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Monitoring for Aldicarb Residues in Ground Water of the Central Valley of California

S. J. Marade and D. J. Weaver

Environmental Hazards Assessment Program, Department of Pesticide Regulation, California Environmental Protection Agency, 1220 N Street, Sacramento, California 95814, USA

Aldicarb is a systemic carbamate pesticide used to control insects, mites, and nematodes on a wide range of crops including cotton, potatoes, citrus, and dry beans. Groundwater contamination by aldicarb was first discovered in Suffolk County, New York in August, 1979 (Zaki et al. 1982). During the next several years, numerous aldicarb-monitoring studies were conducted in the United States. In a summary report, Lorber et al. (1990) indicated that by 1990, aldicarb sulfoxide and aldicarb sulfone had been detected in groundwater in 61 counties and in 19 states.

In response to detections in Long Island, well-water monitoring for aldicarb was initiated in California in 1979 (Oshima 1980). No residues were found in that study. However, in 1983, aldicarb sulfoxide and aldicarb sulfone were detected in samples from Del Norte County, located in northwestern California where aldicarb had been used in commercial lily bulb production. Subsequently, residues were also found in well water sampled from lily bulb production areas in neighboring Humboldt County in 1986. After 1986, aldicarb was no longer used on outdoor crops in Del Norte or Humboldt County. Aldicarb sulfoxide and aldicarb sulfone continued to be detected in well water sampled in Del Norte County.

The detections of aldicarb residues in Humboldt County initiated the response process of the Pesticide Contamination Prevention Act (PCPA), a law enacted in California in 1985 to protect groundwater from pesticide contamination (State of California 1985). Under the law, any detection of a pesticide active-ingredient in the groundwaters of California must be investigated by the Department of Pesticide Regulation (DPR), formerly part of the California Department of Food and Agriculture (CDFA). Aldicarb contamination was determined to be the result of an agricultural use, and its continued use, with some modifications, was allowed in all areas of California except Del Norte and Humboldt Counties.

The DPR has continued to test for the presence of aldicarb residues in groundwater through annual monitoring activities in

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Send reprint requests to S.J. Marade at the above address.

counties where usage of aldicarb is high over several years. This report presents findings from well surveys conducted in 1989-91.

MATERIALS AND METHODS

Well-sampling surveys for aldicarb residues were conducted in September, 1989, September and October, 1990, and December, 1991. To prepare for each survey, statewide pesticide-use report information for 1986, 1987, and 1988 (CDFA 1986, 1987, 1988) was reviewed. All use of aldicarb was required to be reported to the state because it is classified as a restricted-use compound. Based on mass applied, the nine counties with highest use were selected for monitoring. Within each county, aldicarb use was spatially identified for each section of land. A section of land is approximately 259 ha (1 sq mi) as based on the U.S. Geological Survey's (USGS) Public Lands Survey Coordinant System (Davis and Foote 1966). Depth-to-groundwater maps (U.S. Department of Interior Bureau of Reclamation 1988, 1989, 1990) prepared in the spring of the survey year were also used to determine the sampling sequence of areas to be sampled in each county. Sections that were treated with larger amounts of aldicarb and that had shallower groundwater tables were chosen first. Between 3 and 10 wells were sampled in any one county depending on the number of treated sections and the availability of wells for sampling. Between 47 and 50 different wells were selected for sampling in a survey year.

Prior to sampling a well, the well's condition was evaluated to ensure that the well had no obvious point of entry that would allow point-source contamination. In addition, the area surrounding the well was observed for signs of pesticide storage or for the presence of open wells. The proximity of the well to cotton or sugar beet fields was recorded. Wells were selected for sampling 30-400 m from cotton or sugar beet fields.

Water samples were collected from a faucet or Schrader® valve sampling port located between the well head and the holding tank after running the pump for 10 min to ensure that a fresh water sample was received. Five replicate well water samples and one field blank sample (distilled water) were collected per well in one-L polypropylene bottles. Bottles were sealed with polypropylene caps, placed immediately on dry ice (-70°C), and kept frozen (-10°C) until analyzed for aldicarb. Samples were stored for a maximum of 3 d after collection.

