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Pesticide Residues in Surface Water from Irrigation-Season Monitoring in the San Joaquin Valley, California, USA

K. Starner,[1] F. Spurlock,[1] S. Gill,[1] K. Goh,[1] H. Feng,[2] J. Hsu,[2] P. Lee,[2]
D. Tran,[2] J. White[2]

[1] California Department of Pesticide Regulation (CDPR), Environmental Monitoring Branch, Post Box 4015, Sacramento, CA 95812, USA
[2] Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA), 3292 Meadowview Road, Sacramento, CA 95832, USA

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California's San Joaquin Valley is one of the most productive agricultural areas in the United States. In 1987, approximately 5 percent of the total value of agricultural production in the US was generated in the San Joaquin Valley (Gronberg et al. 1998). During arid spring and summer months, production of vegetables, hay and grains, fruit and nuts, and cotton requires extensive irrigation. A wide variety of pesticides are applied throughout the irrigation season (California Department of Pesticide Regulation (CDPR) 2004a). Consequently the potential exists for pesticide contamination of surface waters that receive irrigation runoff. Relatively little recent surface water monitoring for pesticides has been conducted in the San Joaquin basin during the late irrigation season (July through September). This study reports concentrations of select late irrigation season-applied pesticides in San Joaquin Valley surface waters sampled in 2002.

MATERIALS AND METHODS

The primary surface water analytes in this study were the organophosphate insecticides diazinon and chlorpyrifos, the pyrethroid insecticides permethrin and esfenvalerate, the herbicide metolachlor, and the two primary metolachlor degradation products, metolachlor ethanesulfonic acid (ESA) and metolachlor oxanilic acid (OXA). These pesticides were chosen due to their relatively high use and lack of recent monitoring data in the area. Other pesticides included in the analyses were alachlor, alachlor ESA, alachlor OXA, azinphos-methyl, dichlorvos, dimethoate, disulfoton, ethoprop, fenamiphos, fonofos, malathion, methidathion, methyl parathion, phorate, profenofos, tribufos, atrazine, bromacil, diuron, hexazinone, metribuzin, norflurazon, prometon, prometryn, simazine, and three triazine degradates, deethyl-atrazine (DEA), 2-amino-4-chloro-6-ethylamino-s-triazine (ACET) and 2,4-diamino-6-chloro-s-triazine (DACT).

Four surface water monitoring sites (Figure 1) were selected in areas of the San Joaquin Valley with high recent pesticide use during the late irrigation season. One sampling site, the San Joaquin River at Vernalis, is a major perennial river that flows to the Sacramento-San Joaquin Delta and eventually into the San Francisco Bay. This site receives streamflow from the entire San Joaquin basin, and as such it characterizes the overall water quality in the entire basin (Panshin

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Correspondence to: K. Starner

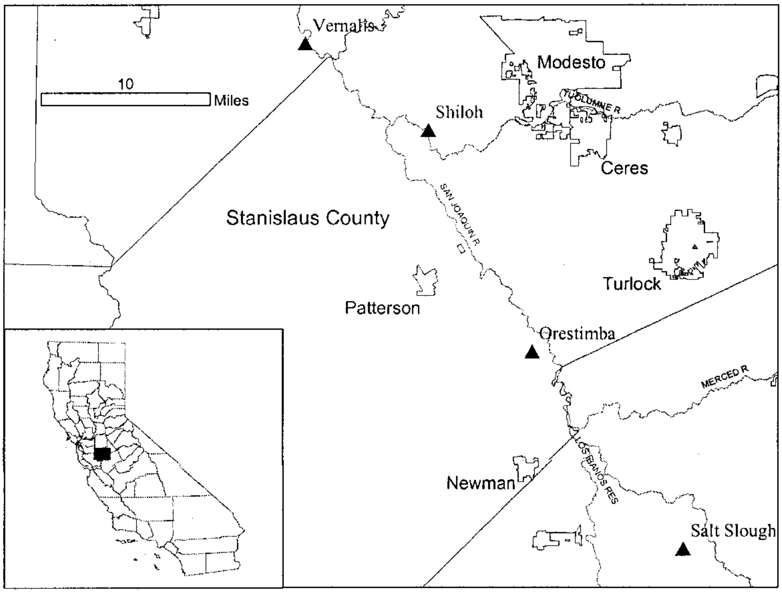

Figure 1. Sampling sites in the San Joaquin Valley (▲). Shaded area in inset map shows location within California.

