

A TEST OF PROCEDURES FOR DETERMINING THE GROUND WATER PROTECTION LIST

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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"A Test of Procedures for Determining
the Ground Water Protection List"

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PURPOSE

The Environmental Hazards Assessment Program conducted a well water monitoring study to examine the validity of the procedure the Branch uses to establish the Ground Water Protection List contained in the regulations implementing the Pesticide Contamination Prevention Act.

BACKGROUND

Although the Department of Pesticide Regulation's (DPR) ground water program began before its passage, the current centerpiece of ground water protection is the Pesticide Contamination Prevention Act (PCPA, AB 2021, Chapter 1298, Statutes of 1985). It added Article 15 to Chapter 2 of Division 7 of the Food and Agricultural Code. The purpose of the PCPA is to prevent further pesticide pollution of the ground water aquifers of the State.

The PCPA requires the Director of DPR to establish, by regulation, a list (called the Ground Water Protection List) of pesticide active ingredients that could potentially leach to ground water. These potential leachers are identified to help focus DPR monitoring efforts on those pesticides most likely to move to ground water.

These potential leachers are pesticide active ingredients that have not been detected in ground water due to agricultural use. However, they have physical and chemical properties, which characterize their persistence and mobility, similar to active ingredients that have been detected due to such agricultural use. They are identified by examining data on these physical and chemical properties which has been submitted by registrants. These data are compared to standards, called Specific Numerical Values. The Department has established these Specific Numerical Values based on characteristics of known, leaching pesticides. An active ingredient is considered a potential leacher when its Specific Numerical Values exceed certain levels, and when the chemical is applied to the soil or the application is followed by irrigation.

STUDY METHODS

Two hundred and sixteen wells were sampled, six wells for each of 36 compounds. The total number of wells was based on the maximum that time and resources would allow. Particular wells were selected for



sampling based on location in sections with the highest reported use in 1988 of the particular compound. Of the 36 compounds, 27 were potential leachers and nine were compounds unlikely to leach to ground water, based on a comparison of their physical and chemical properties to the Specific Numerical Values.

RESULTS

Four of the 27 potential leachers were detected in ground water: atrazine, bromacil, diuron, and simazine. Of the 162 wells sampled, two contained residues of diuron, four contained residues of simazine, one contained residues of bromacil, and one contained residues of atrazine. The four were all chemicals previously detected in California ground water.

None of the nine compounds in the non-leacher group were detected in well water samples.

CONCLUSIONS

The results of this study support using the current methodology to identify potential leachers to be placed on the Ground Water Protection List because there was a significantly higher rate of positive wells amongst wells sampled for Ground Water Protection List compounds. Since the four compounds detected in ground water in this study have been found previously in ground water in California, the results of this study are inconclusive for determining whether the Ground Water Protection List procedures are capable of correctly identifying leachers which have not yet been detected. However, future ground water monitoring conducted by this Department will continue to sample for compounds on the Ground Water Protection List and will address this question.



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8/13/92

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

ABSTRACT

The Pesticide Contamination Prevention Act mandates the establishment of the Ground Water Protection List (GWPL). Compounds on this list are monitored for in ground water. To examine the validity of the procedure used to establish the GWPL, 216 wells were sampled, 6 wells for each of 36 compounds. The 36 compounds represented nine compounds unlikely to leach into ground water and 27 compounds with the potential to leach to ground water. Only four compounds, all on the list of potential leachers, were detected in ground water: simazine, atrazine, diuron and bromacil. None of nine compounds on the potential non-leacher list were detected. The difference in rate of positives was statistically significant when comparing the number of wells in each group, but not significantly different when comparing the number of pesticides. The latter nonsignificance was likely due to the low statistical power of the test when using pesticides as the experimental unit. The results support the methodology used to identify potential leachers to be placed on the Ground Water Protection List. Since the four detected compounds have been found previously in ground water in California, the results of this study do not clarify whether the GWPL procedures are capable of correctly identifying previously undetected leachers.

Both the procedures used to establish the Ground Water Protection List and the techniques employed to target and sample wells are subject to variability. This variability is caused by variability in the estimation of physicochemical properties and potential under-reporting in the 1988 and 1987 pesticide use reports which were used for locating high use sections in this study. Variability also occurred in the procedure to identify wells to be sampled because wells were not available for sampling in some sections that had high pesticide use. Specific Numerical Values (SNVs), which are cut off points based on physicochemical properties of known leachers, embody a conservative bias in the sense that they are set to minimize the possibility of failing to detect a potential leacher. The sampling results were consistent with this conservative bias. As a screening model, the SNV procedure is susceptible to criticism including the applicability of laboratory measured adsorption compared to field adsorption, the possible influence of agronomic practices and ambiguity in the application of soil degradation rates.

Suggestions are made to improve the criteria and data used to establish the GWPL, and to facilitate sampling for compounds on the GWPL.

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such product.

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INTRODUCTION

The Pesticide Contamination Prevention Act (AB2021) outlined a procedure for identifying pesticides with the potential to leach to ground water. According to this procedure, pesticides that are determined to be both mobile and persistent in soil, and are applied in a specified manner, are considered potential leachers. Presumably, mobility and persistence are indicators of leachability because mobile compounds do not adhere to the soil or are highly water soluble, and persistent compounds do not degrade quickly. In AB2021, it is assumed that certain physicochemical characteristics can be used to characterize the relative mobility and persistence of a pesticide. Water solubility and soil adsorption coefficients are used to indicate relative pesticide mobility, while hydrolysis half-life, aerobic and anaerobic soil metabolism half-lives, and field dissipation half-life are used to indicate relative pesticide persistence.

To determine relative mobility and persistence of pesticides, the Department of Pesticide Regulation (DPR) is required to establish specific numerical values (SNVs) for these six physicochemical characteristics (Wilkerson, 1986; Johnson, 1988; Johnson, 1989) and then compare actual values developed for each pesticide against these SNVs. Pesticides with values that exceed (or are less than in the case of soil adsorption coefficient) these SNVs for any characteristic of mobility and any characteristic of persistence are placed on the B2 list (Food and Agricultural Code Section 13144 (b)(2)). Any pesticides on the B2 list which are intended to be applied to or injected into the soil by ground-based application equipment or by chemigation, or the labels of which require or recommend that application be followed within 72 hours by flood or furrow irrigation, are placed on the Ground Water Protection List (GWPL). Compounds on GWPL are targeted in the monitoring program to determine if they have reached or threaten

to reach ground water. "Soil applied" and "ground-based application equipment" are defined in regulation by a list of phrases which are found on pesticide labels and connote pesticide application to soil (California Code of Regulations, Section 6000.5).

Before sampling begins, the GWPL is stratified according to the Protocol for Ranking the Ground Water Protection List (Environmental Hazards Assessment Program (EHAP) 1988). In brief, this establishes three categories of priority for sampling. The first priority category consists of pesticides which have been detected in ground water due to non-point sources or which are ranked as high on the SB950 priority list, which ranks chemical by their toxicity. The second category is based on sales data or physicochemical factors. The third category consists of those compounds left over. Categories of priority indicate the order in which compounds should be monitored and the number of wells to be sampled for each. This stratification protocol will not be examined further in this study.

The question arises as to whether compounds placed on the GWPL are more likely to be found in ground water than compounds not on the list. It is the aim of this study to examine the validity of the procedure to identify compounds that leach to ground water.