For each well, one well sample and the field blank were analyzed by the CDFA's Chemistry Laboratory Services Branch located in Sacramento, California (Lee and Richman 1991). One hundred mL of the water sample was extracted three times with 100 mL of methylene chloride; the extract was concentrated to 3-5 mL and dried with 1 g of anhydrous sodium sulfate. The extract was filtered, transferred to a centrifugal tube, and evaporated to approximately 200 µL in a nitrogen evaporator at 35°C. Six hundred µL of methanol was added. The volume of extract was

reduced to 100 µL and then transferred to an autosampler vial insert precalibrated to 200 µL. The tube was washed with 60 µL of methanol which was added to the same insert, and the final volume was brought to 200 µL with more methanol. Samples were separated by high performance liquid chromatography (Hewlett-Packard 1090 Liquid Chromatograph). The eluant is derivatized by post-column reaction (Pickering Labs Post-Column Derivatization System using a C18 4.6 mm x 25 mm x 5 µm column) and detected with a fluorescence detector (Hitachi F1000 Fluorescence Spectrometer). Minimum detection limit (mdl) was 0.05 ppb. Aldicarb standards that were acquired as needed between September, 1989 and December, 1991 were USEPA certified as 99% pure before the onset of chemical analysis. CDFA's standard operating procedure included testing the old standard against the new to ensure that no decomposition had occurred. One spiked sample containing aldicarb, aldicarb sulfoxide, and aldicarb sulfone was submitted with each extraction set. Mean percent recoveries ± standard deviation (sd) for aldicarb, aldicarb sulfoxide, and aldicarb sulfone were 88.6% (sd = 6.27), 81.6% (sd=8.7), and 91.9% (sd=8.26), respectively. In addition, blind spike samples were submitted containing either aldicarb, aldicarb sulfoxide, and/or aldicarb sulfone. Mean percent recoveries for seven aldicarb, seven aldicarb sulfoxide, and six aldicarb sulfone blind spike samples were 96.7% (sd=22.19), 74.6% (sd=14.12), and 88.5% (sd=8.38), respectively.

RESULTS AND DISCUSSION

Aldicarb, aldicarb sulfoxide, or aldicarb sulfone residues were not detected (<0.05 ppb) in samples from 146 wells selected from nine counties in the Central Valley (Figure 1 and Table 1). Annually, the nine counties selected for monitoring had received over 90% of the aldicarb applied in California. Total amounts of aldicarb applied over a 3-year period in sections containing sampled wells ranged from 0 to 823 kg ai. Twenty-seven of the 146 sampled wells were sampled in sections that had no reported aldicarb use because they were surrounded by sections in which large quantities of aldicarb were applied and/or they were located in areas of relatively shallow depth to groundwater of 30 meters or less. One-hundred and nineteen wells were sampled in sections that had in any one year total amounts of 1 to 528 kg applied.

In another recent survey, no aldicarb residues were detected in 100 wells sampled from four counties of the Central Valley of California (Rhone-Poulenc 1990). Since 1979, over 1500 wells have been sampled for aldicarb and none other than those in Del Norte and Humboldt counties have contained aldicarb residues (Maes et al. 1992).

The lack of aldicarb detections is surprising because well samples were taken from areas where residues of other pesticides have been found in well water and attributed to non-point source contamination. Aldicarb was used primarily for insect control on cotton in the sections sampled. Cotton (82.7%) and sugar beets (7.7%) account for nearly 90% of the total amount applied in