et al. 1998). Three additional sampling sites (Tuolumne River at Shiloh, Orestimba Creek at River Road and Salt Slough at Highway 165) in three separate subbasins were chosen to represent a variety of subbasin and stream characteristics. These characteristics include overall subbasin size, amount of agricultural land and pesticide use in the subbasin, stream discharge, and percent of discharge from irrigation return water. The sites chosen range from an ephemeral stream comprised almost entirely of irrigation return flow and located in a small subbasin where the land use is predominantly agriculture (Orestimba Creek) to a major perennial tributary in a larger subbasin consisting of predominantly forest land (Tuolumne River at Shiloh) (Panshin et al. 1998, Gronberg et al. 1998).

Collection of surface water samples began on July 2, 2002, and continued until September 30, 2002. Each of the four sampling sites was sampled once per week for fourteen weeks. All pyrethroid samples were collected directly into 1-L amber glass bottles using an extendable sampling pole or a weighted container lowered from a bridge. All other samples were collected either directly into 1-L amber glass bottles using an extendable sampling pole or, when necessary for access reasons, into a 3-L Teflon bottle using a D-77 isokinetic sampler (Geotech Environmental Equipment, Inc., Denver, CO) lowered from a bridge. The bulk samples collected into the 3-L bottle were immediately transferred to 1-L amber glass bottles.

Method detection limits (MDL) and reporting limits (RL) for detected pesticides are presented in Table 1. Reporting limits for the remaining pesticides were between 0.03 and 0.05 µg/L. Residues determined to be present in a sample at or above the RL are reported here as detections. Residue concentrations between the RL and MDL that are determined by the analytical chemist to be likely due to the analyte of interest are reported as trace detections. The analytical chemist uses his/her best professional judgment to make this determination. No attempt is made to quantitate trace detections.

For metolachlor and metolachlor degradate analysis, a 150ml aliquot of each filtered water sample was passed through a Waters SepPak Vac 6cc C-18 solid phase extraction column (Waters, Millford, MA). The analytes were eluted with 10ml methanol, and the methanol was evaporated to just below 0.40ml. A 0.1ml acetonitrile aliquot was added and the final extract volume adjusted to 0.50ml with water. The extract was analyzed using a Waters model 2690 high performance liquid chromatograph (HPLC) (Waters, Millford, MA) equipped with a Finnigan LCQ Deca mass spectrometer (Finnigan, Thermo Electron Corporation, San Jose, CA) and a Zorbax SB-C-8 column (Agilent, Palo Alto, CA).

The pyrethroid whole water samples, including any suspended sediment, were extracted with hexane:acetone (80:20, v/v). Sample bottles were rinsed with extraction solvent and added to the sample extracts for analysis. Extracts were concentrated using a Brinkmann R110 rotary evaporator (Brinkmann, Westbury, NY), and analyzed using a Hewlett-Packard model 5890 gas chromatograph equipped with a HP-1 column (Hewlett Packard, Avondale, PA) and an electron capture detector (ECD). The pyrethroid analysis results are reported on a whole sample basis (water plus suspended sediment).

The organophosphate insecticides samples were extracted with methylene chloride and the extract was passed through sodium sulfate to remove residual water. The anhydrous extract was evaporated to near dryness on a rotary evaporator and diluted to a final volume of 1.0ml with acetone. The extract was then analyzed by a Hewlett-Packard model 5890 gas chromatograph (Hewlett Packard, Avondale, PA) equipped with an Rtx OPPesticides column (Restek, State College, PA) and a flame photometric detector (FPD).

For herbicide analysis, the water samples were passed through two Oasis MCX Cartridges (Waters, Millford, MA) connected in tandem. The cartridges were then eluted under vacuum with 5% ammonium hydroxide in methanol. The eluant was filtered through a nylon Acrodisc 0.2-micron filter (Gelman Sciences, Ann Arbor, MI), concentrated, reconstituted in 75/25 water/methanol and analyzed by a ThermoQuest/ThermoSeparation HPLC with a Finnigan LCQ Deca mass spectrometer (Finnigan/ThermoQuest, San Jose, CA).

