge at 15-minute intervals. Peak flow of the Sacramento River at Colusa occurred at 1900 hours on January 25 and at Verona at 0130 hours on January 27. The gaging station at Verona is just downstream from the confluence of the Sacramento and Feather Rivers. The principal sources of water that flow to the Sacramento River at Verona are the Feather River, the Colusa Basin Drain, and Sacramento Slough (Figure 1, inset). Daily mean discharge data for the Feather River, the Colusa Basin Drain, and Sacramento Slough for January 22 through 29, 1994, are shown in Figure 4. Peak flow on the Feather River was at least one day before that of Sacramento Slough and two days before peak flow on Colusa Basin Drain.

Diazinon concentrations measured in water samples from the Sacramento River at Colusa and Sacramento sites are shown in Figure 5. Diazinon concentrations peaked on January 25 at the Sacramento River at Colusa; measured concentrations then decreased and stabilized. The January 24 sample was taken just as the hydrograph started to rise (Figure 3). The January 25 sample was taken on the upper part of the hydrograph, just before peak discharge (Figure 3). All other samples were taken on the declining part of the hydrograph.

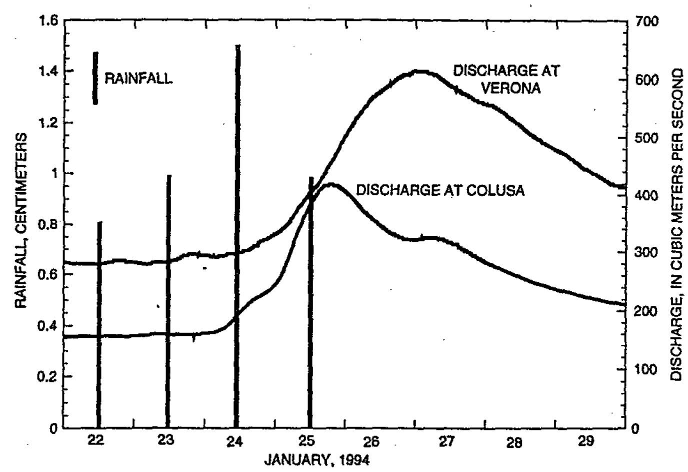

Figure 3. Discharge Measured at the Sacramento River at Colusa and Verona, California, January 22 Through January 30, 1994; and Rainfall Measured at Colusa, January 22 Through January 25, 1994.

The diazinon concentrations and discharge measured at the Sacramento River at Sacramento were considerably higher than those measured at the Sacramento River at Colusa. Therefore, the measured diazinon must have entered the Sacramento River

TABLE 2. Concentrations of Pesticides Detected in Water Samples Collected on January 12, 1994, at Selected Sites, Sacramento Valley, California.
(See Figure 1 for site locations. Concentrations are reported as nanograms per liter.)

Site Number	Location	Diazinon	Methidathion	Carbofuran	Molinate	Simazine
1	Sacramento River at Colusa	10*	–	–	–	–
2	Feather River at Yuba City	33	56	–	–	–
3	Butte Slough	79	–	49	140	8*
4	Feather River Below Yuba City	44	–	13*	11*	–
5	Colusa Basin Drain	20*	–	27*	98*	–
6	Sacramento Slough	86	–	35	116	–
7	Sacramento River at Sacramento	10*	–	–	–	–

*Concentrations are below lower limit of reliable detection. The presence of these pesticides was confirmed by mass spectrometry, but the reported concentrations are estimates.
(–, not detected.)

C—035254

C-035254

downstream from Colusa. Discharge and measured diazinon concentrations for the Sacramento River at Sacramento are shown in Figure 6. The diazinon concentrations measured in samples from the Sacramento River at Sacramento rose with the hydrograph. The highest concentration was from a sample taken near peak discharge at 1000 hours on January 27. Both concentration and flow dropped on January 28. This general pattern of increasing concentrations on the rising limb and decreasing concentrations on the falling limb of the stream hydrograph has been observed for other locations where pesticides enter the streams as a result of rainfall-induced runoff (Richards and Baker, 1993; Domagalski, 1995).

