

# Department of Pesticide Regulation

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DATE:	June 30, 2002
SUBJECT:	SUMMARY OF RESULTS FOR FISCAL YEAR 2000/01 GROUND WATER PROTECTION LIST MONITORING FOR FENAMIPHOS, FENAMIPHOS SULFOXIDE, AND FENAMIPHOS SULFONE

## SUMMARY

Fenamiphos was chosen for monitoring from active ingredients (AIs) on the Ground Water Protection List (GWPL). Sixty wells were sampled in nine counties during September-November, 2001. No residues of fenamiphos or the degradates fenamiphos sulfoxide or fenamiphos sulfone were detected in any of the wells. Thirty-four wells did contain residues of one or more herbicides or herbicide degradates.

# BACKGROUND

In 1987, a group of 45 pesticide AIs was put into regulation as the Ground Water Protection List (Title 3, California Code of Regulations section 6800[b]), compounds which have the potential to pollute ground water through normal agricultural use. A monitoring protocol for GWPL AIs developed in 1988 required that compounds on the list be prioritized before monitoring was conducted (1). From 1992 through 1999, a total of 20 of the highest priority AIs (2)(3)(4)(5)(6)(7)(8)(9) were monitored with between 25 and 40 wells sampled for each AI.

A revised protocol for GWPL monitoring was approved in 1997 (10) and is now used to select Als for monitoring. Under the new protocol, compounds on the GWPL are not formally prioritized. Rather, Als are selected for monitoring based on current information about their physico-chemical characteristics, cultural practices for crops on which they are applied, detections in ground water anywhere in the United States, and any other pertinent information.



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Alachlor and metolachlor, along with two degradates of each, were selected using the revised protocol and were monitored during fiscal year (FY) 2001/02 (11).

The nematicide fenamiphos, along with the degradates fenamiphos sulfoxide and fenamiphos sulfone, was also selected for monitoring during FY 2001/02. Monitoring for these chemicals in California had been conducted by the Environmental Monitoring Branch (EM) in 1987 (12). In that study, 41 wells were sampled in Fresno, Kern, and San Joaquin counties but no fenamiphos residues were detected. Since that time, use of fenamiphos has increased in the state.

## **METHODS**

Wells were sampled for fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone during September-November, 2001. EM staff conducted some of the monitoring and some were done in collaboration with a study being conducted by the U.S. Geological Survey (USGS) and included samples collected by USGS staff and some co-sampling done by the two agencies.

The collaborative effort with the USGS included 29 wells. An EM staff member was present to co-sample 18 wells, including 3 monitoring wells. One bottle of water was taken for analysis by the California Department of Food and Agriculture (CDFA) laboratory. Eleven wells were sampled only by USGS personnel and one sample from each of seven of those wells was submitted to EM for analysis of the three fenamiphos compounds. For the remaining four wells, two primary well samples and a field blank sample were submitted to EM. One bottle was used for fenamiphos analysis and the other for analysis of herbicides in an analytical screen.

EM sampled an additional 31 wells. Areas to be surveyed for well sampling were selected based on Pesticide Use Report information for 1994-1999. Counties were listed in descending order for use of fenamiphos, and the counties with the greatest use were selected. Sections were chosen within each county where the greatest quantities of the pesticides had been applied. Those sections that had coarse soil types and shallow depth to ground water were targeted as primary locations for monitoring. Sampling crews drove through pre-selected sections of land in each county with the goal of sampling one well per section. For each well sampled, two primary, four backup, and two field blank samples were collected.

The CDFA laboratory performed analyses for fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone using APCI/LC/MS/MS with a reporting limit (RL) of 0.05 parts per billion (ppb) for all chemicals. Water samples from 60 different wells were analyzed. When more than one sample was submitted per well, the PTRL West, Inc. laboratory analyzed the second sample for 10 herbicide chemicals using a LC/MS/MS analytical screen. The analytes and their reporting limits were: atrazine 0.031 ppb, simazine 0.035 ppb, DEA 0.035 ppb, ACET 0.032 ppb, DACT 0.057 ppb, prometon 0.022 ppb, hexazinone 0.082 ppb, norflurazon 0.021 ppb, bromacil 0.022 ppb, and diuron 0.022 ppb. This analytical method was determined to

be unequivocal for the ten analytes (13). The CDFA laboratory also analyzed backup samples from five wells using a LC/MS/MS analytical screen with a RL of 0.05 ppb for the same chemicals analyzed for by the PTRL laboratory.

Use of fenamiphos was documented from Pesticide Use Reports for 1994-1999. The total number of pounds applied was determined for each section in which a well was sampled and also for the eight adjoining sections surrounding the monitored section. Land use characteristics were also determined for each section of land in which a well was sampled. The percentage of each land use type was determined based on 1993-1996 Department of Water Resources maps.

