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Occurrence of Dicofol in the San Joaquin River, California

J. Domagalski

U.S. Geological Survey, Water Resources Division, 2800 Cottage Way, Room W-2233, Sacramento, California 95825, USA

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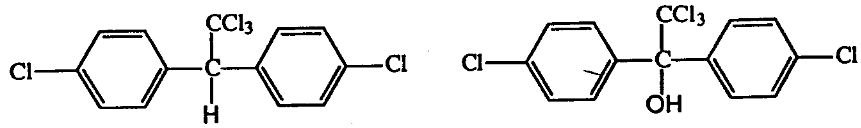
The San Joaquin River and its tributaries were sampled intensively for pesticides during the irrigation season-April through October of 1993. The purpose of the sampling was to determine the occurrence of pesticides defined operationally as those dissolved in the water column. A pesticide detected frequently in these samplings was dicofol (2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol). Although other pesticides were detected in that study, dicofol is discussed separately in this paper because of its potential toxicity. Dicofol is similar in structure to DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) (Figure 1) and has been implicated as one of a group of chlorinated hydrocarbon pesticides that can induce endocrine disruption in wildlife populations and humans (Colborn and Clement, 1992; Colborn et al, 1993; Hileman, 1993; Guillette Jr. et al, 1994). Scientific concern over these chemicals has been directed toward the different effects on the offspring of the exposed organism relative to the adult. The effects may be highly dependent on the timing of exposure, especially with respect to fetal development (Colborn and Clement, 1992). Low concentrations, such as those routinely detected in environmental samples, may result in the onset of these endocrine disruptive effects. The San Joaquin River and its tributaries are known to have elevated concentrations of DDT and its degradation products in bed sediments (Gilliom and Clifton, 1990) and fish (Rasmussen and Blethrow, 1990). The bed sediment concentrations measured at the time were among the highest for any major river system in the United States (Gilliom and Clifton, 1990).

The structure of dicofol relative to DDT is sufficient to alter significantly some chemical properties, such as water solubility. Therefore, the type of exposure for aquatic organisms will be different. Dicofol is principally transported as a dissolved constituent in the San Joaquin River and its tributaries as opposed to DDT, which principally occurs in bed or suspended sediment or aquatic tissue. DDT can bioaccumulate because of its low water solubility, but dicofol should not. The presence of an endocrine disrupting chemical dissolved in the water column may have implications for aquatic organisms. At present the toxicological significance of dicofol, with respect to endocrine disruption, has not been fully evaluated and no studies have reported on the widespread occurrence of dicofol as a dissolved constituent in a major river system.

The purpose of this paper is to present the results of dicofol occurrence in the San Joaquin River and its tributaries, during the irrigation season of 1993, and to relate that occurrence to land use within the basin and to the physical properties of dicofol.



DDT

Solubility: 0.0017 mg/L
Log Koc: 5.38

Dicofol

Solubility: 0.8 mg/L
Log Koc: 3.7

Figure 1. Diagram showing structures, solubility, and log organic carbon partitioning coefficients for DDT and Dicofol. Solubility and log K_{oc}, for DDT from Kenaga (1980); solubility and log K_{oc}, for dicofol from Wauchope et al., 1991.

MATERIALS AND METHODS

Water samples were collected at 22 sites within the perennial reach of the San Joaquin River in the San Joaquin Valley (Figure 2). The sites were selected to represent inputs from major tributaries to the river and the different agricultural land uses and soil types of the valley. Because the flow of the San Joaquin River is intermittent upstream of the Salt Slough (Figure 2, location 3), and measurements had to be made in a steady stream, all sampling locations were selected downstream of the confluence of the San Joaquin River and Salt Slough. Soil textures of the San Joaquin Valley are dependent on the provenance of the sediments from which they were derived. Soils of the western San Joaquin Valley tend to be of finer texture relative to the more sandy soils of the eastern San Joaquin Valley. As a result, there is considerable surface runoff from agricultural fields of the western valley during winter rain storms and following irrigation events. In contrast, there is much less runoff from fields of the eastern valley because of more rapid infiltration of rain or irrigation water. The difference in soil types also affects agricultural land uses. For example, orchards tend to be more extensive in locations east of the San Joaquin River because of the presence of well-drained soils. Orchards are also present in the western valley but row crops are more pervasive. The San Joaquin Valley is arid to semiarid, with almost all precipitation occurring in the winter. The lack of summer rain necessitates the use of irrigation water for successful agricultural production.

The uses of dicofol in the San Joaquin Valley are shown in Table 1. Most of the use occurs during June through August. The crops receiving the greatest amount of dicofol applications are cotton and beans. A map of locations of dicofol applications is displayed in Figure 3. There is a distinct zonation of use with bean applications primarily in the western part of the northern valley and cotton applications in the southern part of the study area.