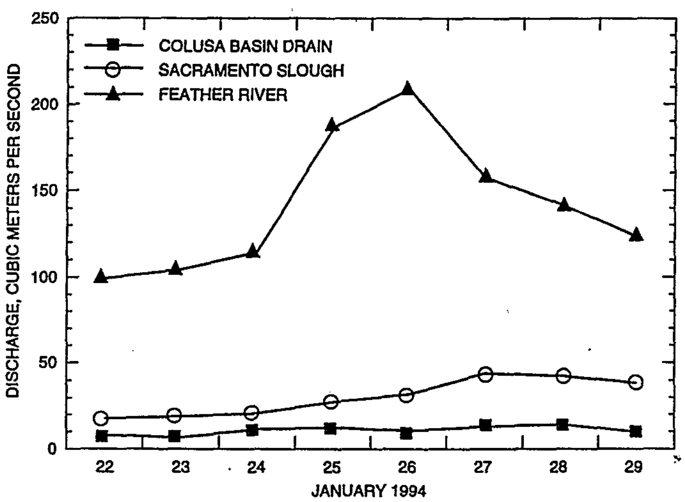

Figure 4. Daily Mean Discharge at the Feather River, the Colusa Basin Drain, and the Sacramento Slough, Sacramento Valley, California, January 22 Through January 29, 1994.

The western part of the valley was not a major source of diazinon during or after the storm of January 22-26. In samples collected from the Colusa Basin Drain (Figure 1), the highest measured concentration was 60 nanograms per liter (Figure 7). In contrast, diazinon concentrations in streams east of the Sacramento River were considerably higher (Figure 7). Of these, measured diazinon concentrations were lowest for the Feather River at Yuba City because this site was upstream from most of the orchards. Concentrations were intermediate for the Butte Slough. The highest concentrations were measured in samples from the Feather River downstream from Yuba City and at Sacramento Slough. The highest concentrations occurred near peak discharge on the Feather River downstream from Yuba City on January 26 and on Sacramento Slough on January 27.

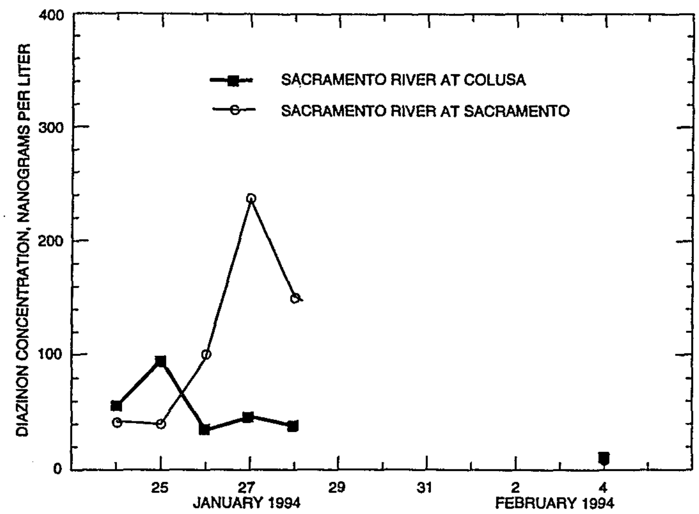

Figure 5. Diazinon Concentrations Measured in the Sacramento River at Colusa and at Sacramento, California, January 24 Through February 4, 1994.