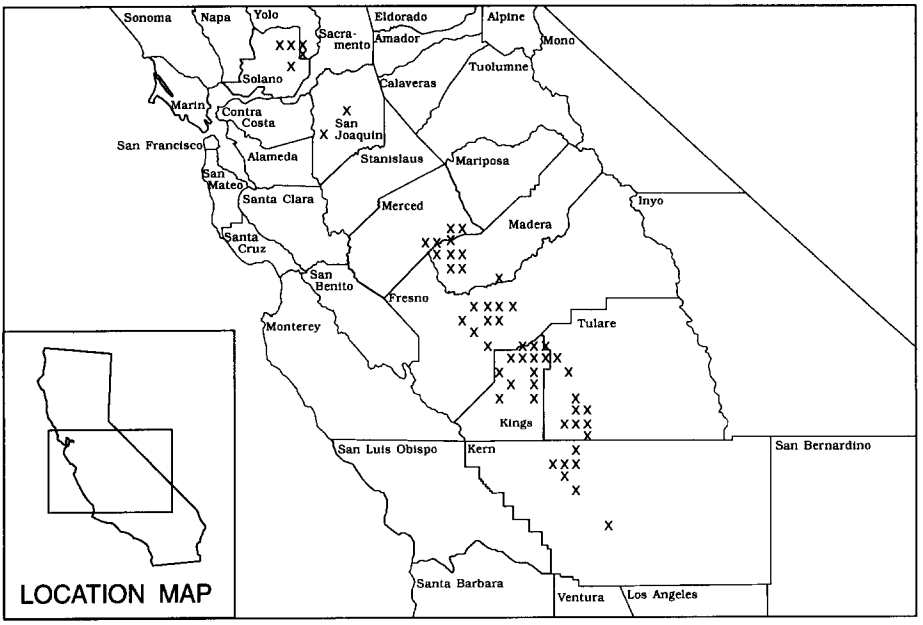

Figure 1. Each X represents an area in the Central Valley in which 1 or more wells were sampled during the three annual aldicarb surveys.

Table 1. The total number of wells sampled by year(s) and depth to groundwater for each of the counties that were included in 1989 - 1991 aldicarb well-monitoring surveys.

County	Number of Wells Sampled 1989	1990	1991	Total	Depth (m) to Groundwater
Fresno	7	9	10	26	12 - 52
Kern	5	10	10	25	27 - 81
Kings	5	10	10	25	8 - 34
Madera	8	7	7	22	18 - 34
Merced	8	3	3	14	20 - 43
San Joaquin	5	0	0	5	6 - 30
Solano	4	0	0	4	6 - 18
Tulare	4	8	10	22	17 - 58
Yolo	3	0	0	3	6
Totals	49	47	50	146	

California (CDFA 1987, 1988). In cotton, most aldicarb is placed 5-15 cm below the surface in raised beds at planting (Chemical and Pharmaceutical Press 1989). The shallow placement could reduce the potential for leaching because granules are above the area

where the greatest potential for drainage of irrigation water occurs. If placed where irrigation water contacts residues, then leaching could occur (Jones 1986). The extent of leaching would depend on the amount of percolated water produced from irrigation (Wyman et al. 1985, Bouwer 1987, Troiano et al. 1992).

Timing of applications may also be important in affecting the degradation of aldicarb. The majority of combined applications to cotton and sugar beets were made between April and June, after most of the year's rainfall was completed and when soil temperatures increased. Jones (1986) indicated that increasing soil temperatures in the unsaturated zone resulted in faster degradation of aldicarb residues. Soil temperatures measured at a depth of 15 cm in Central Valley counties during 1986 and 1987, ranged from 15.5 to 20°C in April and from 22.2 to 26.7°C in July (California Department of Water Resources 1992). In addition, a soil coring study conducted in Fresno County demonstrated that aldicarb sulfoxide, applied through drip irrigation over the spring and summer months, did not leach below 2 m in a sandy soil (Weaver et al. 1990).

In conclusion, contamination of groundwater by aldicarb appears to be dependent on the timing of applications and the placement of the active ingredient. Residues have been found in Del Norte and Humboldt counties of California where aldicarb had been applied in the fall and then subsequently exposed to large amounts of winter rain. Exposure to rainfall would cause a high probability for residues to be removed from the intended site of application. In contrast, aldicarb use in crops grown in the Central Valley is typified by spring applications and shallow placement in raised beds. This placement reduces the possibility for contact of residues with drainage water produced from irrigation. Spring applications would promote more rapid degradation of residues due to increases in soil temperatures.

Acknowledgments. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Department of Pesticide Regulation. The authors wish to express their gratitude to John Troiano for his advice and technical assistance and to Linda Heath Clark for preparing the map found in this article.

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