METHODS

Study Design

Selection of chemicals. For this experiment, 153 active ingredients with sufficient information to classify were placed into four groups. These groups are as follows: (1) B2 list compounds applied to soil (B2-SA, equivalent to the GWPL); (2) B2 list compounds not applied to soil (B2-NSA); (3) non-B2 list compounds applied to soil (NB2-SA); and (4) non-B2 list compounds not applied to soil (NB2-NSA). The SNV cutoff values used to produce the B2 list were soil adsorption coefficient (K_{oc}) 2400 cm³/g, hydrolysis half life 9 days, aerobic soil metabolism half life 730 days and solubility 4 ppm (Johnson 1988). Physicochemical data developed by registrants for each compound was obtained from the physicochemical database. Because of resource constraints, ground water sampling was limited to active ingredients from the two extreme groups: NB2-NSA and B2-SA. By not sampling the other two groups, the experiment lost the ability to determine which selection factor, physicochemical characteristics or soil application, may have had the largest influence on identifying pesticides that leach to ground water.

In addition to physicochemical properties and soil-applied status, the following information was collected, if available, for each compound: the index of chemical analytical method feasibility, pounds of active ingredient (a.i.) used in 1988, and the number of nationwide studies where the pesticide was detected in ground water due to non-point sources (Tables 1 and 2).

The study was limited to active ingredients for which chemical analytical techniques currently existed or could easily be developed (method index 1 or 2 in Tables 1 and 2). Consequently, compounds with a method rating of 3 had no existing reliable chemical analysis techniques and were not considered for sampling. Of the 82 compounds on the B2 list, 50 were soil applied, and of those, 29 compounds had a method index of 1 or 2. Of the 70 compounds on the NB2 list, 24 were soil applied, 18 were not soil applied and 28 either had no active registrations or no reported use. Of the 18 that were not soil applied,

10 compounds had a method index of 1 or 2 (Table 1). Because the number of chemicals in both the NB2-SA and B2-SA groups with an index of 1 or 2 was small, the Protocol for Ranking the Ground Water Protection List (EHAP 1988) was not used for this study.

Table 1. Non-B2, non-soil applied compounds (NB2-NSA) with available chemical analytical techniques (method index 1 or 2) NA = not available.

<u>Code</u> [†]	<u>Name</u>	<u>Method Index</u> [‡]	<u>Reported Lbs used in 1988</u>	<u>G.W. Detect</u> [¶]
1552	benomyl	1	71373	0
834	bromoxynil octanoate	2	97409	NA
2171	cypermethrin	2	106052	0
346	dicofol	2	391067	0
1963	fenvalerate	2	103104	0
111	formetanate	2	159679	NA
418	naled	2	236623	0
335	phosmet	1	120916	0
445	propargite	2	1650087	0
190	S,S,S-tributyl phosphorotrithioate	2	921590	0

[†]Internal CDFA chemical code.

[‡]Index of 1 and 2 indicates chemical analytical techniques exist or could easily be developed, respectively.

[¶]A '0' indicates compound has been sampled for in 1 or more ground water studies in the U.S.A. and no positive samples have been found. A positive number denotes the number of different studies which have found positive detections of compound in ground water.

Statistical methods. The ideal sampling unit would consist of the individual pesticides in each of the two categories, B2-SA and NB2-NSA. However, because the sample size of both groups was small, the statistical power using chemicals as the sampling unit would be low. Consequently, data were analyzed using both chemicals and samples (=wells) as the experimental unit. For either analysis the hypothesis structure was as follows:

Null: $p_1 = p_2$
 Alternate: $p_1 - p_2 > 0$

where p1 and p2 are both respectively for B2-SA and NB2-NSA, the fractions of either positive chemicals or positive wells . There is, however, a subtle difference between the hypothesis structure with the two different kinds of experimental units. With pesticides as the experimental unit, the statistical procedure tests for the difference between the two pesticide populations identified by the administrative procedures developed to create and administer the GWPL. With wells as the experimental unit, the test compares two populations of wells. These two well populations can be described as wells in high-use sections of the

Table 2. B2, soil applied compounds (B2-SA) with available chemical analytical techniques. See footnotes in Table 1.

<u>Code</u>	<u>Name</u>	<u>Method</u>	<u>Reported Lbs used in 1988</u>	<u>G.W. Detect</u>
806	2,4-d dimethylamine salt	1	354758	NA
678	alachlor	1	43360	21
575	aldicarb	1	367452	10
45	atrazine	1	86923	31
314	azinphos-methyl	1	529069	1
70	bensulide	2	43239	0
83	bromacil	1	53123	3
1640	cyanazine	1	233255	8
198	diazinon	1	751123	1
1995	diethatyl-ethyl	2	16974	NA
216	dimethoate	1	521703	0
230	disulfoton	1	160852	0
231	diuron	1	548198	3
404	ethoprop	1	4700	1
1857	fenamiphos	1	85970	0
254	fonofos	1	42876	3
361	linuron	1	25583	1
2132	metalaxyl	2	51864	1
375	methiocarb	1	8446	0
1996	metolachlor	1	14203	13
1692	metribuzin	1	12903	10
449	molinate	1	1515856	0
2017	oxadiazon	2	10995	0
382	oxydemeton-methyl	2	127048	0
459	parathion	1	1103494	0
499	prometon	1	1434	2
502	prometryn	1	49589	0
531	simazine	1	299797	13
1810	tebuthiuron	2	11178	NA

potential leacher and non-leacher pesticides. Consequently, any difference in the rate of positive wells between potential leacher and non-leacher well groups would be interpreted as being due to the nature of the pesticide and its propensity to leach. Various rules were adopted in well selection to assure that sampled wells were distributed over at least two or more counties. Testing for the difference between the two groups of compounds using wells as the experimental unit was judged to be a reasonable substitute for the lower power test using compounds as the experimental unit.

Sampling data were analyzed using both wells and chemicals as the experimental unit with Pearson chisquare and likelihood ratio chisquare (Dixon et al. 1988). The one-sided significance levels were determined by halving the 2-sided significance levels reported by BMDP (Dixon et al. 1988). Zeros in the tables were included in the analysis since they represented sampling results. With wells as the experimental unit, and assuming a 10% detection difference between NB2-NSA and B2-SA, a rough calculation yielded 6 wells per chemical as an adequate sample size.

Selection of sections. California is divided into surveying units designated by a township and range measurements in relation to a base meridian. These square units are 36 square miles in area and, in turn, are subdivided into 1 square mile units called sections. Pesticide use information includes location information in the form of township, range and section. To increase the probability of detecting a compound in ground water, sections with the highest use history in 1987 and 1988 were selected for potential sampling. Use history was not available for 1989. Additional spatial constraints were employed in selecting sections: (1) For each chemical, wells from at least two counties were sampled (ie. three wells in each of two counties or two wells in each of three counties). This constraint attempted to prevent a single hot spot from biasing the results. (2) Only one compound was sampled for in any particular well. This constraint prevented correlation between samples which could occur if two or more pesticides were sampled for from the same well. Also, we attempted to select sections from as small a group of counties as possible in order to provide the most uniform conditions, both within each treatment group and between

treatment groups.

Sampling Methods

Well sampling methods are described in Sava (1986).

Chemistry Methods/Quality Control

Quality control procedures included blind spikes, method validation, continuing matrix spikes, confirmation analysis and analysis of field blanks if positive detections occurred. Methods are detailed in Appendix 4.

RESULTS

Three of the original 39 compounds were removed from the study. Formetanate and bensulide were removed because the chemical methods could not be developed within the time frame of the study. Tebuthiuron did not have adequate use data available.

Four of 27 compounds on the B2-SA list were found in ground water (Table 3). These compounds were diuron, simazine, atrazine, and bromacil. None of the nine compounds on the NB2-NSA list were detected. In terms of well samples, eight of 162 samples for the B2-SA list were positive (two diuron, four simazine, one bromacil, one atrazine). For each compound, dates of sampling, extraction and analysis, analytical method, detection limits and blind spike recoveries are shown in Table 3. All positive detections were confirmed by a second sample and second method. In most cases samples were extracted within a week of sampling, though a few chemicals were extracted up to four weeks after sampling.