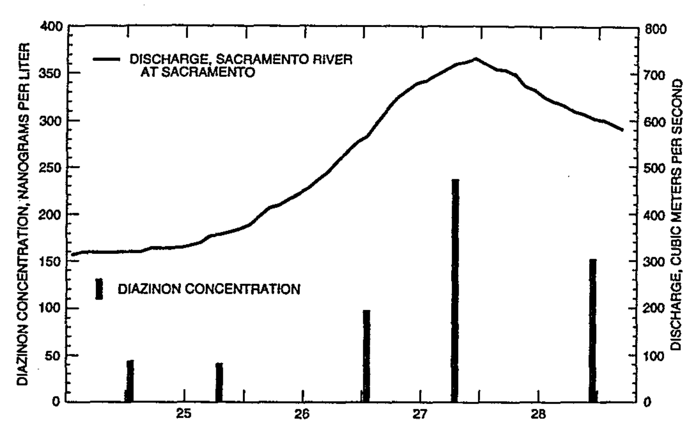

Figure 6. Diazinon Concentrations and Discharge Measured in the Sacramento River at Sacramento, California, January 1994.

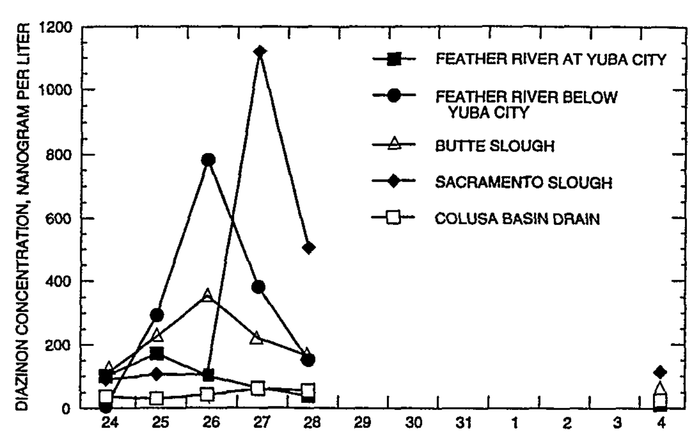

Figure 7. Diazinon Concentrations Measured in Selected Waterways, Sacramento Valley, California, January 24 Through February 4, 1994.

C—035255

C-035255

The most likely source of diazinon for the concentrations measured in samples taken from the Sacramento River at Sacramento is the Feather River. The peak concentration at the Feather River downstream from Yuba City was measured on January 26 at about 0900 (Figure 7). This peak corresponded to the rising limb of the hydrograph. The highest measured diazinon concentrations for the Sacramento River at Sacramento were measured the next day (Figure 5). The sampling location for the Feather River downstream from Yuba City is approximately 10 miles upstream from the confluence with the Sacramento River. The travel time of partial water from the Sacramento River from the confluence with the Feather River to the sampling site at Sacramento is 9 to 10 hours, based on peak discharges measured at the gaging stations. The travel time of a parcel of water from the Feather River sampling site downstream from Yuba City to the sampling site at Sacramento is approximately 15 to 16 hours. Therefore, peak concentrations should be recorded at the Sacramento River at Sacramento site the day after those of the Feather River site, if the Feather River is the principal contributor of the diazinon load. The highest concentration at Sacramento Slough was measured on January 27 (Figure 7). The diazinon measured at Sacramento Slough on January 27 would be detected at the Sacramento River at Sacramento the next day, when diazinon concentrations were decreasing in the Sacramento River. The Colusa Basin Drain has been ruled out as a substantial source of diazinon because of generally low concentrations (Figure 7). Therefore, the Feather River was probably the principal source of measured diazinon in samples taken from the Sacramento River at Sacramento. Pesticides were measured on January 24, 1994, at eight additional sites in small tributaries (Figure 1). These samples were collected during or shortly after the rainfall. Pesticide concentrations measured at these sites are shown in Table 3.