Sampling was done at various levels of frequency. All sites were sampled during two synoptic surveys that took place during March and August, 1993. At a subset of locations, additional sampling varied from twice monthly to monthly for the period March through September, 1993. The sampling sites with the greatest sampling frequency were the Central California Irrigation District Canal (15), Orestimba Creek (6), the Spanish Grant Drain (13), and the Salt Slough (9).

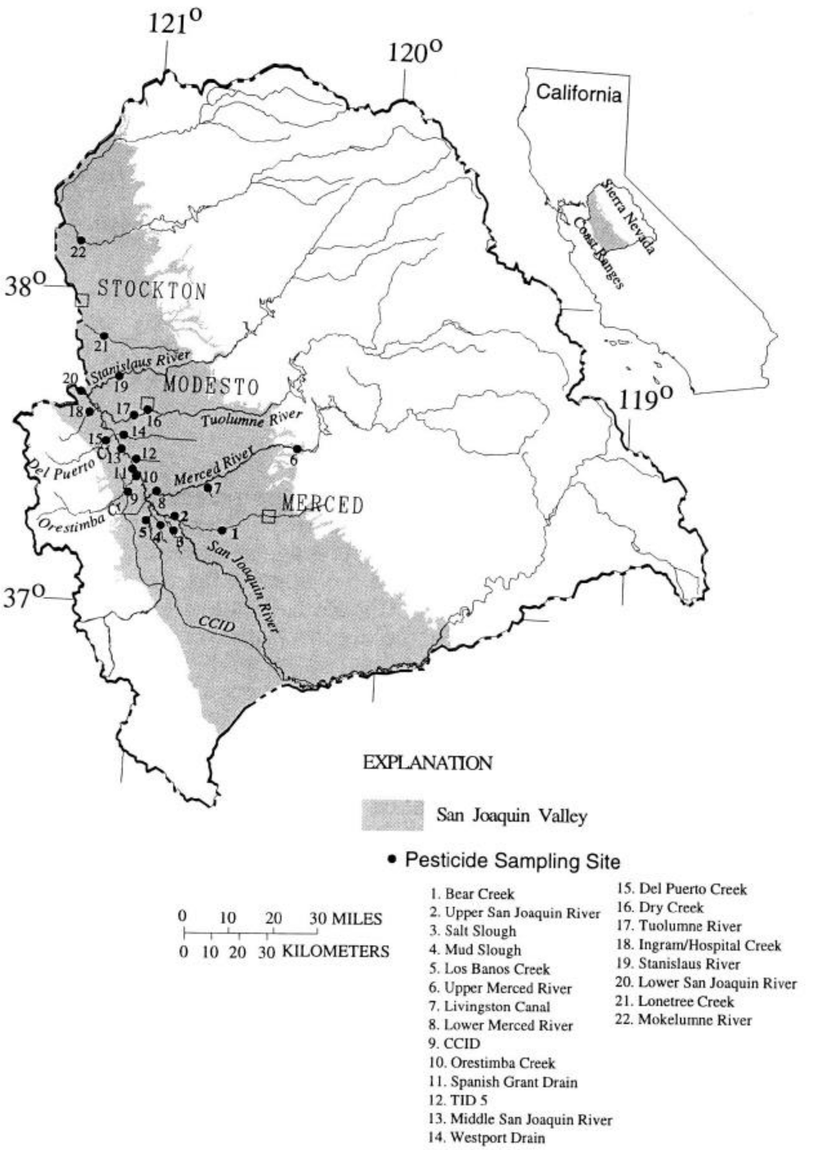


Figure 2. Study area and locations of sampling sites.

Table 1. Use of dicofol, 1991, San Joaquin Valley

Commodity	Dicofol applied in kg
Almonds	30
Apples	58
Beans	12,930
Cantaloupes	561
Cotton	38,768
Grapes	772
Melons	1,181
Peppers	211
Pumpkins	101
Squash	34
Tomatoes	256
English Walnuts	954
Watermelons	731
Total Dicofol Used	56,587

Water samples were width and depth integrated across the entire river or stream channels. Dicofol was extracted from one liter filtered water samples onto 500 µg C_{18} solid phase extraction cartridges. The cartridges were dried with nitrogen and extracted with 6 µL of hexane and ether (1:1 mix). Following concentration to 100 µL, dicofol was analyzed by gas chromatography-ion trap detector. Dicofol was positively identified by comparing the mass spectra obtained and gas chromatographic retention times from the water sample extracts to an authentic standard. The detection limit was 0.05 µg/L.

RESULTS AND DISCUSSION

The first synoptic sampling, which took place during March 1993, resulted in no detections of dicofol at any of the sampling stations. This was the expected result as the sampling took place prior to dicofol applications. All 21 sites were again sampled in the second synoptic of late August 1993. Dicofol was detected at seven of the eight western valley sites during the August synoptic sampling. The only western valley site for which dicofol was not detected was Los Banos Creek. Dicofol was not detected in any of the 10 sites of the eastern San Joaquin Valley.

