TRANSPORT AND TRANSFORMATION OF DISSOLVED RICE PESTICIDES IN THE SACRAMENTO RIVER DELTA, CALIFORNIA

U.S. GEOLOGICAL SURVEY

OPEN-FILE REPORT 91-227

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Open-File Report 91-227

Sacramento, California
1991

U.S. DEPARTMENT OF THE INTERIOR
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TABLE

Multiply	By	To obtain
acre	4,047	square meter
feet (ft)	0.3048	meter
pound (lb)	4.536	kilogram
mile (mi)	1.609	kilometer

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F=1.8(°C)+32.$$

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Abstract

A large quantity of pesticides and herbicides is applied to flooded ricefields in the Sacramento Valley, California, during April, May, and June. Residues of molinate, thiobencarb, carbofuran, and methyl parathion have been detected in the Sacramento River and are of concern because of their effect on aquatic life. A Lagrangian study of the transport and transformation of these compounds was made along a 45-mile reach of the Sacramento River and the tidally influenced delta. Slow degradation rates of molinate, thiobencarb, and carbofuran resulted in conservative transport during the 4-day timeframe of the study. In contrast, methyl parathion apparently was degraded in the ricefields to para-nitro phenol and only this product was detected.

INTRODUCTION

Rice is one of the most abundant crops of the Sacramento Valley of California. As much as 500,000 acres are used in the production of rice in a given year. This production is attributable partly to the abundance of high-quality irrigation water from the Sacramento River. Rice growers use a continuous-flood method of irrigation and apply a considerable amount of herbicides and pesticides from April to June. Field drainwater containing dissolved residues of these compounds is discharged to the Sacramento River. Drainwater from ricefields was estimated to comprise 30 percent of the total flow in the Sacramento River during drainage of these fields (California State Water Resources Control Board, 1984).

The compounds of interest include two thiocarbamate herbicides (molinate and thiobencarb): a carbamate insecticide (carbofuran) and an organophosphate insecticide (methyl parathion). These compounds are soluble in water to concentrations of 30 to 800 milligrams per liter at 25 °C (degrees Celsius) and, therefore, are transported primarily in the dissolved phase. Residues of these compounds were detected in the Sacramento River and may have an effect on the larval stage of fish in the Sacramento River and the San Francisco Bay estuary. California has attempted to control this discharge by prohibiting field drainage for 19 days following application of molinate.

A Lagrangian study was done on the transport and transformation of rice pesticides in a 45-mi (mile) reach of the Sacramento River downstream from the Colusa Basin Drain, one of the principal sources of ricefield drainage (fig. 1). A Lagrangian study involves following a "parcel" of water between previously chosen upstream and downstream sites. The "parcel" then can be sampled periodically and chemical reactions can be monitored within the same body of water. Typically, the inflow of the American River into the Sacramento River is significant, but during the week of the study, the inflow was low (less than 5 percent of the total). The inflow from ground water is insignificant throughout the study reach. Inflow of other sources of agricultural return water, below the Colusa Basin Drain, also are insignificant. The goals of the study were to determine the effect on the concentrations of rice pesticides by dilution and dispersion and by various degradation mechanisms which might include photolysis, hydrolysis, microbial degradation, and volatilization. A solute-transport model is being developed to quantitatively describe these processes. This paper describes the river concentrations and chemical reactions affecting the pesticides.

The quantities of pesticides used on rice and the degradation mechanisms of the residues are listed in table 1. The pesticide-use data were collected during 1988 and are the most current data available.

Molinate and thiobencarb are used for control of water weeds and grasses, carbofuran is used to control rice water weevils, and methyl parathion is used to control tadpole-shrimp larvae.