As expected, some concentrations of diazinon and other pesticides are higher in samples from these sites because the streams are relatively small and are closer to the orchards. Honcut Creek, Jack Slough, the Yuba River, and the Bear River all discharge into the Feather River (Figure 1). Of those sites, Jack Slough had the highest concentrations of pesticides. Jack Slough may have been the principal source of diazinon to the Feather River; however, other possible sources were not sampled. In addition, concentrations can change rapidly in small tributaries; therefore, some of the other sites may have been important for the transport of diazinon. The other four drains or canals (additional sampling sites, Figure 1) all drain to Sacramento Slough. The highest individual concentration of diazinon was detected in a sample collected from the Main Drainage Canal (Figure 1; Table 3). Although some drains that discharge into Sacramento Slough had high concentrations, the diazinon load of Sacramento Slough to the Sacramento River was apparently less than that of the Feather River.

The measured concentrations of diazinon in the Feather River and Sacramento Slough, as well as several of the additional sites, were of toxicological significance. At concentration above 350 nanograms per liter, diazinon is toxic to *Ceriodaphnia dubia*, a zooplankton species used in bioassays developed by the U. S. Environmental Protection Agency (Amato *et al.*, 1992). Diazinon concentrations exceeded 350 nanograms per liter for at least two days in the Feather River, at least one day in Butte Slough, and possibly two days in Sacramento Slough. The Sacramento River samples were always below this value and would not provide a positive response on the bioassay unless other toxicants were present. Therefore, sufficient dilution water was present in the Sacramento River to mitigate toxic effects from these

TABLE 3. Pesticide Concentrations Measured in Water Samples from Small Tributaries in the Sacramento Valley, California, January 24, 1994.
(See Figure 1 for Site Locations. Concentrations are in nanograms per unit. –, not detected.)

Site Number	Location	Diazinon	Methidathion	Carbofuran	Molinate	Simazine
8	Main Drainage Canal	1340	55	45	200	–
9	Honcut Creek	105	–	21	–	–
10	Jack Slough	767	1100	135	264	1350
11	Yuba River at Yuba City	35	–	–	–	36
12	Wadsworth Canal	569	58	15	57	86
13	O'Bannion Drain	122	–	41	272	30
14	Department of Water Resources Drain	230	49	157	475	803
15	Bear River	203	57	82	91	132

C —0 3 5 2 5 6

C-035256

rganophosphate pesticides. A proposed water-quality riterion for diazinon for the protection of aquatic life ; 80 nanograms per liter (Menconi and Cox, 1994). iazinon concentrations exceeded this criterion at all ampling stations except the Colusa Basin Drain and e Yuba River.

Diazinon oxon, a degradation product of diazinon rmed by the substitution of oxygen for sulfur bound the phosphorous atom (Figure 2), was found in 10 amples. The presence of diazinon oxon was verified sing an authentic standard. The mass spectrum of e sample matched that of the standard. The linkage f phosphorous to oxygen, rather than to sulfur, can esult in greater toxicity (Buchel, 1983; Woodrow *et l.*, 1983). Therefore, it was of interest to determine e relative abundance of that degradation product. iazinon oxon was only detectable in samples that ad high concentrations of diazinon in excess of 100 anograms per liter. The oxon-to-diazinon ratios anged from a low of 0.006 to a high of 0.04. The average ratio was 0.025. Diazinon oxon, therefore, ccounts for about 2.5 percent of the total diazinon ad on average. The relatively small amount of diazion oxon present and the relative constant ratio of egradation product to parent pesticide indicate that xon is a transient species. In contrast, much higher atios of oxon to parent pesticide have been detected n fog samples collected in the Central Valley (Glotfel-y *et al.*, 1990; Seiber *et al.*, 1993). In some fog samles, the amount of oxon exceeded that of the parent esticide. In surface water, the conversion rate of liazinon to diazinon oxon may be relatively slow or he hydrolysis rate may be relatively fast. Oxon anaogues of organophosphate pesticides are known to ave faster hydrolysis rates relative to the parent ompounds (Buchel, 1983). Under either scenario, the atios would be less than one. Apparently, the converion of diazinon to diazinon oxon is facilitated in fog ut not in surface water. The occurrence of diazinon xon in fog would be of interest if atmospheric transort of diazinon to the rivers occurred. Atmospheric ransport of pesticides can be important. A thorough eview of pesticide transport in the atmosphere has een given by Majewski and Capel (1995).

