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DATE: February 26, 2010

SUBJECT: STUDY 182/228-PRELIMINARY SUMMARY OF RESULTS FOR WELL SAMPLING FROM 1999 THROUGH 2009

SCOPE OF THE MEMORANDUM

This memorandum summarizes results of a monitoring program that documents pesticide concentrations in domestic wells located in the San Joaquin Valley of California. The wells were sampled annually from 1999 through 2009. This memorandum summarizes the annual sampling with respect to number of wells sampled, the number of wells with detections of residues, and the mean concentration of detected residues. A subsequent report will present in depth statistical analysis and discussion of measured trends.

BACKGROUND

In 1982 the Department of Pesticide Regulation (DPR) reported the first incidence of simazine in groundwater in California (Weaver et al., 1983). In 1983 DPR found simazine in soil to a depth of 28 feet at concentrations of 2 to 55ug/L (ppb) (Zalkin et al., 1984). In 1985 California Assembly Bill AB2021, called the Pesticide Contamination Prevention Act, was passed in an attempt to prevent further contamination of California groundwater by pesticides (Food and Agriculture Code, Section 13141-13152). DPR first developed regulations for use of pesticides detected in groundwater in the late 1980’s. Use was regulated in areas denoted as Pesticide Management Zones, which were sections of land where residues were detected in well water. DPR’s Ground Water Protection Program obtains samples primarily for domestic wells because they are more susceptible to contamination than municipal wells due to location in rural, agricultural areas and to harvesting of water from shallow aquifers. The groundwater regulations were revised in May of 2004. The revisions increased the definition of a vulnerable area to include geographic data and they increased restrictions on use by requiring a conditional permit for use in vulnerable areas that are now designated as Ground Water Protection Areas (Troiano, et al., 2000).

This monitoring well network was developed as a measure of success of regulations enacted to protect groundwater from further contamination by pesticide residues. In anticipation of the passage of revised regulations, well water sampling was initiated in the Fall of 1999.

This study will extend many years because Spurlock et al., 1997 concluded that a median estimated time between herbicide application and subsequent detection in groundwater was around six to nine years. The last sampling interval covered in this summary is for the Spring of 2009 so the results are considered as a background indication of effects occurring prior to the onset of the 2004 revised regulations. Potential effects on well water concentration due to the revisions are not expected until at least one to four more years.

MATERIALS AND METHODS

The wells chosen for this study are located in Tulare and Fresno Counties in areas that have been identified as being susceptible to the movement of pesticides to groundwater based on soil type and average depth to ground water (Troiano et al., 1987). Sections of land determined to be the most susceptible are those containing coarse soils because pesticides may leach to groundwater, and those containing a hardpan layer because pesticides may move off site in runoff water to areas or structures that provide fast movement to groundwater. Wells were chosen in 1999 that had been sampled previously by DPR and that were found to have positive finds for simazine, bromacil, or diuron (Garretson, 1999). Permission to sample each well was obtained from 75 well owners; 33 in Fresno County coarse soil sections, 18 in Fresno Co. hardpan, 3 in Tulare County coarse, and 21 in Tulare County hardpan. Sampling began in the fall of 1999 following procedures in DPR SOP#FSWA001.00 **(**Marade, 1996). A chain of custody record was completed and accompanied each sample.

Collection and transport of samples followed DPR SOP#QAQC004.01 Transporting, Packaging and Shipping Samples from the Field to the Warehouse or Laboratory (Jones, 1999). The California Department of Food and Agriculture, Environmental Monitoring Section conducted chemical analysis of all samples. Quality control was conducted in accordance with DPR SOP#QAQC001.001 Chemistry Laboratory Quality Control (Segawa, 1995).

RESULTS

Yearly Summary of Number of Wells Sampled and Pesticide Residues Monitored:

<u>1999</u>
Fall: 75 wells were sampled in August and September.

The samples were analyzed for: atrazine, simazine, diuron, bromacil, prometon, prometryn, hexazinone, cyanzine, metribuzin, norflurazon, DEA (a metabolite of atrazine), ACET and DACT (metabolites of atrazine and simazine).