Most of the sampled wells were located in San Joaquin, Fresno, or Tulare Counties (Figure 1). Four wells, two each from Fresno and Tulare, showed positive concentrations of simazine between 0.1 and 0.5 ppb (Table 4). Two wells in Tulare were positive for diuron at 0.5 and 0.6 ppb. One well in Fresno was positive for bromacil at 0.17 ppb. And one well in Sacramento County was positive for atrazine at 0.14 ppb.

The results of the statistical tests are shown in Table 5. Using wells as the experimental unit, there was a significant difference ($p < .05$) in positive detections between B2-SA and NB2-NSA groups. The Pearson chisquare test for the difference between proportions with wells as the sampling unit was reasonably powerful with an 81% chance of finding significance at 0.05 level for an assumed 10% rate of positives in B2-SA versus a 1% positive rate for NB2-NSA (Borenstein and Cohen 1988).

Table 3. List of chemicals sampled for, dates, analytical techniques and results.

Active Ingredient	Sample Dates	Extraction Date	Analysis Date	Method	Blind Spike Level (ppb)	Blind Spike Recovery (%)	Results
Dicofol	2/25-2/26	3/25 §	3/26 ††	GC/ECD	0.4	58	N.D.
Propargite	2/5-2/6	2/21 §	2/22 ††	GC/HALL/ECD	0.3	50	
S,S,S-Tributyl-phosphorotrithioate	2/27-2/28	3/1 §	3/4 ††	GC/FPD	0.3	83	N.D.
Naled	----- Unstable, analyzed for metabolite only. See DDVP -----						
Phosmet	2/25-2/26	3/8 ¶	4/5 ¶¶	GC/MS	0.2	115	N.D.
Benomyl	2/19-2/21	2/25 §	2/25 ††	LC/UV	0.5	50	N.D.
Bromoxynil	3/18-3/21	3/22 §	3/22 ††	GC/MSD	--	--	N.D.
Fenvalerate	3/11-3/13	3/15 §	3/18 ††	GC/ECD	--	--	N.D.
Cypermethrin	3/19-3/20	3/25 §	3/28 ††	GC/ECD	--	--	N.D.
Diazinon	3/5-3/6	3/7 §	3/8 ¶¶	GC/FPD/MSD	0.3	107	N.D.
	2/19-2/21	2/25 §					
Molinate	2/19-2/21	2/22 §	2/25 ††	GC/TSD	0.4	85	N.D.
Diuron	2/5-2/7	2/12 #	2/20 ††	LC/MS	0.2	100	0.6/0.5 0.5/0.5
Simazine	2/5-2/7	3/5 ¶	4/2 ††	LC/MS/MS	0.2	115	0.33/0.48, 0.30/0.41, 0.19/0.27, 0.29/0.45
Dimethoate	2/6-2/7	3/5 ¶	4/2 ¶¶	GC/MS	0.1	120	N.D.
2,4-d dimethylamine salt	3/14-3/15	3/19 §	3/21 ††	GC/ECD	0.2	110	N.D.
Parathion	2/5-2/8	2/11 §	2/11 ††	GC/TSD	0.4	98	N.D.
Azinphos-methyl	2/26	3/13 ¶	4/6 ††	GC/MS	0.2	110	N.D.
Aldicarb	3/5-3/6	3/8 §	3/8 ††	LC/Post col.	0.4	88	N.D.
Atrazine	3/5-3/8	3/13 ¶	4/18 ††	LC/MS/MS	0.2	75	0.14/0.19
Cyanazine	2/12-2/13	2/21 ¶	2/27 ††	LC/MS/MS	0.2	100	N.D.
Disulfoton	3/6-3/8	3/16 ¶	4/20 ¶¶	GC/MS	0.2	130	N.D.
Metolachlor	2/5-2/7	2/13 §	2/14 ††	GC/ECD/TSD	0.3	107	N.D.
Prometryn	2/11-2/13	2/21 ¶	2/27 ††	LC/MS/MS	0.3	70	N.D.
Bromacil	2/27	3/13 ¶	4/17 ††	LC/MS/MS	0.4	60	0.17/0.16
Diethatyl-ethyl	3/5-3/6	3/11 §	3/12 ††	GC/ECD	0.4	110	N.D.
Alachlor	2/25-2/27	3/1 §	3/4 ††	GC/ECD/TSD	0.2	90	N.D.

Table 3. (Cont'd)

Active Ingredient	Sample Dates	Extraction Date	Analysis Date	Method	Blind Spike Level (ppb)	Blind Spike Recovery (%)	Results
Fenamiphos	2/11-2/12	3/6 ¶	4/3 ¶¶¶	GC/MS	0.3	87	N.D.
Oxydemeton-methyl	3/12-3/13	3/21 §	3/25 ††	GC/TSD/FPD	0.3	90	N.D.
Metalaxyl	2/13-2/15	2/20 §	2/21 ††	GC/ECD	0.3	73	N.D.
Linuron	3/11-3/13	3/19 #	4/4 ††	LC/MS	0.3	87	N.D.
Fonofos	3/4-3/7	3/16 ¶	4/19 ¶¶¶	GC/MS	0.2	105	N.D.
Metribuzin	2/19-2/20	3/1 ¶	4/18 ††	LC/MS/MS	0.2	85	N.D.
Oxadiazon	3/19-3/21	3/22 §	3/22 ††	GC/ECD	0.2	105	N.D.
Methiocarb	3/25-3/27	4/1 §	4/1 ††	LC/Post col.	0.3	97	N.D.
Prometon	2/12-2/14	2/21 ¶	2/27 ††	LC/MS/MS	0.3	80	N.D.
Ethoprop	3/12-3/14	3/21 ¶	4/22 §§	GC/MS	0.3	140	N.D.
Metabolites							
Diazoxon	3/5-3/6	3/7 §	3/8 ††	GC/FPD/MSD	--	--	N.D.
	2/19-2/21	2/25 §	3/8 ††	GC/FPD/MSD	--	--	N.D.
Paraoxon	2/5-2/8	2/11 §	2/11 ††	GC/TSD	--	--	N.D.
Azinphos-methyl OA	2/26	3/13 ¶	4/6 ##	GC/MS	--	--	N.D.
Aldicarb sulfoxide	3/5-3/6	3/8 §	3/8 ††	LC/Post col.	--	--	N.D.
Aldicarb sulfone	3/5-3/6	3/8 §	3/8 ††	LC/Post col.	--	--	N.D.
Fenamiphos sulfoxide	2/11-2/12	3/6 ¶	4/3 ¶¶¶	GC/MS	--	--	N.D.
Fenamiphos sulfone	2/11-2/12	3/6 ¶	4/3 ††	GC/MS	--	--	N.D.
Methiocarb sulfoxide	3/25-3/27	4/1 §	4/1 ††	LC/Post col.	--	--	N.D.
Methiocarb sulfone	3/25-3/27	4/1 §	4/1 ††	LC/Post col.	--	--	N.D.
Phosmet OA	2/25-2/26	3/5 ¶	3/8 ††	GC/MS	--	--	N.D.
DDVP	2/11-2/13	3/7 ¶	4/4 ¶¶	GC/MS	0.2	85	N.D.

† Methods are gas chromatography (GC), electron capture detector (ECD), electrolytic conductivity detector (HALL), flame photometric detector (FPD), mass spectrometry (MS), liquid chromatography (LC), post column derivitization (Post col.), thermionic specific detector (TSD), ultra violet (UV), mass selective detector (MSD).