## RESULTS

A total of 60 wells were sampled in nine counties but no fenamiphos, fenamiphos sulfoxide, or fenamiphos sulfone residues were detected in any of the wells (Table 1). Several wells contained one or more herbicide residues, including nine in Fresno County, four in Kern County, two in Madera County, five in Merced County, three in Monterey County, three in San Joaquin County, three in Stanislaus County, and four in Tulare County. No herbicide residues were detected in any of the Sonoma County wells.

Atrazine was found in 4 wells, simazine in 19, bromacil in 9, diuron in 13, and norflurazon in 6. Also detected were degradates of atrazine and simazine:

DEA (2-amino-4-chloro-6-isopropylamino-s-triazine or deethylatrazine),

ACET (2-amino-4-chloro-6-ethylamino-s-triazine, also known as deisopropylatrazine or deethylsimazine), and DACT (2,4-diamino-6-chloro-s-triazine, also known as didealkylated triazine when it is not known if parent compound is atrazine or simazine). Residues of DEA were found in 3 wells, ACET in 24, and DACT in 20.

The analytical method used by the PTRL West laboratory is unequivocal for ten herbicide analytes; thus no verification of those results are necessary. When both laboratories analyzed water from the same wells, detections of the same herbicide compounds were made for 23 analyses. The PTRL West laboratory detected herbicide residue in five more samples where the CDFA laboratory did not; this was due to the lower RLs reported for the PTRL West laboratory.

Fenamiphos use data and land use characteristics are presented by county in Tables 2-10. In each table, the total number of pounds of fenamiphos, bromacil, diuron, simazine, and norflurazon applied during the years 1994-1999 are presented for the section in which a well was sampled (in section) and also as a total for that section plus the eight adjoining sections (9-section).

### DISCUSSION

Monitoring was first conducted for fenamiphos residues in California ground water in 1987. In that study 41 wells were sampled in Fresno County, Kern County, and San Joaquin County but no fenamiphos, fenamiphos sulfoxide, or fenamiphos sulfone was detected. Monitoring for these compounds was conducted again in 2001, approximately 14 years later. Again, none of the fenamiphos compounds were detected in any of 60 wells. The same counties used in the first study were again monitored, plus six additional counties where fenamiphos had been applied. Use of the compound in California showed a general increase over the past several years.

The widespread use of fenamiphos in the areas sampled suggested a potential for ground water contamination. Although no residues were detected, residues of certain herbicides were found in well water in 8 of the 9 counties tested. These detections indicated spatial vulnerability to ground water contamination in those areas. However, the lack of detections of the fenamiphos compounds indicates that movement is mitigated as a result of specific use practices, some aspect of the physical/chemical properties, or some combination of these factors.

## **REFERENCES CITED**

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- 2. Weaver, D. and J. Marade. July 15, 1992. Memorandum to K. Goh: Summary of results for FY 1991-92 ground water protection list monitoring.
- 3. Weaver, D. and J. Marade. August 23, 1993. Memorandum to J. S. Sanders: Summary of results for FY 1992-93 ground water protection list monitoring.
- 4. Weaver, D. and J. Marade. August 19, 1994. Memorandum to K. S. Goh: Summary of results for FY 1993-94 ground water protection list monitoring.
- 5. Weaver, D. and J. Marade. June 30, 1995. Memorandum to K. S. Goh: Summary of results for FY 1994-95 ground water protection list monitoring.
- 6. Weaver, D. and J. Marade. August 21, 1996. Memorandum to K. S. Goh: Summary of results for FY 1995-96 ground water protection list monitoring.
- 7. Weaver, D. and J. Marade. June 30, 1997. Memorandum to K. S. Goh: Summary of results for FY 1996-97 ground water protection list monitoring.

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- 9. Weaver, D. and J. Marade. March 19, 1999. Memorandum to K. S. Goh: Summary of results for FY 1998-99 ground water protection list monitoring.
- 10. Weaver, D. J. April 8, 1997. Revised protocol for selecting Ground Water Protection List active ingredients to be monitored under certain agricultural conditions.
- 11. Weaver, D. J. and C. Nordmark. May 6, 2002. Memorandum to Bob Rollins: Summary of results for fiscal year 2001-02 ground water protection list monitoring for alachlor, metoloachlor and two degradates of each.
- 12. Troiano, John, Bonnie Turner, and Nancy Miller. 1987. Sampling for residues of Fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone in well water. California Department of Food and Agriculture, Environmental Hazards Assessment Program, EH 87-8. 31 pp.
- 13. Spurlock, Frank. May 17, 2002. Memorandum to Kean S. Goh: Determination if the PTRL West, Inc., liquid chromatography/atmospheric pressure chemical-ionization/mass spectrometry/mass spectrometry method for selected herbicides and degradates in water (PTRL Method 1000Wymsms7b), meets the "unequivocal detection" criteria.