This is consistent with the known application patterns which show that little dicofol is used in that part of the San Joaquin Valley. Dicofol began to be detected during mid-June at sampling sites located in the western San Joaquin Valley. The sampling sites given the greatest sampling frequency were the Central California Irrigation District (CCID) Canal, Orestimba Creek, the Spanish Grant Drain and the Salt Slough. Results of dicofol analyses for those sites are shown in Figure 4. The highest concentration, near 2,500 ng/L, was detected at Orestimba Creek. The detections followed the known use pattern in that most of the use occurred during June through August. The concentrations of dicofol measured at Del Puerto Creek and Ingram/Hospital Creek, two sites sampled only during the synoptic samplings, during August, were 519 and 684 ng/L, respectively, somewhat higher relative to the other western valley sites for that time period. Dicofol detections at Orestimba Creek, Spanish Grant Drain, Del Puerto Creek, and Ingram/Hospital Creek likely

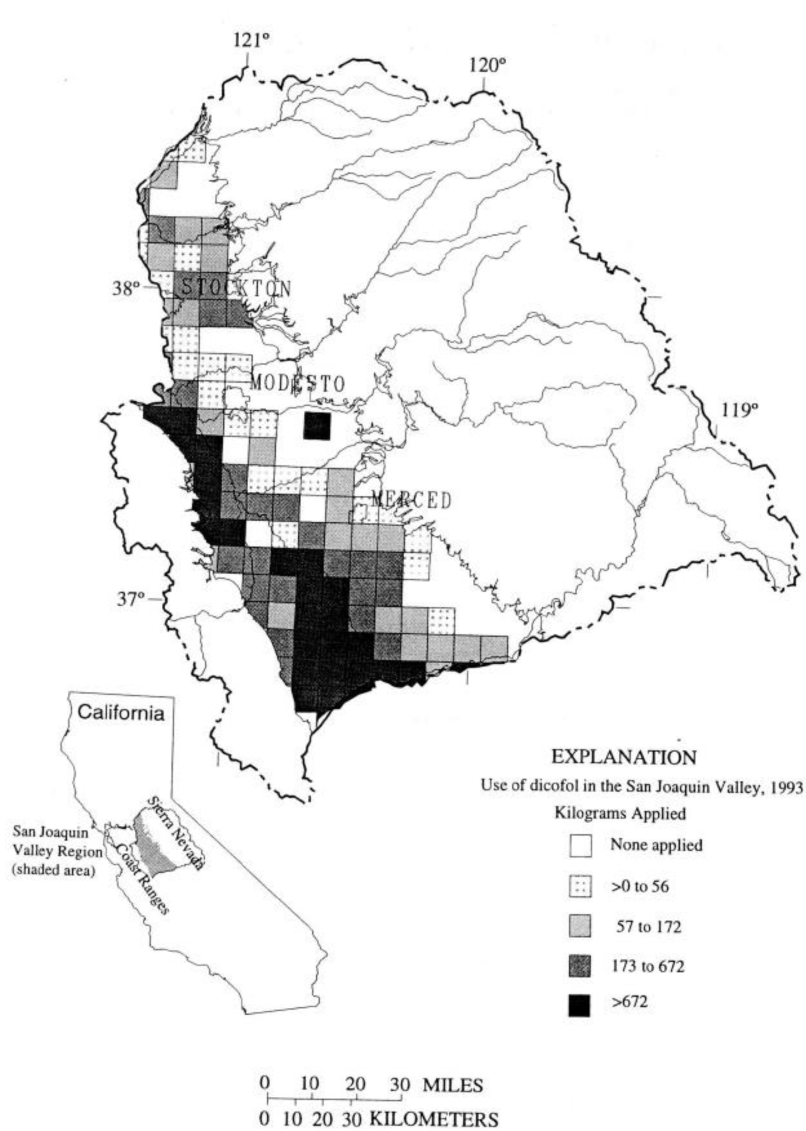


Figure 3. Locations of dicofol applications within the San Joaquin Valley.