Two other organophosphate pesticides that are ised on dormant orchards are methidathion and chlorpyrifos. The amount of methidathion applied is similar to that of diazinon, but the amount of chloryrifos used is about 25 percent of that of diazinon. The lower use of chlorpyrifos might, in part, account for the lack of detections of that pesticide. Methidathion was detected at the Feather River and Sacramento Slough at concentrations much lower than those of diazinon. The measured concentration of methidathion was 143 nanograms per liter on January 25 at the Feather River downstream from Yuba City; it decreased to 26 nanograms per liter on January 26. The peak concentration of methidathion was observed one day prior to that for diazinon. While the diazinon concentration was increasing, the methidathion concentration probably was decreasing, because the supply from the orchards was exhausted. The most likely source of methidathion to the Feather River was the Jack Slough. A concentration of 1,102 nanograms per liter was measured in a sample collected on January 24. The highest concentration at the Sacramento Slough was 104 nanograms per liter, measured on January 27, which decreased to 75 nanograms per liter on January 28. The high concentration occurred near peak discharge, and the lower concentration was measured in a sample collected during the declining part of the hydrograph. Sources of methidathion to the Sacramento Slough are unknown. Methidathion was detected at several agricultural drains that discharge to the slough, but the highest concentration measured was 50 nanograms per liter.

Molinate and carbofuran were detected in samples from the Colusa Basin Drain, Sacramento Slough, Butte Slough, and the smaller drainages that are used for rice cultivation. Molinate is an herbicide used to control water grasses, and carbofuran is an insecticide. These pesticides are applied mainly in May and June, the period of the seeding and early growth of rice. Rice cultivation is one of the largest agricultural land uses in the study area. Concentrations of molinate and carbofuran for Butte Slough, Colusa Basin Drain, and Sacramento Slough are shown in Figures 8 and 9. In contrast to diazinon, the concentrations of molinate had only a slight variation in concentration during the storm of January 22-26. Furthermore, concentrations measured prior to the storm and a week after the storm were not significantly different. The concentrations measured before, during, and after the storm are within the analytical error. Carbofuran concentrations increased slightly on January 27 and 28, and the concentrations measured on February 4 were slightly less than those of the previous week. Carbofuran concentrations measured on January 12, prior to the storm, were similar to those measured during and after the storm (Table 2). The concentration profiles of rice pesticides probably are not attributable to storm runoff, but rather to current management practices for the elimination of rice stubble. Following the harvest, rice fields in the Sacramento Valley traditionally have been burned to destroy the residual stubble. Rice stubble does not degrade rapidly and would interfere with planting the subsequent year's crop. The burning of rice fields has been discouraged because of potential health risks from smoke released to the atmosphere. A new technique, currently being evaluated, is the flooding of rice fields after the

C—035257

C-035257

harvest to promote more rapid degradation of the stubble. Flooded fields were being drained during this study and were the probable source of the rice pesticides.