Table 1. Detections of pesticides in wells sampled for fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone during 2000-2001 Ground Water Protection List monitoring. No fenamiphos residues were found in any of the wells. Only data for pesticides that were detected are presented. For samples analyzed by two laboratories, CDFA<sup>a</sup> laboratory results are shown on the first line, PTRL<sup>b</sup> laboratory results are shown on the second line. One line of data is presented for samples analyzed only by the PTRL Laboratory or not analyzed for herbicides.

		Concentration, parts per billion										
County	Township/Range- Section	Well sampled by <sup>c</sup>	Atrazine	Simazine	DEA	ACET	DACT	Diuron	Bromacil	Norflurazon		
Fresno	13S/17E-28	USGS	_ d	-	-	-	-	-	-	-		
	13S/18E-21	USGS	-	-	-	-	-	-	-	-		
	14S/18E-15	USGS	-	-	-	-	-	~	-	-		
	14S/18E-30	DPR	ND <sup>e</sup>	ND	ND	0.041	0.064	ND	ND	ND		
	14S/19E-05	USGS	-	-	-	-	-	-	-	-		
	14S/21E-14	DPR/USGS	ND ND	0.141 0.131	ND ND	0.761 0.528	1.115 0.896	ND ND	ND ND	ND ND		
	14S/22E-03	DPR	ND ND	0.057 0.048	ND ND	0.347 0.249	0.473 0.461	0.145 0.096	1.054 0.971	0.05 0.03		
	14S/22E-08	DPR/USGS	ND 0.046	0.053 0.071	ND ND	0.410 0.347	0.456 0.450	0.434 0.310	0.231 0.226	ND 0.032		
	15S/19E-25	DPR	ND	0.05	ND	ND	ND	ND	ND	ND		
	15S/22E-03	DPR	ND	0.056	ND	0.041	ND	0.258	ND	ND		
	16S/19E-11	USGS	-	-	-	-	-	-	-	-		
	16S/19E-22	DPR	ND	0.063	ND	0.099	0.059	ND	ND	ND		

	Township/Range- Section		Concentration, parts per billion								
County		Well sampled by	Atrazine	Simazine	DEA	ACET	DACT	Diuron	Bromaci	Norflurazon	
Fresno	16S/20E-09	DPR/USGS	ND	0.064	ND	0.236	0.273	ND	ND	ND	
	16S/20E-15	DPR	ND	0.073	ND	0.126	0.104	ND	ND	ND	
	16S/20E-26	DPR	ND	0.096	ND	0.323	0.209	ND	ND	ND	
	16S/22E-34	USGS	-	-	-	-	-	-	-	-	
Kern	25S/25E-31	DPR	ND	0.054	ND	ND	ND	ND	ND	ND	
	25S/26E-01	DPR	ND	0.04	ND	0.052	ND	ND	ND	ND	
	25S/26E-16	DPR	ND	0.121	ND	0.203	0.118	0.186	0.025	ND	
	26S/25E-09	DPR	ND	ND	ND	ND	ND	0.023	ND	ND	
	28S/26E-11	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
Madera	11S/17E-28	DPR/USGS	ND 0.048	ND ND	0.050 0.062	0.084 0.125	0.231 0.225	ND ND	ND 0.033	ND ND	
	12S/17E-22	DPR/USGS	0.115 0.106	0.154 0.126	0.073 0.084	0.502 0.530	0.563 0.505	0.157 0.120	ND 0.033	ND ND	
	12S/18E-29	DPR/USGS	ND	ND	ND	ND	ND	ND	ND	ND	
Merced	05S/11E-34	DPR/USGS	ND	0.092	ND	0.298	0.594	ND	ND	ND	

			Concentration, parts per billion								
County	Township/Range- Section	Well sampled by	Atrazine	Simazine	DEA	ACET	DACT	Diuron	Bromacil	Norflurazon	
Merced	06S/12E-05	DPR/USGS	ND	ND	ND	ND	ND	ND	0.025	ND	
	06S/12E-34	DPR/USGS	ND	ND	ND	ND	ND	ND	0.025	ND	
	06S/12E-34 Monitoring Well	DPR/USGS	ND	ND	ND	ND	ND	0.034	ND	ND	
	07S/12E-18	DPR/USGS	ND	ND	ND	0.043	ND	ND	ND	0.046	
Monterey	15S/04E-08	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
	15S/04E-16	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
	15S/04E-26	DPR	ND	ND	ND	ND	ND	0.078	ND	ND	
	15S/04E-35	DPR	ND	0.041	ND	0.048	ND	ND	ND	ND	
	15S/04E-35	DPR	ND	ND	ND	ND	ND	ND	0.036	ND	
	15S/04E-36	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
	16S/04E-35	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
	20S/08E-21	DPR	ND	ND	ND	ND	ND	ND	ND	ND	
San Joaquin	04N/06E-20	USGS	-	-	-	-	-	-	-	-	