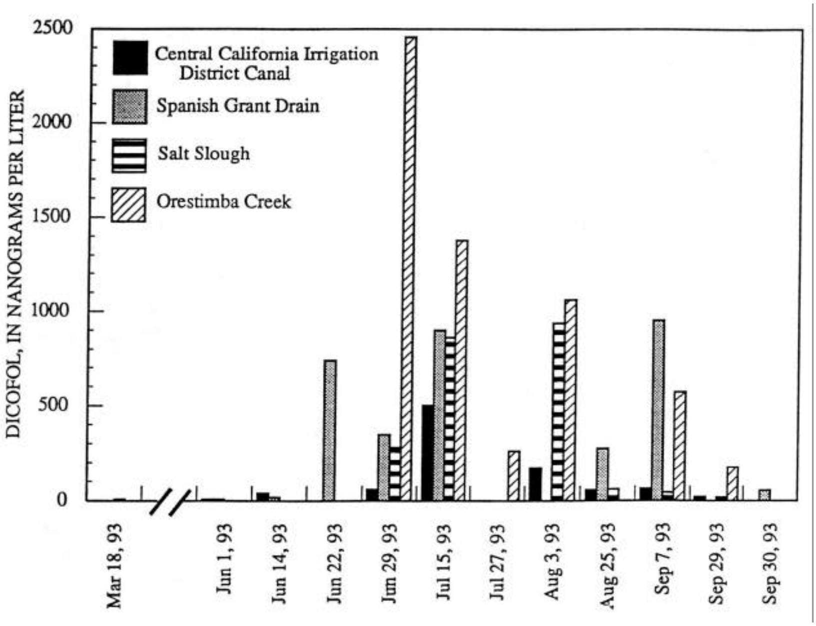


Figure 4. Concentrations of dicofol measured at the Central California Irrigation District (CCID) Canal, Spanish Grant Dram, Salt Slough, and Orestimba Creek. Nine samples collected between March 18 and June 1 had no detectable dicofols.

are due to applications on beans. The detections at Salt Slough are most likely due to applications on cotton and those of the CCID Canal to applications on beans and cotton.

Water samples were collected monthly at the middle San Joaquin River site (site 13, Figure 2). This site was sampled more frequently than other sites on the San Joaquin River because it should be the most representative of water quality with respect to pesticides. The site is centrally located within the perennial reach of the San Joaquin River, receives irrigation drainage from both sides of the valley, and is just upstream of a point where water from the river is diverted for local irrigation projects. The dicofol concentrations are shown in Table 2.

The dicofol concentrations measured in the San Joaquin River are lower relative to concentrations measured in the western tributaries. The lower concentrations are attributed to dilution of water from the eastern valley, primarily the Merced River.

Table 2. Concentrations of dicofol measured at the middle San Joaquin River site

Date	Dicofol concentration in ng/L
June 23, 1993	0
July 26, 1993	40
August 24, 1993	71
September 28, 1993	51

Dicofol was measured less frequently in samples collected at the lower San Joaquin River site (site 20, Figure 2). The concentrations measured on June 29 and August 25, 1993 were both 50 ng/L. Dicofol was not detected in a sample collected on September 29, 1993. There were no samples collected in July. Dicofol was not detected at the upper San Joaquin River site on any occasion.

The water solubility of dicofol is 0.8 mg/L (Wauchope and others, 1991). The organic-carbon-normalized partition coefficient (K_{oc}) of dicofol, defined as the quantity of dicofol (in µg) per g of sedimentary organic carbon divided by the quantity in solution (µg mL^{-1}), is 5000 [log K_{oc} = 3.7 (Wauchope and others, 1991)]. During the irrigation season, the amount of suspended sediment in a stream such as Orestimba Creek is on the order of 100 mg/L. The total amount of organic carbon on the sediments as measured during this study was 2%. Under those conditions, the amount of dicofol in solution is 99% of the total. That is, only 1% is associated with the suspended sediment. If the suspended sediment concentrations increase to 500 mg/L, then the dicofol in solution would be 95% of the total. During winter rainstorms, the amount of suspended sediment in streams such as Orestimba Creek can increase to over 1000 mg/L. Even under relatively high sediment load, at least 90% of the dicofol would be transported in solution and only 10% sorbed to suspended sediment.

In contrast, the water solubility of DDT is 0.0017 mg/L and the K_{oc}, is 238,000 (log K_{oc} = 5.38) (Kenaga, 1980). At the suspended sediment concentration of 100 mg/L, found at Orestimba Creek, 68% of the transported DDT will be in solution and 32% will be sorbed to the sediment. At a suspended sediment concentration of 500 mg/L such as during storm runoff, only 30% of the DDT will be in solution and under conditions of high sediment load, 1000 mg/L, up to 83% of the transported DDT will be sorbed to the sediment. DDT will, therefore, accumulate in the bed sediments of Orestimba Creek and the San Joaquin River and be available for bioaccumulation. The bioaccumulation will probably occur, initially, through uptake by benthic organisms. DDT can be bioaccumulated by other aquatic species, including fish, through various food webs. Dicofol will be present mainly in solution and will not undergo appreciable bioaccumulation. Nevertheless the presence of dicofol in the water column for most of the irrigation season may have implications for endocrine disruption of aquatic organisms, particularly in the tributaries where concentrations are the highest. Further research is needed on the toxicology, with respect to endocrine disruption, from chemicals dissolved in water at low concentrations.

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