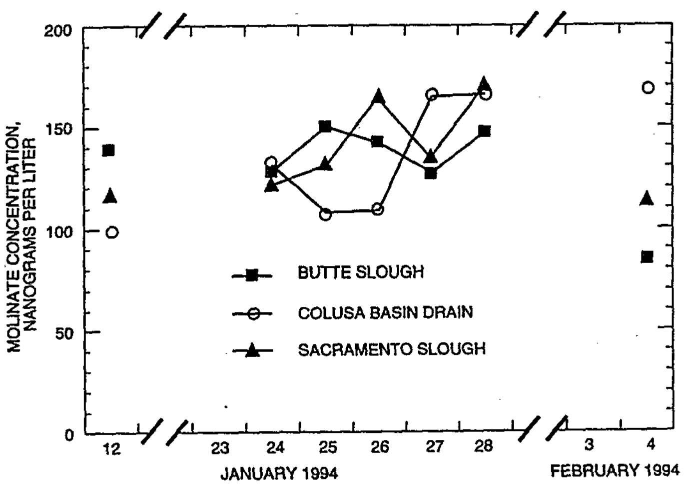

Figure 8. Concentrations of Molinate Measured at the Butte Slough, the Colusa Basin Drain, and the Sacramento Slough, Sacramento Valley, California, January 12 Through February 4, 1994.

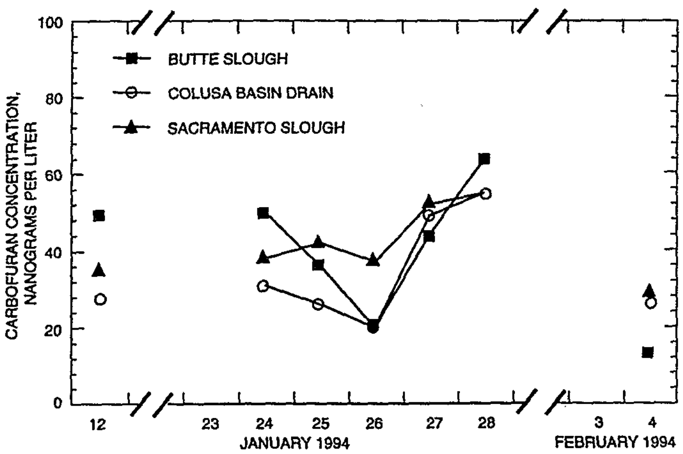

Figure 9. Concentrations of Carbofuran Measured in Butte Slough, the Colusa Basin Drain, and the Sacramento Slough, Sacramento Valley, California, January 12 Through February 4, 1994.

Molinate is applied to flooded rice fields during May and June to protect the emerging rice shoots from competing water grasses. This is the only use of molinate in California. The major pathways for the degradation or removal of molinate from these fields are volatilization and photolysis (Soderquist *et al.*, 1977). A photo-degradation product of molinate, 4 keto molinate, was detected in all samples with detectable molinate. A plot of the ratios of 4-keto molinate to molinate for samples taken from Butte Slough, the Colusa Basin Drain, and Sacramento Slough is shown in Figure 10. The highest recorded ratio was for one Colusa Basin Drain sample. Most other ratios for this site were close to one. Ratios for samples collected from Butte Slough and from Sacramento Slough were slightly less than one. The ratios for samples collected from the additional sites, sampled on January 24, 1994, are similar to those shown in Figure 10. This degradation product has previously been measured in water samples collected from the Sacramento River (Domagalski and Kuivila, 1991). The sampling area for that study was just downstream from the confluence of the Sacramento River and the Colusa Basin Drain and extended downstream from the city of Sacramento. The ratios recorded in that study were between 0.1 and 0.3. The higher ratios measured in January 1994 were probably the result of the longer time available for the photolysis reaction to occur