Quality Control (QC) for this study was conducted in accordance with CDPR

Table 1. Analytical limits for detected pesticides.

Compound	Method Detection Limit (µg/L)	Reporting Limit (µg/L)
Chlorpyrifos	0.0109	0.04
Diazinon	0.011	0.04
Dimethoate	0.0079	0.04
Diuron	0.042	0.05
Malathion	0.0117	0.04
Metolachlor	0.0207	0.05
Metolachlor ESA	0.0434	0.05
Metolachlor OXA	0.0235	0.05

Standard Operating Procedure QAQC001.00 (Segawa 1995). Reagent blank samples were run with each extraction set to monitor for laboratory contamination. No contamination was detected. Blank-matrix spike samples were analyzed with each extraction set. Blank-matrix spikes are blank water samples fortified with an analyte or analytes at a known concentration and extracted and analyzed with an extraction set. For the data presented here, blank-matrix spike recovery performances were 65 to 125%. Blind spike samples were also added to some analytical sets. A blind spike is a blank-matrix sample which has been spiked and submitted to the lab disguised as a field sample. Blind spike recoveries for the data presented here ranged from 64 to 115%. In general, no duplicate samples were analyzed.

Pesticide concentrations were compared to Water Quality Criteria (WQC) (California Department of Fish and Game (CDFG) 2000, US EPA 1986, 1998) and to US EPA ECOTOX aquatic toxicity data (US EPA 2004). WQC are estimations of the highest chemical concentrations in water that should not cause unacceptable acute or chronic effects on aquatic organisms and their uses (US EPA 1985). Data in the US EPA ECOTOX database are compiled from peer-reviewed literature and US and international government agencies.

RESULTS AND DISCUSSION

Pesticide analytical results and use data (CDPR 2004a) are summarized in Table 2, and the complete analytical data set is available on-line (CDPR 2004b). In general, the number of detections for each parent pesticide was greater at sites where greater pesticide use was reported (Table 2). Pesticides that exceeded established WQC included chlorpyrifos, diazinon and malathion (Table 3).

Although detection of chlorpyrifos was relatively infrequent (ca. 5% detection frequency), measured concentrations at all four sites were potentially harmful to aquatic species. Based on the high reporting limit relative to established chlorpyrifos WQC, even trace concentrations of this pesticide might have exceeded the WQC. A more sensitive analytical method for chlorpyrifos has since

Table 2. Summary of pesticide use[a] and surface water monitoring results for four sites sampled weekly for 14 weeks in the San Joaquin Valley, California, USA.

Sampling Site	Chlorpyrifos	Diazinon	Dimethoate	Diuron	Malathion	Metolachlor	Metol ESA	Metol OXA
Orestimba Creek								
subbasin pesticide use	200	40	900	10	250	15	15	15
no. detects/trace detects	1 / 1	3 / 0	12 / 0	6 / 6	1 / 1	8 / 5	14 / 0	9 / 5
max. conc. (μg/L)	0.0705	0.276	0.696	0.354	0.111	0.689	0.502	0.113
Salt Slough								
subbasin pesticide use	15	1	5	3	1	25	25	25
no. detects/trace detects	1 / 2	0 / 2	1 / 0	11 / 3	0 / 0	9 / 5	5 / 9	2 / 12
max. conc. (μg/L)	0.046	trace	0.046	0.582	---	0.951	0.063	0.059
Shiloh								
subbasin pesticide use	140	1	12	2	14	2	2	2
no. detects/trace detects	1 / 0	0 / 2	3 / 3	3 / 6	0 / 0	0 / 1	0 / 8	0 / 0
max. conc. (μg/L)	0.056	trace	0.223	0.07	---	trace	trace	---
Vernalis								
basin pesticide use	38	1	20	2	6	6	6	6
no. detects/trace detects	0 / 1	0 / 0	7 / 2	9 / 4	0 / 0	3 / 11	14 / 0	11 / 3
max. conc. (μg/L)	trace	---	0.073	0.124	---	0.062	0.151	0.079
Totals								
total detects/trace	3 / 4	3 / 4	23 / 5	29/19	1 / 1	20 / 22	33 / 17	22 / 20
max. conc. (μg/L)	0.0705	0.276	0.696	0.582	0.111	0.951	0.502	0.113

[a] Approximate pounds of parent active ingredient applied in the associated basin per 1000 acres of agricultural land, July – September 2002 (DPR 2004a).