<u>2000</u>
Spring: 74 wells were sampled in March and April.

Fall: 70 wells were sampled in November and December.

<u>2001</u>
Spring: 71 wells were sampled in March, April and May.

Nitrate was added at the request of the owners in Spring 2001 and was included in all future sampling.

Fall: 71 wells were sampled in August and September.

Prometryn, cyanzine and metribuzin were not detected in the four previous samplings so they were excluded from the analysis as of Fall 2001.

<u>2002</u>
Spring: 70 wells were sampled in March, April and May.

Three degradation products of hexazinone (A1-G3453, B-A3928, IN-G3710) were added to the analysis when the laboratory had the capability to include them in the screen. The ratio of a degradation product to its parent compound may be one factor that can help to determine if positive results are due to new pesticide application. None of the hexazinone degradation products were found in the Spring 2002 sampling and they were not included in the analysis for any future sampling.

Fall: 69 wells were sampled in October.

The objective of the well monitoring study is to determine if there are changes in pesticide concentrations over time. Single samples are obtained and analyzed for each well annually. In 2002, duplicate samples were obtained and analyzed for each well. This provided a measure of the variability due to lab procedures, instruments, and sample handling. The amount of variability was compared to that measured by the annual single well sampling. This comparison facilitated a estimate of the sensitivity of analytical tests, especially for pesticide residues measured in low concentrations in wells. This was a onetime study and was not repeated.

2003

Spring: 72 wells were sampled in April and May.

The Fall sampling interval was dropped from the schedule due to personnel and budget limitations. Sampling was initially scheduled for twice a year, once in the Spring and then again in the Fall for each well. The concern was that aquifer levels normally drop between the Spring and Fall due to pumping for crop irrigations. This drop in water level could have caused variation in concentrations. An analysis of the paired Spring and Fall data indicated that for wells where concentrations remained similar throughout the years, the Spring and Fall concentrations were also similar. For wells where trends were noted the fall concentrations followed the trend line. The conclusion was that a single Spring sampling was adequate to track changes and that a long term commitment was the more important factor in measuring potential trends in concentration.

2004

Spring: 68 wells were sampled in May and June.

Desmethyl norflurazon, a metabolite of norflurazon, was added to the analysis when the laboratory was able to add it to the screen. It was found in almost half of the wells and was included in all future sampling.

2005

Spring: 68 wells were sampled in May and June.

2006

Spring: 66 wells were sampled in May and June.

2007

Spring: 69 wells were sampled in April and May.

2008

Spring: 68 wells were sampled in March, April and May.

2009

Spring: 68 wells were sampled in March, April and May.
Tebuthiuron was added to the analysis when the laboratory was able to add it to the screen. There were no detections of tebuthiuron.

Summary of Detection Frequency and Concentration of Residues:

A summary of the detection frequency is presented in Table 1 and Figure 1 where the specific number of wells with detections is given in Table 1 and a visual representation of the annual fluctuations of the percentage of wells with detections is graphed in Figure 1. Simazine and its degradation products, ACET and DACT, were the most frequently detected residues where residues were present in nearly all the wells at one or more sampling intervals. Simazine is a pre-emergence herbicide with use on a wide variety of crops in this area of the valley. The high frequency of detection is a reflection of its high use pattern and high potential for the parent and degradation products to move to ground water. Diuron was found in at least half the wells and bromacil was present in at least a third of them. These are both pre-emergence herbicides where diuron again has a broad spectrum of use. Bromacil’s use is restricted to citrus crops and it is in the citrus belt along the Eastern foothills in Fresno and Tulare Counties where the detections were concentrated. Norflurazon was present in over 20% of the wells, but its degradation product was found in almost half the wells. Norflurazon is another pre-emergence herbicide with a high potential to move to groundwater. As the other pre-emergence herbicides are being detected in groundwater and their use subject to restrictions, norflurazon’s use increased over time, as potentially reflected by the increase in detection frequency over time (Figure 1). Atrazine, prometon and hexazinone are pre-emergence herbicides with much lower use rates in this area and the residues were found at a much lower frequency in three wells or less during the course of the study.