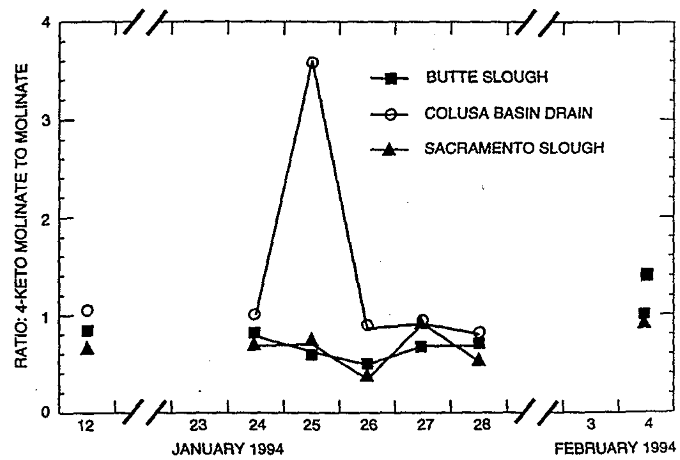

Figure 10. Ratio of 4-Keto Molinate to Molinate Measured in the Butte Slough, the Colusa Basin Drain, and the Sacramento Slough, Sacramento Valley, California, January 12 Through February 4, 1994.

Simazine is an herbicide with widespread agricultural and non-agricultural uses throughout the Central Valley of California. One principal non-agricultural use is for the control of weeds along roadways. Simazine is used during much of the year, but use is highest during the winter months. Measured concentrations of simazine during the storm of January 12, 1994, ranged from near the detection limit to

C—035258

C-035258

350 nanograms per liter. Simazine was detected at ıly one site on the January 12, 1994, sampling. ꞉cause of multiple uses of this compound, sources to e rivers are unknown. Concentrations increased ter the rainfall, indicating that simazine was in the noff water.

SUMMARY AND CONCLUSIONS

Pesticides were detected during January and bruary of 1994 in the Sacramento River and vari- s tributaries as a result of runoff or drainage from o distinct land uses: rice fields as well as fruit chards, such as almonds, prunes, and peaches. Pes- ides from the orchards entered the surface-water eams mainly because of rainfall-induced runoff. azinon was the most frequently detected pesticide d had the highest concentrations. The measured ızinon concentration increased during the rising ıge of the individual stream hydrographs and tend- to have the highest concentration and, therefore, ıding, at or near peak discharge. The concentra- ns then decreased slowly on the declining part of e hydrograph. Strategies for pesticide sampling in e waters of the Sacramento Valley should include is rainfall-induced runoff and river stage to docu- nt the variability in pesticide concentration and ıds

A potential degradation product of diazinon – diazi- n oxon – was detected in several samples, but at v amounts relative to diazinon. The low concentra- ns probably are attributed to rapid hydrolysis in e streams or to slow degradation of diazinon. sults of this study also demonstrate that rice pesti- les, molinate, and carbofuran can be relatively long- ed and can persist beyond the fall rice harvest. though rice pesticides were detected, the concentra- ns tended to be low and were difficult or impossible detect in larger rivers, such as the Sacramento and ather Rivers.

Results of this study indicate that the Feather ver drainage contributed the greatest loading of ızinon to the Sacramento River during the storm of nuary 1994. Diazinon concentrations were of toxico- ical significance in this major river for at least two ys following rainfall. Precipitation patterns in the ntral Valley may not distribute rainfall equally at potential orchard areas. During this study, the rthern and western parts of the valley did not con- bute a significant load of pesticides. Additional mpling under various rainfall scenarios will be quired to determine if other parts of the valley con- bute significant loads of pesticides to the Sacra- nto River during winter rainfall.

LITERATURE CITED

Amato, J. R., D. I. Mount, E. J. Durhan, M. T. Lukasewycz, G. T. Ankley, and E. D. Robert, 1992. An Example of the Identification of Diazinon as a Primary Toxicant in an Effluent.Environmental Toxicology and Chemistry 11:209-216

Bertoldi, G. L., R. H. Johnston, and K. D. Evenson, 1991. Ground Water in the Central Valley, California – A Summary Report. U.S. Geological Survey Professional Paper 1401-A, 44 pp.

Buchel, K. H., 1983. Chemistry of Pesticides. John Wiley and Sons, New York, New York, 581 pp.

Crepeau, K. L., J. L. Domagalski, and K. M. Kuivila, 1994. Methods of Analysis and Quality-Assurance Practices of the U.S. Geological Survey Organic Laboratory, Sacramento, California – Determination of Pesticides in Water by Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry. U.S. Geological Survey Open-File Report 94-362, 17 pp.