II ND= Not detected in any samples for the chemical. First number is original analysis. Second number is confirmation. See Appendix 3 for additional analysis of positives.

§ Chemical analysis at California Department of Food and Agriculture in Sacramento/CDFA.

¶ Chemical analysis at California Analytical Laboratory in West Sacramento/CAL.

Chemical analysis at Agriculture Priority Pesticide Laboratory in Fresno/APPL.

†† Detection limit 0.10 ppb.

‡‡ Detection limit 0.05 ppb.

§§ Detection limit 0.025 ppb.

¶¶ Detection limit 0.01 ppb.

Detection limit 0.20 ppb.



Figure 1. Number of wells sampled by county (A/B, A = number of wells in B2-SA category, B = number of wells in NB2-NSA category) and number of positive wells (C).

Table 4. Number, location and concentration of positive detections.

	<u>Fresno</u>		<u>Tulare</u>		<u>Sacramento</u>	
	<u>Positive Wells</u>	<u>Conc. (ppb)</u>	<u>Positive Wells</u>	<u>Conc. (ppb)</u>	<u>Positive Wells</u>	<u>Conc. (ppb)</u>
Atrazine	0	ND	0	ND	1	(0.14)
Bromacil	1	(0.17)	0	ND	0	ND
Diuron	0	ND	2	(0.5,0.6)	0	ND
Simazine	2	(0.19,0.30)	2	(0.29,0.3)	0	ND

The tests using chemicals as the sampling unit did not show significant differences. However, the Pearson chisquare had only a 26% chance of showing a significant difference at the 0.05 level between an assumed 10% detection rate for B2-SA and an assumed 1% detection rate for NB2-NSA (Borenstein and Cohen 1988). Given the low power of the test using chemicals as the experimental sampling unit, the nearly significant results (0.11 and 0.058, Table 5) present modest evidence that there was a difference

Table 5. Statistical analysis of sampling results using Pearson and likelihood ratio chisquare tests (Dixon et al. 1988). Probabilities less than 0.05 are considered statistically significant.

<u>Statistic</u>	<u>Using Wells As Exper. Unit</u>			<u>Using Chemicals As Exper. Unit</u>		
	<u>Value</u>	<u>D.F.</u>	<u>Probability</u>	<u>Value</u>	<u>D.F.</u>	<u>Probability</u>
Pearson						
Chisquare	2.77	1	0.048	1.5	1	0.110
Likelihood						
Ratio						
Chisquare	4.71	1	0.015	2.46	1	0.058

in the rate of positive detections between the two groups of compounds.

DISCUSSION

Since few compounds on the GWPL (B2-SA) were found in ground water, the methodologies for (a) establishing the GWPL and (b) selecting wells to be sampled may not be adequate to identify pesticides with a high potential to leach to ground water following normal agricultural use. In spite of these possible limitations, the procedure correctly placed the 4 detected compounds on the GWPL list. In addition, the statistically greater level of positive detections in B2-SA wells suggested that it is likely that there will be a higher incidence of residues in wells in sections with high use of GWPL pesticides than in sections of high use of the NB2-NSA category pesticides. Since no previously undetected compounds were found in ground water, this study is less convincing as to whether the GWPL procedures correctly identify previously undetected leachers.

Atrazine, simazine, diuron and bromacil have all been found in other studies of California ground water, collected and published annually in the Well Inventory Data Base (WIDB) (Cardozo et al. 1985, Brown et al. 1986, Ames et al. 1987, Cardozo et al. 1988, Cardozo et al. 1989, Miller et al. 1990). Prometon, though not found in ground water in this study, has been found in ground water due to normal agricultural use. Of the remaining B2-SA compounds, there have been unconfirmed detections or point source findings of 2,4-D, diazinon, dimethoate and molinate. Generally a confirmed detection is defined when a second sample, analyzed by a different laboratory or a different technique, is positive. Unconfirmed detections are all other types of detections, for example, when an initial sample is positive, but subsequent samples are negative.

Aldicarb and its metabolites have been found in Del Norte and Humboldt ground water due to historical use. Currently it is illegal to use it in those 2 counties. A confirmed detection of tebuthiuron was made in San Diego. However, follow-up monitoring studies failed to detect it. On the NB2-NSA list, benomyl is the only compound detected and that detection was unconfirmed. It's difficult to draw hard conclusions from the unconfirmed detections. However, historical confirmed detections of prometon and

aldicarb in ground water, both on the B2-SA list, tend to support the GWPL procedures. Since these previously detected compounds were not found in ground water in this study, the sample size per compound may have been too low or the methodology for selecting wells to sample may be inefficient.

Conservative bias. If a conservative bias is defined as a greater tendency to incorrectly classify non-leachers as potential leachers than to incorrectly classify leachers as potential non-leachers, then the use of the SNV and label screens to produce the GWPL appears to be conservative. In this study 23 of 27 active ingredients that were classified as potential leachers were not found in ground water, whereas 0 potential non-leachers were found in ground water (Table 6). Therefore the dominant 'error' consisted of possible misclassification of non-leachers as potential leachers. Using nationwide detections, fewer 'errors' were made since only 9 active ingredients which were classified as potential leachers were without positive ground water detections. Yet none of the potential non-leachers are found in ground water according to nationwide studies.

Table 6. Number of compounds classified in ground water based on nationwide detection data (Tables 1 and 2, except three omitted pesticides). Numbers in parentheses indicate compounds for which no studies were found.

		<u>This Study</u>		<u>Nationwide Detections</u>	
		<u>Found in GW</u>	<u>Not found in GW</u>	<u>Found in GW</u>	<u>Not found in GW</u>
GWPL Procedures	B2-SA	4	23	16	9 (2)
	NB2-NSA	0	9	0	8 (1)

The SNV screen introduces a conservative bias primarily because the cutoff points are determined as those points which capture 90% of the leacher population, where leacher is defined as an active ingredient with 3 or more nationwide studies in which the active ingredient has been found in ground water (Johnson 1989). Other features of the SNV procedure contribute towards making it conservative. The leacher and non-leacher probability distributions overlap for each test type (Johnson et al. 1991). This

overlap, in conjunction with the setting at 90% of the SNVs, tends to increase the error of misclassifying non-leachers as potential leachers. Also a conservative bias is fostered by the logical nature of the legally mandated SNV comparison which uses inclusive 'or' to combine the various degradation and mobility parameters (Johnson et al. 1991). This results in a more conservative procedure because by checking more parameters in the inclusive 'or' sense, there is more opportunity for a compound to be classified as a potential leacher. Other screening procedures use fewer characteristics. For example, the ground water ubiquity score (GUS) index uses only adsorption and soil degradation to define an abstract region representing potential leachers (Gustafson 1989).

With the possible exception of aerobic metabolism, the California SNVs are more conservative than those described by the EPA's Working Group on Pesticides in Ground Water (USEPA 1986). The following are the California SNVs versus the EPA proposed cutoff points for various parameters, respectively: soil adsorption (K_{oc}) 2400 cm^3/g vs 300-500 cm^3/g , hydrolysis half-life 9 days vs 175 days, solubility 4 ppm vs 30 ppm. Because there was no statistically significant difference in aerobic soil metabolism half-life between known leachers and non-leachers, an artificially high SNV value of 730 days was set to reduce its impact on the screening process (Johnson 1988). There has not yet been sufficient information to establish the field dissipation half-life SNV in California.