The average concentration for wells with detections at each sampling is given in Table 2 and the annual average concentration for wells with detections is given in Figure 2. Figure 2 provides a visual for potential changes in concentration over time. Bromacil concentration was the highest for a single residue with the average value close to 1ug/L. The triazine breakdown products, ACET and DACT had the next highest levels and were generally found at higher levels than their parent, simazine (Troiano and Nordmark, 2002). ACET is formed first and then DACT is formed next during degradation. The levels of DACT are the highest, reflecting long-life and stability in ground water.

Visual observation of Figure 2 indicates potential decreasing concentration for simazine and diuron with a concomitant increase in norflurazon concentration. As indicated previously, this effect may be related to changes in use patterns that were fostered by the previous enactment of regulations: Growers would switch use from a regulated to a nonregulated pesticide where simazine and diuron were regulated before norflurazon. Further analysis is being conducted to determine a statistical basis for potential trends in the data.

Table 1: Number of wells sampled annually that contained residues for each pesticide residue.

	# Sampled	Atrazine	Simazine	Diuron	Prometon	Bromacil	Hexazinone	Norflurazon	DEA	ACET	DACT	DMN
Fall 1999	75	4	65	45	1	30	0	13	6	71	64	
Spring 2000	74	3	61	37	1	28	1	13	3	66	66	
Fall 2000	70	3	63	43	1	26	0	14	5	69	60	
Spring 2001	71	3	61	42	1	28	1	16	6	67	61	
Fall 2001	71	3	57	42	2	26	1	13	5	63	60	
Spring 2002	70	3	65	45	1	27	0	11	9	66	62	
Fall 2002	69	3	60	42	1	28	1	14	8	60	59	
Spring 2003	72	3	62	44	1	29	0	15	7	64	62	
Spring 2004	68	3	55	39	1	23	0	17	6	59	58	30
Spring 2005	68	3	48	37	1	23	0	16	4	60	51	31
Spring 2006	66	3	48	34	1	25	0	15	5	55	55	29
Spring 2007	69	2	53	32	1	22	0	20	4	59	59	31
Spring 2008	68	3	47	34	1	23	0	14	4	58	58	30
Spring 2009	68	2	41	31	1	21	0	14	3	60	58	32

Figure 1: Plot of the annual percentage of wells sampled that contained residues for each pesticide residue.