			Concentration, parts per billion							
County	Township/Range- Section	Well sampled by	Atrazine	Simazine	DEA	ACET	DACT	Diuron	Bromacil	Norflurazon
San Joaquin	04N/07E-21	USGS	ND	ND	ND	ND	ND	ND	ND	ND
	01S/07E-27	DPR/USGS	ND	ND	ND	ND	0.065	ND	ND	ND
	02S/07E-20	DPR/USGS	ND	ND	ND	ND	ND	ND	ND	ND
	02S/07E-20 Monitoring Well	USGS	ND	ND	ND	0.068	0.513	ND	ND	ND
	02S/07E-22	USGS	ND	ND	ND	ND	ND	ND	ND	ND
	02S/09E-09	DPR/USGS	ND	ND	ND	0.057	0.262	0.044	ND	ND
Sonoma	09N/09W-02	DPR	ND	ND	ND	ND	ND	ND	ND	ND
	10N/09W-27	DPR	ND	ND	ND	ND	ND	ND	ND	ND
	10N/09W-36	DPR	ND	ND	ND	ND	ND	ND	ND	ND
	10N/10W-12	DPR	ND	ND	ND	ND	ND	ND	ND	ND
	10N/10W-12	DPR	ND	ND	ND	ND	ND	ND	ND	ND
	11N/10W-08	DPR	ND	ND	ND	ND	ND	ND	ND	ND
Stanislaus	03S/08E-05	USGS	ND	ND	ND	ND	ND	ND	ND	ND
	03S/10E-35	DPR/USGS	ND	ND	ND	ND	ND	ND	ND	ND
	03S/11E-30	DPR/USGS	0.054	ND	0.074	0.032	ND	ND	ND	ND

			Concentration, parts per billion							
County	Township/Range- Section	<sup>inge-</sup> Well sampled by	Atrazine	Simazine	DEA	ACET	DACT	Diuron	Bromacil	Norflurazon
Stanislaus	04S/11E-31	DPR/USGS	ND	ND	ND	0.064	0.094	ND	ND	ND
	04S/11E-31 Monitoring Well	DPR/USGS	ND	ND	ND	ND	0.072	ND	ND	ND
Tulare	17S/26E-30	DPR	ND	0.096	ND	1.172	1.955	0.290	1.015	0.03
	17S/26E-35	DPR	ND	0.109	ND	0.539	0.775	0.155	ND	0.039
	18S/26E-04	DPR	ND	0.101	ND	0.249	0.288	0.053	ND	ND
	18S/27E-31	DPR	ND	0.064	ND	0.052	ND	0.038	ND	0.102
	24S/25E-23	DPR	ND	ND	ND	ND	ND	ND	ND	ND

<sup>a</sup> All samples analyzed by the CDFA laboratory were tested for fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone. Some samples were also tested for atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, deethylatrazine (DEA), deisopropylatrazine (ACET), and didealkylated triazine (DACT). The reporting limit for all chemicals was 0.05 parts per billion (ppb).

<sup>b</sup> All samples analyzed by the PTRL West laboratory were tested for atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, simazine, deethylatrazine (DEA), deisopropylatrazine (ACET), and didealkylated triazine (DACT). The reporting limits in ppb for the PTRL West laboratory were: atrazine (0.031), bromacil (0.022), diuron (0.022), hexazinone (0.082), norflurazon (0.021), prometon (0.022), simazine (0.035), DEA (0.035), ACET (0.032) and DACT (0.057).

<sup>c</sup> Wells were sampled by staff from the Department of Pesticide Regulation (DPR), staff from the U. S. Geological Survey (USGS) or co-sampled by staff from both agencies.

 $^{d}$  - = not analyzed for.

<sup>e</sup> ND = none detected at the reporting limit (RL) for that chemical. The RL is the smallest amount that can be reliably detected in a laboratory test; the RL is set by the testing laboratory for each chemical.

Contact <u>GWPP@cdpr.ca.gov</u> for tables that have been removed and references not currently available on the web. Tables that have been removed are listed below.

Table 2. Fresno County -Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 3. Kem County -Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more well were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 4. Madera County -Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 5. Merced County -Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 6. Monterey County-Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

TabJe 7. San Joaquin County-Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 8. Sonoma County-Use of fenamiphos and selected herbicides for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 9. Stanislaus County-Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.

Table 10. Tulare County -Use of fenamiphos and selected herbicides and land use characteristics for sections of land in which one or more wells were sampled for 2000-2001 Ground Water Protection List monitoring.