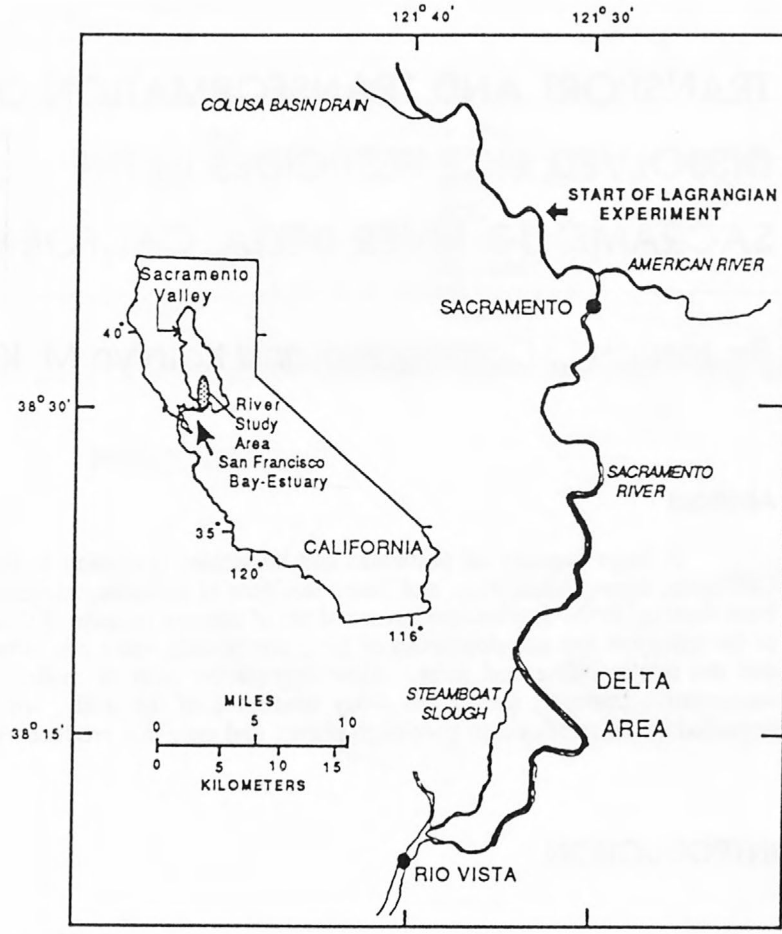

Figure 1. Study area.

Table 1. Quantities of pesticides used on rice during 1988 and degradation mechanisms of pesticide residues

Pesticide	Total pesticide application (pounds)	Degradation mechanisms
Molinate	1,467,761	Volatilization, photolysis (Soderquist and others, 1977)
Thiobencarb	421,954	Photolysis (Crosby, 1983)
Methyl parathion	71,072	Hydrolysis (Wolfe and others, 1986) or microbial degradation (Walker, 1976).
Carbofuran	58,630	Hydrolysis (Sharom and others, 1980) or microbial degradation (Chaudry and Ali, 1988)

METHODS

Sampling began June 3, 1990, at 1800 hours. The initial parcel of water was followed by use of a drogue, which was designed to flow with the current and be unaffected by wind. The parcel was followed through Steamboat Slough (fig. 1) instead of the main reach of the Sacramento River because that path represents the shortest traveltime to the delta. Water samples, integrated from 3 ft (feet) below water surface to a depth of 9 ft, were collected every 6 hours for a total of 96 hours. Discharge measurements and, therefore, pesticide load calculations were not made for any of the sampling stations. Because most of the study reach is tidally influenced, load calculations would require averaging discharge and concentrations over the entire tidal cycle. Load calculations are further complicated by the splitting of the waterflow between the main river channel and Steamboat Slough and other diversions. Instead, concentrations of pesticides within the "parcel" of water were plotted against time. This approach is valid because dilution of the "parcel" with surface- or ground-water inflows is not significant.

Pesticides were extracted from 2-L (liter) samples onto C_{18} solid-phase extraction cartridges and were analyzed by gas chromatography-ion trap detector (GC-ITD). Four-L samples, collected for phenolic degradation products, were extracted with dichloromethane at acid pH. Trimethyl silane derivatives of the phenols were analyzed by GC-ITD. Detection limits are as follows: molinate [100 ng/L (nanograms per liter)]; carbofuran (50 ng/L); methyl parathion (100 ng/L); thiobencarb (25 ng/L); carbofuran phenol (25 ng/L); and para-nitro phenol (50 ng/L).

RESULTS AND DISCUSSION

The results for the Lagrangian study are shown in figure 2. The points labeled as outflow near the Colusa Basin Drain are from a sample collected prior to the start of the Lagrangian study and therefore represent a separate parcel of water. Molinate, thiobencarb, and carbofuran were detected at all sampling stations. In addition, two photolysis degradation products of molinate, 2-keto molinate and 4-keto molinate, and the hydrolysis or microbial degradation product of carbofuran, carbofuran phenol, were detected. Although methyl parathion was not detected, the hydrolysis or microbial degradation product, para-nitro phenol, was detected. Analyses for the phenolic degradation products were not done on the Colusa Basin Drain sample.

Molinate shows a slight trend of decreasing concentrations with time (fig. 2A). The ratio of the abundance of molinate photolysis degradation products to molinate (fig. 2B) shows some scatter but no clear trend. Furthermore, the ratio in the drainwater is not significantly different than that detected in the river; therefore, these photolysis products probably were synthesized in the ricefield and photolysis is not an important reaction occurring in the river. Volatilization is the most important degradation mechanism for molinate in a ricefield (Soderquist and others, 1977), but volatilization is not an important degradation mechanism in the Sacramento River because of the much greater channel depths (20-30 ft) relative to the depth of a flooded ricefield (0.5-1 ft).

Carbofuran and thiobencarb seem to be transported conservatively (figs. 2C and 2D). Concentrations of carbofuran phenol are variable and show no clear trend (fig. 2E). A preliminary degradation experiment for carbofuran and thiobencarb showed no change in concentration in unfiltered Sacramento River water after 1 week.