The soil applied screen could also be a source of conservative bias. A search is made for certain label language connoting pesticide applications to soil. A compound is deemed to be soil applied if any one label contains the appropriate language, even though the majority of the use may be otherwise. Finally, the results may be biased in an unknown way because a criterion for including compounds in the study was how readily available were the necessary chemical analytical techniques. However, with respect to the two chemical groups, B2-SA and NB2-NSA, it is not clear how this criteria would have biased the results because assessing this possible bias requires speculation on the relative detection in ground water of B2-SA and NB2-NSA compounds for which no chemical analytical techniques are readily available.

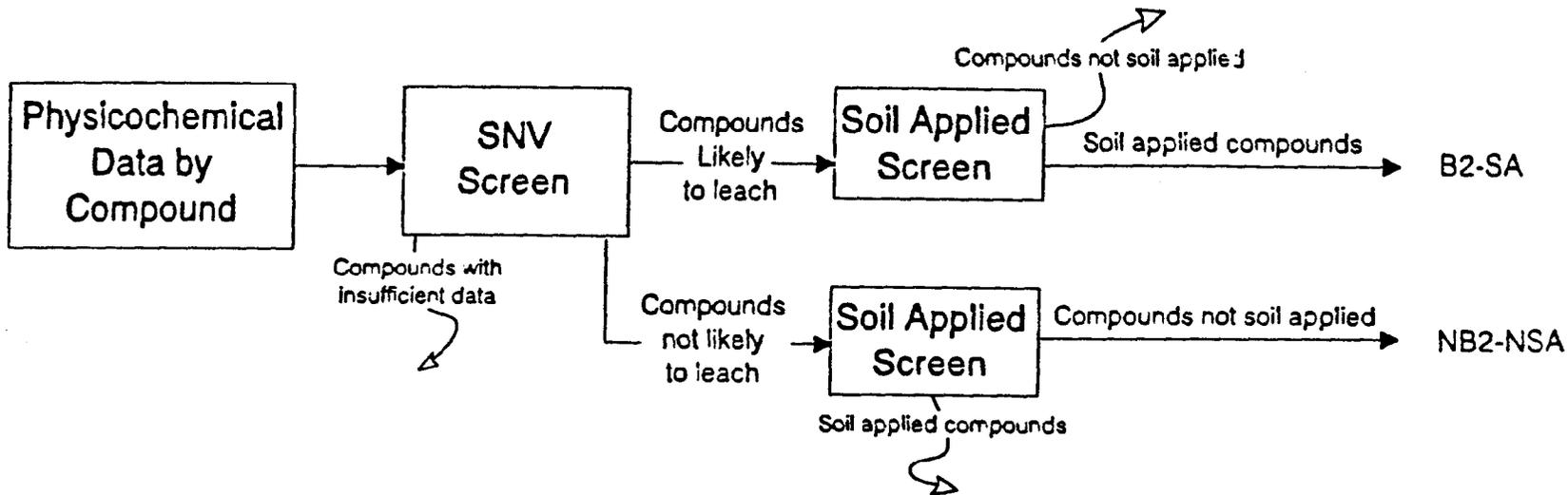
Sources of Variability. Two previously detected compounds, prometon and aldicarb, were not detected in this study and no previously undetected compounds were found. A factor contributing to these results was variability. Variability was important in determining the overall success of first, classification of a compound and second, field sampling to determine its presence in ground water. This variability most likely causes a lower level of positive detections because it tends to undermine precision in identifying potential leachers and to undermine the ability to sample ground water from areas with the highest use rates. The introduction of variability into the procedure begins with the construction of the SNVs (Figure 2). In part, their construction depends on published scientific studies which utilize different methods and media (Kollig 1988, Kollig and Kitchens 1990). For example, soil degradation and adsorption studies utilize different soil types.

The EHAP has operated under the assumption that, all other considerations being equal, wells in the highest use areas for an active ingredient will have the highest probabilities of exhibiting residues of that active ingredient. To locate wells within the highest use areas, the use database is queried to obtain section by section use of an active ingredient. This information is screened for obvious errors and then manually transferred to county maps. Prior to 1990, complete use information was obtained only for restricted compounds. For non-restricted compounds, use information was voluntary and incomplete. Consequently, since pre-1990 use information was the primary source available for conducting this work, some high use sections may have been overlooked.

Moreover, all other considerations may not be equal. High use areas may or may not correlate with aquifer vulnerability. Consequently, the intrinsic vulnerability of an aquifer adds another dimension of variability to the sampling procedure. Recent work has begun to focus on a pesticide by vulnerability screening procedure (Goss and Wauchope 1991, Wauchope et al. 1991).

Another source of variability arises in the field with the set of wells that can actually be sampled.

SELECTION OF COMPOUNDS AND WELLS FOR SAMPLING



Pesticide Use Report

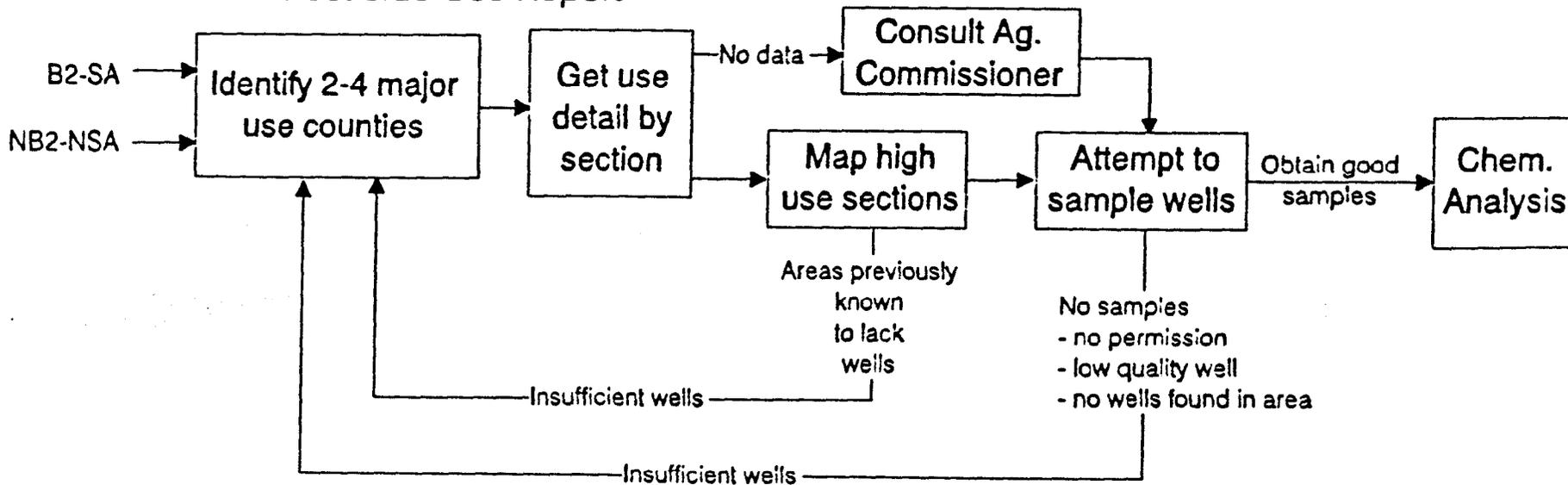


Figure 2. Flow chart of procedures for determining B2-SA and NB2-NSA categories and selecting sampling locations.

Some wells in high use sections were not sampled because they were in poor condition or permission was not granted. In addition, some sampling was conducted in wells located in a section adjacent to, but not in, the targeted, high-use section. Such adjacent section sampling is avoided if possible. But when necessary, it is conducted with the understanding that the sampled wells will be 'across the street' from the designated high-use section.

Physical factors that may affect sampling results include direction of ground water flow, depth to ground water, well casing perforation depth, possible undisclosed dry wells or other sources of point contamination. These factors could result in failure to detect compounds which may be in ground water or in detection of compounds which are present in ground water for reasons other than leaching.