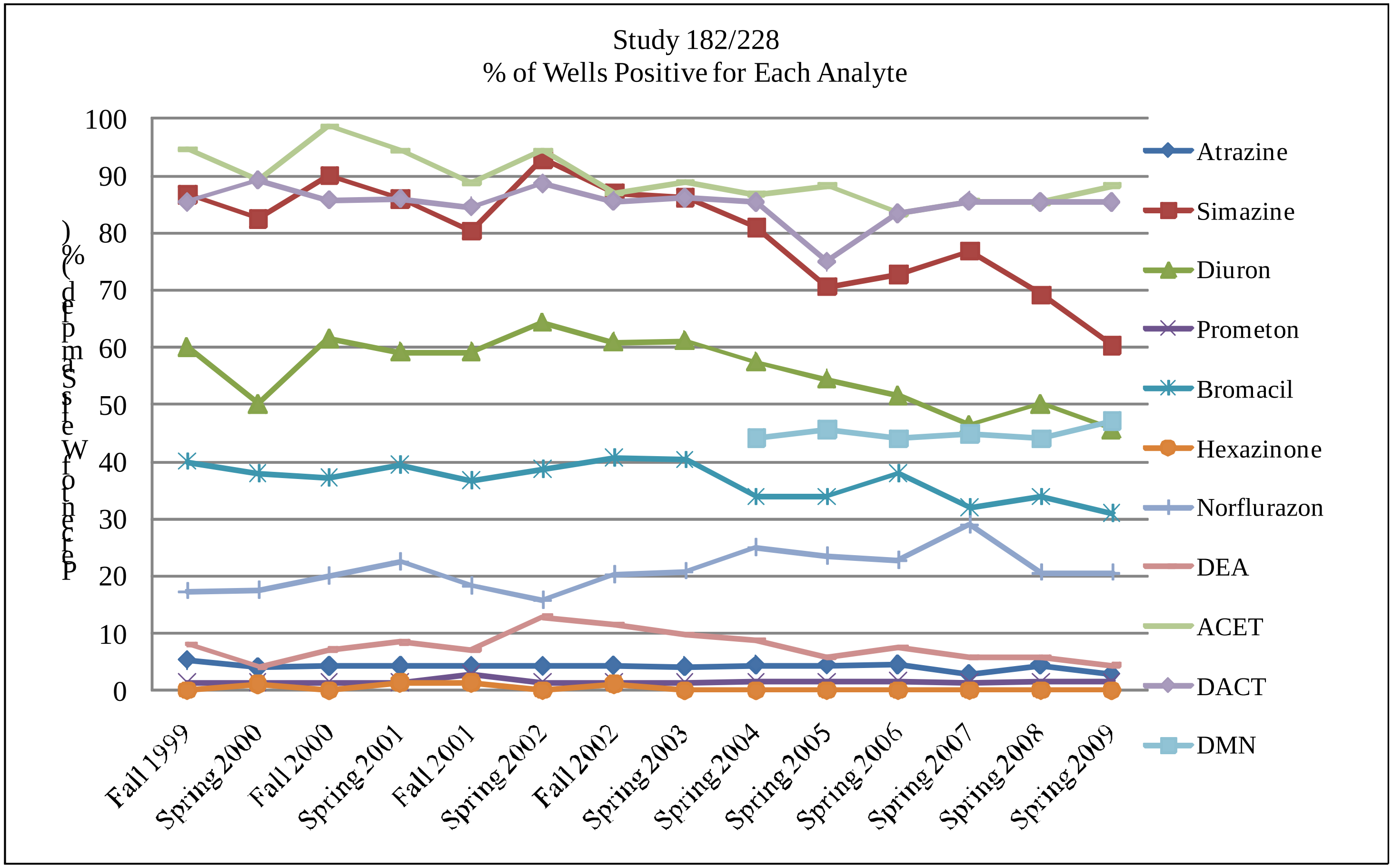
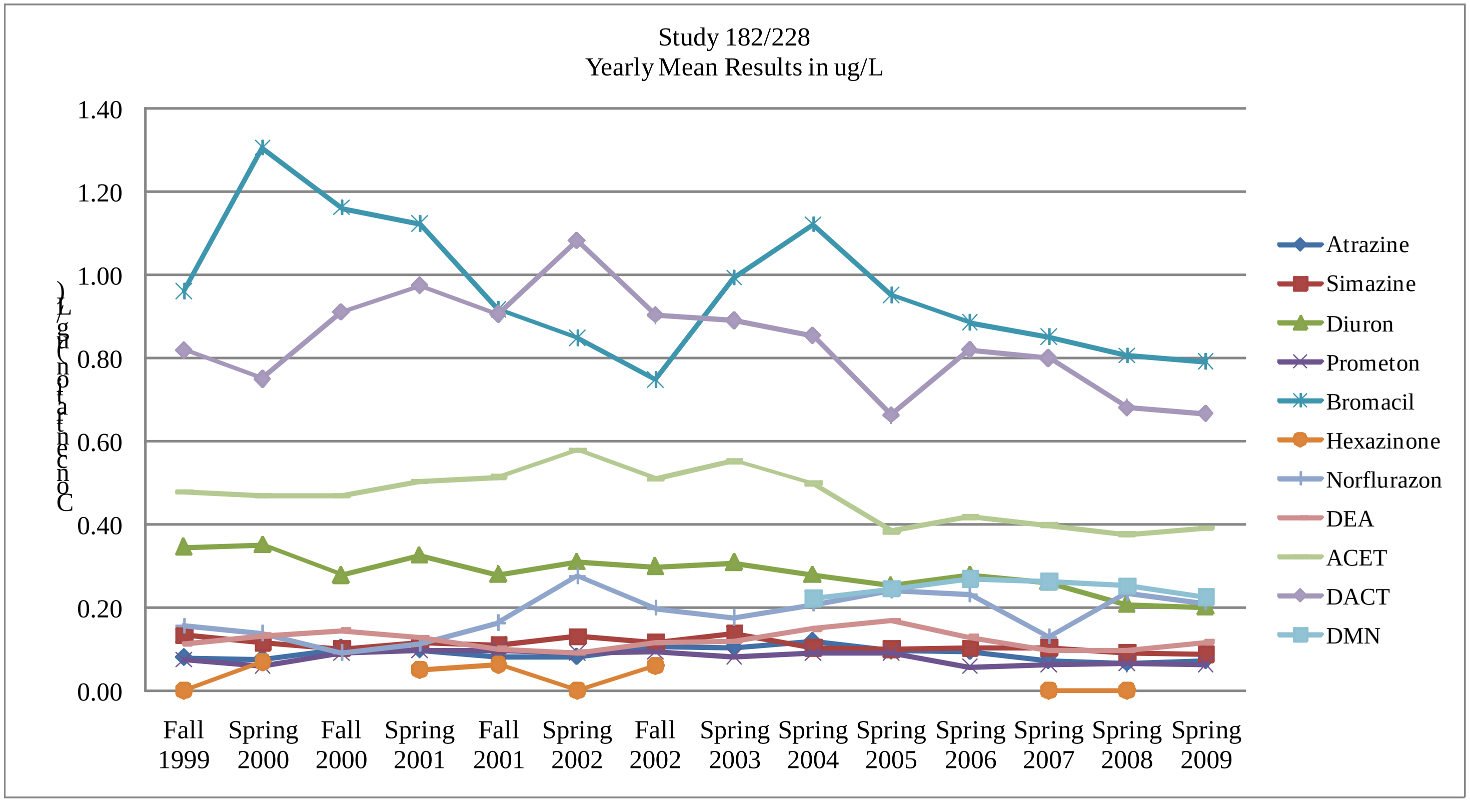