Table 3. Number of exceedances of toxicity benchmarks at each sampling site.

Benchmark Type	Level (μg/L)	No. of exceedances per sampling site			
		Orestimba	Salt Sl.	Shiloh	Vernalis
Chlorpyrifos					
chronic WQC[a], CDFG	0.014	1	1	1	0
acute WQC, CDFG	0.02	1	1	1	0
chronic WQC, US EPA	0.041	1	1	1	0
ECOTOX data, US EPA	0.053[b]	1	0	1	0
Diazinon					
acute WQC, CDFG	0.08	1	0	0	0
chronic WQC, CDFG	0.05	1	0	0	0
acute WQC, US EPA	0.09	1	0	0	0
ECOTOX data, US EPA	0.21[c]	1	0	0	0
Malathion					
WQC USEPA	0.1	1	0	0	0

[a]WQC = water quality criteria
[b] *C. dubia* 96-hour LC_{50}
[c] *D. magna* 96-hour LC_{50}

been developed for use in future monitoring studies.

Overall, detections of diazinon and malathion were also relatively infrequent (ca. 5% and 2% detection frequencies, respectively). The highest diazinon detection exceeded all three established WQC for diazinon. This was the only diazinon detection that exceeded established WQC. However, diazinon was detected at trace concentrations or greater in all three subbasins, even under relatively low use conditions (Table 2). Since trace detections of diazinon could potentially approach established WQC, these detections are also of concern.

Malathion was detected above the RL in a single sample at 0.111 μg/L. This concentration exceeds the US EPA WQC of 0.1 μg/L, but does not exceed the CDFG acute WQC of 0.43 μg/L. There were no other detections of malathion at any sampling site. These results suggest that use of malathion in this area during the summer irrigation season does not frequently result in concentrations that are harmful to the aquatic environment.

Diazinon and chlorpyrifos have reportedly shown additive toxicity to *Ceriodaphnia dubia* (Bailey et al. 1997, CDFG 1999, 2000). In this study there were no instances of detectable concentrations of both diazinon and chlorpyrifos occurring in a single sample.

Although dimethoate, diuron and metolachlor were detected frequently (> 35% detection rate each), concentrations were below the available toxicity levels for these compounds (US EPA 2004). There are no currently established WQC for these pesticides.

The authors are not aware of any existing aquatic toxicity test data for the metolachlor degradation products, metolachlor OXA and metolachlor ESA. These degradates were frequently detected in this study; nearly 70% of all samples collected had detections of at least one degradation product. In order to interpret the relevance of these detections, reliable aquatic toxicity information is needed.

The remaining pesticides that were detected were detected infrequently and at concentrations well below available toxicity levels: methyl parathion, 1 detection at 0.048 μg/L, simazine, 3 detections, from 0.050 to 0.082 μg/L, hexazinone, 5 detections, from 0.070 to 0.154 μg/L, norflurazon, 1 detection at 0.281 μg/L and prometryn, 2 detections at 0.057 and 0.129 μg/L. There were no detections of either of the pyrethroid insecticides, permethrin or esfenvalerate, in any water sample. This result is not unexpected, given the hydrophobicity of the pyrethroid insecticides (Laskowski 2002). Stream bed sediment analysis will be included in the design of future efforts to assess the potential impacts of these compounds on aquatic systems.

The detections of chlorpyrifos and diazinon in surface waters of the San Joaquin Valley during the late irrigation season were at or near concentrations potentially harmful to aquatic species. These detections occurred in all three subbasins monitored. The subbasins consist of a variety of hydrology, land use, and pesticide application characteristics. These results indicate that the potential for off-site movement of chlorpyrifos and diazinon under irrigated agriculture conditions may be substantial and warrants further attention. For the additional pesticides detected in this study, comparison of detection concentrations to available toxicity data suggests that use of these pesticides under the conditions studied does not generally result in concentrations harmful to the aquatic environment.

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