Screening models. Jury et al. (1988) defined a screening model as a mathematical or experimental procedure which discriminates between the performance of pesticides in an idealized scenario. Therefore, the SNV procedure, which is used to identify potential leachers based solely on physicochemical properties, qualifies as a screening model. At best screening models only provide a relative index of leachability and probably will never accurately predict leaching in a specific instance. There is, however, reason to doubt that a screening model will be able to attain even this modest goal. The Behavior Assessment Model (Jury et al. 1983) which provides a relative ranking of pesticide behavior, was tested against site specific soil concentrations measured for 5 applied compounds (Clendening et al. 1990). The authors concluded that mobility of the deeply leaching portion of the compounds could not be predicted, even in a relative sense. Even more sophisticated computer simulation models which incorporate the underlying physical processes in pesticide transport have also had their problems. Using aldicarb and bromide in a field test of 5 major models, including LEACHMP (Wagenet and Hutson 1987) and PRZM (Carsel et al. 1985), Pennell et al. (1990) concluded that none of the models accurately described measured solute concentration distributions.

Accurate prediction of potential leachers by screening models is difficult for several reasons. First, screening models normally depend on some measure of pesticide adsorption to soil. However, it is uncertain how well current methods characterize adsorption. The most common method used to determine adsorption of registered pesticides is the batch adsorption method which involves shaking a soil/water/pesticide mixture until equilibrium is achieved. The method has been criticized because of the variable rates at which equilibrium may be achieved (Lee et al. 1988) and because adsorption is sometimes determined by mass balance techniques and sometimes by simple subtraction techniques (Singh et al. 1990). Another criticism relates to the suitability of using laboratory adsorption studies to estimate field adsorption. Partitioning between soil and water may be different in the field because bypass water flow in the field reduces the opportunity for adsorption (Jury et al. 1988). Moreover, soil properties are known to vary significantly within a single field compared to the relatively uniform soil and water conditions used in the batch adsorption procedure. For example, coefficients of variation of saturated conductivity or chemical concentrations in the field routinely exceed 100% (Jury 1986).

Another potential problem for many screening models is the lack of specific definition of soil degradation and understanding of how degradation rates are influenced by soil depth, temperature, moisture conditions or other factors. In the SNV screening procedure, soil degradation is comparatively well defined as three distinct types: aerobic or anaerobic soil metabolism or field dissipation. These definitions arise primarily from Environmental Protection Agency Pesticide Assessment Guidelines as described in Subdivisions D for product chemistry and N for environmental fate. Other screening models simply require a soil degradation half life, leaving it to the user to determine what is appropriate (Jury et al. 1987, Rao et al. 1985, Leonard and Knisel 1988). However, even when well defined, soil degradation is difficult to apply to different field conditions. For example, bentazon is an herbicide that has been found in ground water in California rice growing areas. In one study its field dissipation half life was measured as 7-11 days when used on beans with sprinkler irrigation (Zehr 1989). However, extrapolating from the laboratory-measured anaerobic soil metabolism yielded approximately 3500 days (Johnson 1991).

Degradation of bentazon in flooded, clay rice soil fields where conditions are anaerobic would be grossly overestimated if the field dissipation half life measured in beans was used.

A final weakness in screening models and a contributing factor to the variability found in this study is the impact of agronomic practices. As in the case of bentazon, where different cultural conditions induce large differences in soil degradation half lives, agronomic practices may influence the likelihood of pesticide movement to ground water. Another example is the extent of ground water recharge, determined in part by the quantity of water used for irrigation. Pesticides with only moderate mobility may leach if a large amount of water is applied. On the other hand, mobile pesticides may not leach if irrigation is managed to keep the pesticide high in the soil profile where moisture, temperature and oxygen conditions promote degradation. The variability in agronomic practices must certainly contribute to variability in the presence or absence of pesticides in ground water in California's large and diverse agricultural environments. At least one author has called for the development of pesticide transport models which include the effects of agronomic practices (Shoemaker et al. 1990).

RECOMMENDATIONS

GWPL Procedures

1. The EHAP should evaluate screening methods which might more accurately predict potential leachers. However, the conservative bias in types of errors should be preserved.
2. The EHAP should continue to investigate the relationship between laboratory-derived physicochemical properties and pesticide behavior in the field. At a minimum each EHAP study project leader should attempt to relate field-measured behavior to physicochemical properties in discussing results from field and monitoring studies.
3. The EHAP should continue in its efforts to understand how variability in soils influences the predictions of computer simulation models.
4. The EHAP should consider conducting a systematic study of errors in the use report to identify and avoid sampling sections where use information is likely to be incorrect.

Sampling Procedures

1. The EHAP should consider utilizing computer graphics techniques to automate the process of mapping pesticide use, selecting sections to sample, and scheduling field sampling activities.
2. The EHAP should consider maintaining a database of records of areas with both sufficient and insufficient wells for sampling that could be superimposed on computer-generated use maps.

3. The EHAP should consider conducting soil coring studies to supplement the well sampling in high-use sections that do not contain useful sampling wells.

4. The EHAP may wish to use the Department of Water Resources well information to stratify wells before sampling in order to take into account depth, age, or other characteristics which might be relevant to the sampling procedure and goals.

CONCLUSIONS

To examine the validity of the procedure used to establish the Ground Water Protection List, 216 wells were sampled, 6 wells for each of 36 compounds. The 36 compounds represented nine compounds unlikely to leach into ground water and 27 compounds with the potential to leach to ground water. Only four compounds, all on the list of potential leachers, were detected in ground water: simazine, atrazine, diuron and bromacil. None of nine compounds on the potential non-leacher list were detected. Though the compounds found in ground water were all on the potential leacher list, there was no statistical difference in the rate of positives between the leaching vs. the non-leaching pesticides. However, the lack of significance may have been due to the low statistical power of this test. There was a significant statistical difference in the rate of positive wells between those wells sampled for pesticides on the GWPL and those wells sampled for pesticides not on the GWPL. The significant difference in detection rates by wells suggests that the GWPL procedures do identify a set of potential leachers. Proving this proposition, however, was made more difficult by the impact of several kinds of variability. And the study was inconclusive insofar as detecting new compounds because no previously undetected potential leachers were found in the ground water samples.

Variability enters the GWPL procedures through variability in the estimation of physicochemical properties and potential under-reporting in the pesticide use reports that were used for locating high-use sections. Variability also occurred in the well selection procedure when identified high-use sections could not be sampled. The SNVs are set conservatively to minimize the possibility of not identifying a potential leacher. The sampling results were consistent with the conservative bias of the SNVs. Screening models in general are susceptible to criticism including the applicability of laboratory measured adsorption compared to adsorption in the field, the possible influence of agronomic practices and ambiguity in the application of soil degradation rates.

Suggestions were made to improve the criteria and data used to establish the GWPL, and to facilitate sampling for compounds on the GWPL.

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Appendix 1. Common synonyms for chemicals sampled for in this study.