Table 2: Average annual concentration for wells sampled that contained pesticide residues.

	Atrazine	Simazine	Diuron	Prometon	Bromacil	Hexazinone	Norflurazon	DEA	ACET	DACT	DMN
Fall 1999	0.08	0.13	0.35	0.07	0.96		0.16	0.11	0.48	0.82	
Spring 2000	0.08	0.11	0.35	0.06	1.31	0.07	0.14	0.13	0.47	0.75	
Fall 2000	0.10	0.10	0.28	0.09	1.16		0.09	0.15	0.47	0.91	
Spring 2001	0.10	0.12	0.33	0.10	1.12	0.05	0.11	0.13	0.50	0.97	
Fall 2001	0.08	0.11	0.28	0.10	0.92	0.06	0.16	0.10	0.51	0.91	
Spring 2002	0.08	0.13	0.31	0.09	0.85		0.28	0.09	0.58	1.08	
Fall 2002	0.11	0.12	0.30	0.09	0.75	0.06	0.20	0.12	0.51	0.90	
Spring 2003	0.11	0.14	0.31	0.08	0.99		0.18	0.12	0.55	0.89	
Spring 2004	0.12	0.10	0.28	0.09	1.12		0.21	0.15	0.50	0.85	0.22
Spring 2005	0.10	0.10	0.25	0.09	0.95		0.24	0.17	0.38	0.66	0.25
Spring 2006	0.09	0.10	0.28	0.06	0.88		0.23	0.13	0.42	0.82	0.27
Spring 2007	0.07	0.10	0.26	0.06	0.85		0.13	0.10	0.40	0.80	0.26
Spring 2008	0.07	0.09	0.21	0.07	0.81		0.24	0.10	0.38	0.68	0.25
Spring 2009	0.07	0.09	0.20	0.06	0.79		0.21	0.12	0.39	0.67	0.23
MEAN	0.09	0.11	0.28	0.08	0.96	0.06	0.18	0.12	0.47	0.84	0.25
SD	0.02	0.02	0.04	0.02	0.16	0.01	0.05	0.02	0.06	0.12	0.02
CV	18	14	16	19	17	14	30	18	14	14	8

Figure 2: Plot of the annual mean concentration for each pesticide residue for wells with detections.



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