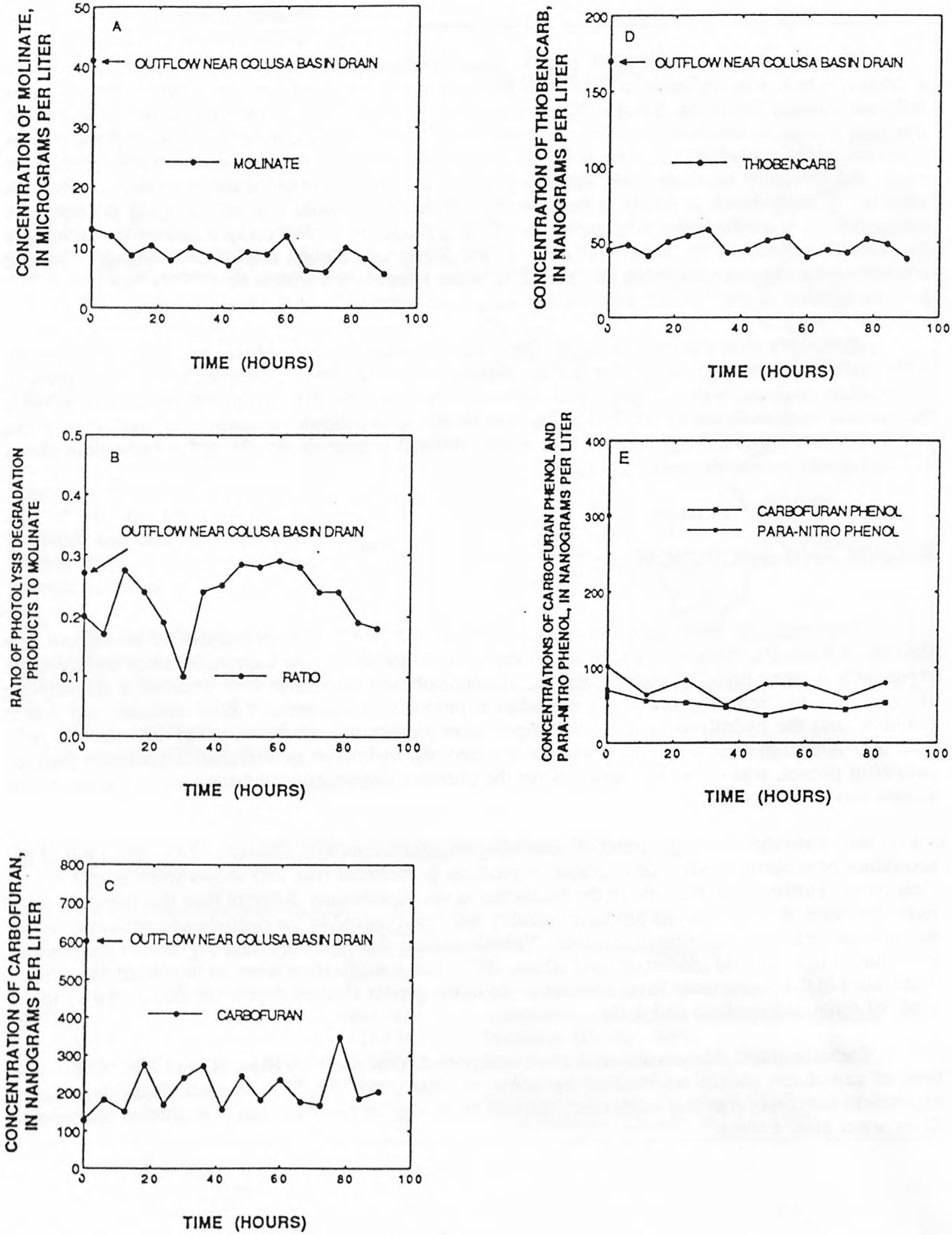

Figure 2. Results of Lagrangian study and concentrations of pesticide residues near the Colusa Basin Drain.

Methyl parathion was not detected but its microbial or hydrolysis degradation product, para-nitro phenol, was detected throughout the reach of the river, suggesting that most of the methyl parathion is degraded in the ricefields. A preliminary degradation experiment for methyl parathion in unfiltered Sacramento River water suggests a half-life of 5 to 6 days. Methyl parathion is applied at about the same time as molinate and therefore is held on the ricefields for 19 days prior to drainage, allowing adequate time for significant degradation to occur.

SUMMARY

Residues of rice pesticides, either the compounds or their degradation products, were detected along a 45-mi reach of the Sacramento River. The transport seemed to be conservative. This preliminary study shows that residues of these compounds are being transported into the delta and possibly into San Francisco Bay. The transport of molinate, thiobencarb, and carbofuran is favored by slow degradation rates within the Sacramento River. In contrast, methyl parathion is rapidly degraded, probably in the ricefields, and is not detected in the river. Future work is planned on the chemical and microbial degradation of these compounds in the river-delta-bay system.

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