Domagalski, J. L., 1995. Nonpoint Sources of Pesticides in the San Joaquin River, California: Input from Winter Storms, 1992-1993. U.S. Geological Survey Open File Report 95-165, 15 pp.

Domagalski, J. L. and K. M. Kuivila, 1991. Transport and Transformation of Dissolved Rice Pesticides in the Sacramento River Delta, California. *In:* U.S. Geological Survey Toxic Substances Hydrology Program – Proceedings of the Technical Meeting, G. E. Mallard and D. A. Aronson (Editors), Monterey, California, March 11-15, 1991. U.S. Geological Survey Water-Resources Investigations Report 91-4034.

Domagalski, J. L. and K. M. Kuivila, 1993. Distributions of Pesticides and Organic Contaminants Between Water and Suspended Sediment, San Francisco Bay, California. Estuaries 16:416-426.

Eichelberger, J. W., T. D. Behymer, and W. L. Budde, 1988. Method 525 – Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Gas Chromatography/Mass Spectrometry in Methods for the Determination of Organic Compounds in Drinking Water: Cincinnati, Ohio. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, pp. 325- 356

Glotfelty, D. W., M. S. Majewski, and J. N. Seiber, 1990. Distribution of Several Organophosphorus Insecticides and Their Oxygen Analogues in a Foggy Atmosphere. Environmental Science and Technology 24:353-357.

Glotfelty, D. E., J. N. Seiber, and L. A. Liljedahl, 1987. Pesticides in Fog. Nature 325:602-605.

Hirsch, R. M., W. M. Alley, and W. G. Wilber, 1988. Concepts for a National Water-Quality Assessment Program. U.S. Geological Survey Circular 1021, 42 pp.

Kuivila, K. M. and C. G. Foe, 1995. Concentrations, Transport and Biological Effects of Dormant Spray Pesticides in the San Francisco Estuary, California, Environmental Toxicology and Chemistry 14:1141-1150.

MacCoy, D., K. L. Crepeau, and K. M. Kuivila, 1995. Dissolved Pesticide Data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-1994. U.S. Geological Survey Open- File Report 95-110.

Majewski, M. S. and P. D. Capel, 1995. Pesticides in the Atmosphere: Distribution, Trends and Governing Factors. *In:* Pesticides in the Hydrologic System (Volume 1), Robert J. Gilliom (Editor). Ann Arbor Press, Inc., Chelsea, Michigan, 214 pp.

Menconi, M. and C. Cox, 1994. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River Systems. State of California, The Resources Agency, Department of Fish and Game, Environmental Services Division Administrative Report 94-2, 60 pp.

Richards, R. P. and D. B. Baker, 1993. Pesticide Concentration Patterns in Agricultural Drainage Networks in the Lake Erie Basin. Environmental Toxicology and Chemistry 12:13-26.

C –0 3 5 2 5 9

C-035259

Seiber, J. N., B. W. Wilson, and M. M. McChesney, 1993. Air and Fog Deposition Residues of Four Organophosphate Insecticides Used on Dormant Orchards in the San Joaquin Valley, California. Environmental Science and Technology 27:2236-2243

Soderquist, C. J., J. B. Bowers, and D. G. Crosby, 1977. Dissipation of Molinate in a Rice Field. Agricultural and Food Chemistry 25:940-945.

Woodrow, J. E., D. G. Crosby, and J. N. Seiber, 1983. Vapor-Phase Photo Chemistry of Pesticides. Residue Reviews 85:111-125.

Zaugg, S. D., M. W. Sandstrom, S. G. Smith, and K. M. Fehlberg, 1995. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Pesticides in Water by C-18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry with Selected-Ion Monitoring. U.S. Geological Survey, Open-File Report 95-181, 49 pp.

C-035260

C-035260