<u>Common Name</u>	<u>Trade Name or Other Name</u>
2,4-dimethylamine salt	2,4-D
alachlor	Lasso
aldicarb	Temik
atrazine	
azinphos-methyl	Guthion
benomyl	Benlate
bromacil	Hyvan, Krovar
bromoxynil octanoate	Buctril, Brominal
cyanazine	Bladex
cypermethrin	Ammo, Cymbush
diazinon	
dicofol	Kelthane
diethatyl-ethyl	Antor
dimethoate	Cygon
disulfoton	Disyston
diuron	Karmex
ethoprop	Mocap
fenamiphos	Nemacur
fenvalerate	Pydrin
fonofos	Dyfonate
linuron	Lorox
metalaxyl	Ridomil
methiocarb	Mesurool
metolachlor	Dual
metribuzin	Sencor
molinate	Ordram
naled	Dibrom
oxadiazon	Ronstar
oxydemeton methyl	Metasystox-R
parathion	
phosmet	Imidan
prometon	
prometryn	Caparol
propargite	Omite
s,s,s-tributyl phosphorotrithioate	DEF, Folex
simazine	Princep

Appendix 2. County, township/range/section for sampling locations, chemical samples, corresponding use information, acidification of samples, and owner reported well depth. With the exception of ethoprop, all wells were sampled for in at least 2 counties. No samples for different pesticides came from the same well. In several cases, the target section could not be sampled and samples were drawn from an adjacent section within 200-300 yards of the target section.

SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
21N01E-23	2,4-D	260 & 176	Butte	535	3/14/91	176	260		yes		n/a
21N01E-26	2,4-D	307	Butte	1137	3/14/91		307		yes		n/a
21N01E-26	2,4-D	307	Butte	1089	3/14/91		307		yes		n/a
23N01W-35	2,4-D	853 & 988	Butte	1401	3/14/91	988	853		yes		n/a
20N02W-06	2,4-D	411	Glenn	253	3/14/91	411			yes		n/a
21N02W-02	2,4-D	777 & 472	Glenn	259	3/14/91	472	777		yes		n/a
01N04E-10	Alachlor	adj 1276	San Joaquin	955	2/26/91				no	01N04E-15 (1988=1276lb)	n/a
01S05E-23	Alachlor	298	San Joaquin	961	2/26/91	298			no		50'
02S05E-34	Alachlor	276	San Joaquin	943	2/26/91	276			no		n/a
07N01E-10	Alachlor	818	Solano	949	2/26/91	818			no		125'
07N01E-25	Alachlor	957	Solano	61	2/25/91		957		no		n/a
07N01E-34	Alachlor	Adj 1243	Solano	703	2/25/91				no	07N01E-33 (1987=261lb; 1988=582lb)	n/a
15S19E-10	Aldicarb	303-357; adj 397	Fresno	1353	3/5/91	303	357		no	15S19E-15 (1988=397lb)	n/a
16S21E-28	Aldicarb	1117 + 500	Fresno	1347	3/5/91	500	1117		no		n/a
16S21E-35	Aldicarb	649; adj to 346	Fresno	1341	3/5/91		649		no	17S20E-02 (1988=346lb)	n/a
02N07E-14	Aldicarb	652	San Joaquin	1365	3/6/91	652			no		260'
02N07E-14	Aldicarb	652	San Joaquin	1359	3/6/91	652			no		260'
03N05E-13	Aldicarb	adj 384, 144	San Joaquin	1377	3/6/91				no	03N05E-11 (1987=144lb; 1988=384lb)	n/a
11S13E-08	Antor	460	Fresno	1065	3/5/91	460			no		80'
11S13E-08	Antor	460	Fresno	1095	3/5/91	460			no		n/a
10S11E-03	Antor	219	Merced	1071	3/6/91		219		no		n/a
10S11E-13	Antor	279	Merced	1467	3/5/91		279		no		n/a
10S11E-16	Antor	195	Merced	1059	3/6/91	195			no		30'
11S12E-09	Antor	313 & 339	Merced	1113	3/6/91	313	339		no		20'
05N04E-15	Atrazine	266	Sacramento	1167	3/7/91		266		no		80'
05N06E-30	Atrazine	314 & 338	Sacramento	1131	3/7/91	338	314		no	positive	250'
07N06E-11	Atrazine	361; adj 494	Sacramento	1077	3/7/91	361			no	07N06E-12 (1987=494lb)	n/a
02N05E-05	Atrazine	adj 645	San Joaquin	1485	3/6/91				no	03N05E-32 (1987=645lb)	n/a
04N07E-04	Atrazine	adj 1293	San Joaquin	999	3/4/91				no	05N07E-33 (1987=1293lb)	300'
05N07E-34	Atrazine	adj 1293	San Joaquin	895	3/8/91				no	05N07E-33 (1987=1293lb)	270'
05S11E-25	Azinphos-m	760	Merced	625	2/26/91	760			yes		180'
05S12E-23	Azinphos-m	1280	Merced	505	2/26/91		1280		yes		260'
06S13E-05	Azinphos-m	adj to 845 & 746	Merced	571	2/26/91				yes	05S13E-32 (1987=845lb); 06S13E-06 (1987=746lb)	85'
18S24E-33	Azinphos-m	550-825	Tulare	511	2/26/91	825	550		yes		n/a
20S25E-25	Azinphos-m	770	Tulare	817	2/26/91		770		yes		n/a

SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
21S/26E-23	Azinphos-m	356, adj 651&537	Tulare	523	2/26/91		356		yes		n/a
10S/16E-15	Benomyl	Adj.3 sctn of use	Madera	169	2/20/91				no	10S/16E-22 (33lb); 10S/16E-23 (30lb); 10S/16E-21 (48lb)	300'
11S/16E-25	Benomyl	170	Madera	367	2/20/91	170			no		160'
11S/16E-26	Benomyl	180	Madera	385	2/20/91	180			no		181'
05S/11E-24	Benomyl	South of Use	Merced	205	2/19/91				no	05S/11E-13 (1987=442lb; 1988=435lb)	190'
05S/13E-17	Benomyl	234	Merced	421	2/19/91	234			no		n/a
08S/15E-34	Benomyl	155	Merced	859	2/21/91	155			no		191'
15S/24E-10	Bromacil	80; adj 3 hi use sctn.	Fresno		2/27/91	41	39		no	15S/24E-11 (1987=10lb, 1988=113lb); -2 (1987=12lb, 1988=151lb); 04 (1988=135lb)	28'
15S/24E-11	Bromacil	123; adj 163&125	Fresno	613	2/27/91	10	113		no	15S/24E-02 (1987=12lb, 1988=151lb); -12 (1987=35lb, 1988=95lb)	80'
15S/24E-12	Bromacil	125, adj to 123	Fresno	847	2/27/91	30	95		no	15S/24E-11 (1987=10lb; 1988=113lb)	100'
16S/25E-17	Bromacil	630, cluster +700	Tulare	583	2/27/91		630		no	16S/25E-16 (1987=144lb); -21 (1988=136lb); 20 (1987=80lb, 1988=310lb)	n/a
17S/25E-34	Bromacil	60, adj 300	Tulare	517	2/27/91	60			no	no ID given; 17S/25E-27 =300lb	n/a
20S/26E-13	Bromacil	304+366, adj3sct	Tulare	763	2/27/91	366	304		no	20S/26E-14 (1987=256lb, 1988=214lb); -12 (1988=89lb); 20S/27E-18 (1987=316lb)	n/a
07S/14E-34	Bromoxynil		Merced	1281	3/21/91		243				n/a
07S/15E-02	Bromoxynil		Merced	987	3/21/91						n/a
21S/25E-18	Bromoxynil		Tulare	1413	3/19/91		131				n/a
09N/01E-04	Bromoxynil	251	Yolo	1597	3/18/91		251				102'
09N/01E-20	Bromoxynil	168	Yolo	1299	3/18/91	168					320'
09N/01W-04	Bromoxynil	198	Yolo	1143	3/18/91	198					90'
13S/18E-28	Cyanazine	702	Fresno	751	2/12/91		702		no		n/a
16S/19E-12	Cyanazine	480	Fresno	727	2/12/91	480			no		220'
17S/19E-13	Cyanazine	680	Fresno	781	2/13/91	680			no		n/a
07S/15E-33	Cyanazine	368	Merced	355	2/13/91		368		no		n/a
08S/14E-01	Cyanazine	300	Merced	379	2/13/91		300		no		50-60'
08S/15E-34	Cyanazine	1100	Merced	415	2/13/91		1100		no		300-35'
15S/18E-28	Cypermethrin		Fresno	1317	3/20/91				yes		150-15'
17S/18E-22	Cypermethrin		Fresno	1491	3/20/91	28			yes		n/a
17S/19E-36	Cypermethrin		Fresno	1221	3/20/91		98		yes		55'
20N/03W-10	Cypermethrin	31 & 20	Glenn	1155	3/19/91	20	31		yes		90'
20N/03W-11	Cypermethrin	adj (north, west)	Glenn	637	3/20/91				yes		80'
	Cypermethrin	30	Glenn	1269	3/20/91				yes	21N/02W-13	65'
14S/18E-35	DEF	595	Fresno	877	2/28/91		595		yes		280'
14S/19E-10	DEF	296	Fresno	799	2/28/91		296		yes		n/a
16S/19E-03	DEF	683	Fresno	589	2/28/91		683		yes		n/a
14S/21E-28	Diazinon	240+217=457	Fresno	891	2/21/91	217	240		yes		n/a
16S/20E-13	Diazinon	1890	Fresno	447	2/21/91		1890		yes		n/a

SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
16S/20E-33	Diazinon	750	Fresno	933	2/20/91		750		yes		n/a
05S/13E-17	Diazinon	1252	Merced	919	2/19/91		1252		yes		180'
09S/16E-07	Diazinon	984	Merced	915	2/19/91		984		yes		315'
10S/10E-02	Diazinon		Merced	925	2/20/91	765			yes		150'
14S/18E-11	Dicofol	804	Fresno	547	2/25/91		804		no		220'
17S/19E-12	Dicofol	886	Fresno	853	2/25/91	886			no	17S/21E-15 (1987=276lb, 1988=300lb)	n/a
17S/21E-16	Dicofol	288; adj to 576	Fresno	541	2/25/91	288			no	17S/25E-25 (1988=482lb); 17S/35E-35 (1988=482lb)	79'
17S/25E-36	Dicofol	643; adj 2 scots	Tulare	529	2/25/91		643		no		200'
17S/27E-29	Dicofol	1445	Tulare	601	2/25/91		1445		no	19S/26E-01 (1988=591lb)	n/a
19S/26E-11	Dicofol	703; adj 591	Tulare	595	2/26/91		703		no		139'
14S/18E-25	Dimethoate	939	Fresno	7	2/6/91	328	611		yes		120'
14S/18E-26	Dimethoate	1164	Fresno	121	2/6/91		1164		yes		n/a
17S/21E-01	Dimethoate	1400	Fresno	685	2/6/91	800	600		yes		n/a
15S/25E-32	Dimethoate	1255	Tulare	133	2/6/91	496	759		yes		n/a
17S/25E-24	Dimethoate	1324	Tulare	691	2/6/91	562	762		yes		100'
17S/26E-31	Dimethoate	931	Tulare	13	2/7/91	447	484		yes		n/a
02N/02E-03	Disulfoton		Sacramento	217	3/8/91	789	687		yes		n/a
06N/06E-03	Disulfoton	1572	Sacramento	1035	3/8/91		1572		yes		n/a
01N/05E-06	Disulfoton	347, 300 hi use	San Joaquin	1473	3/6/91	300	347		yes		30-50'
01N/05E-20	Disulfoton	1068, 818	San Joaquin	1455	3/7/91	818	1068		yes	no ID given	n/a
01N/05E-29	Disulfoton	363, 410	San Joaquin	1461	3/7/91	410	363		yes		40'
11N/02E-34	Disulfoton		Yolo	229	3/7/91		197		yes		n/a
15S/16E-10	Diuron	480	Fresno	655	2/5/91		480		no		180'
16S/17E-05	Diuron	600	Fresno	181	2/5/91	330	270		no		300'
16S/17E-17	Diuron	716	Fresno	37	2/6/91	716			no	no ID given	80-90'
16S/25E-16	Diuron	1234	Tulare	319	2/7/91	452	782		no	positive	90'
17S/25E-22	Diuron	1260	Tulare	331	2/5/91	630	630		no		n/a
19S/26E-01	Diuron	802	Tulare	301	2/6/91		802		no	positive	n/a
13S/15E-18	Fenamiphos	418	Fresno	811	2/11/91		418		yes		90'
15S/20E-22	Fenamiphos	1084-217=1301	Fresno	733	2/12/91	217	1084		yes		220'
15S/21E-32	Fenamiphos	469-220=689	Fresno	805	2/12/91	220	469		yes		226'
16S/23E-12	Fenamiphos	152-87=237	Tulare	289	2/11/91	85	152		yes		n/a
16S/24E-10	Fenamiphos	220	Tulare	271	2/11/91		220		yes		112'
17S/26E-26	Fenamiphos	249	Tulare	211	2/12/91		249		yes		n/a
13S/02E-34	Fenvalerate	215 & 217	Monterey	1275	3/11/91	217	215		yes		240'
14S/02E-01	Fenvalerate	690	Monterey	1203	3/12/91	365	325		yes		350'

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SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
14S-02E-02	Fenvalerate	adj w, e, & s	Monterey	1053	3/11/91				yes	adj secs 14S-02E-01 (1987=365lb, 1988=325lb); 14S-02E-03 (1987=252lb, 1988=200lb)	204'
01S-08E-23	Fenvalerate	120	San Joaquin	981	3/13/91	120			yes		300'
02S-05E-32	Fenvalerate	96 & 82	San Joaquin	481	3/12/91	82	96		yes		115'
03S-06E-28	Fenvalerate	100	San Joaquin	1173	3/12/91	100			yes		119'
09S-14E-23	Folex	148; adj to 710	Merced	577	2/27/91		148		no	adj to 09S-14E-26 (1988=710lb)	n/a
09S-15E-02	Folex	273	Merced	499	2/27/91	273			no		300'
10S-12E-10	Folex	142 & 284	Merced	631	2/27/91				no	10S-12E-11 (1987=294lb, 1988=142lb)	n/a
02S-05E-27	Fonofos	120, 279	San Joaquin	1119	3/7/91	279	120		yes	no ID numbers given	90'
04N-05E-24	Fonofos	328	San Joaquin	247	3/4/91		328		yes		n/a
04N-08E-22	Fonofos	275, 400	San Joaquin	1479	3/4/86	400	275		yes		n/a
04S-07E-21	Fonofos	319 & 159	Stanislaus	1125	3/4/91	159	319		yes		100'
06S-08E-14	Fonofos	adj North	Stanislaus	1107	3/6/91				yes	no pounds given	n/a
06S-08E-34	Fonofos	299	Stanislaus	1419	3/7/91	204	95		yes		300'
16S-05E-32	Linuron	213	Monterey	769	3/12/91		213		no		n/a
22S-10E-08	Linuron	208 & 74	Monterey	793	Mar-91	74	208		no	no "specific" sample date given	110'
22S-10E-16	Linuron	193 & 67	Monterey	439	3/13/91	67	193		no		100'
01S-05E-28	Linuron	473	San Joaquin	1251	3/11/91	473			no		50'
01S-06E-03	Linuron	adj (south)	San Joaquin	1407	3/12/91				no	adj to 01S-06E-34 (1987=255lb)	shallow
02N-05E-34	Linuron	480	San Joaquin	1425	3/11/91	480			no		38'
14S-19E-36	Metolachlor	26-9-35	Fresno	757	2/13/91	9	26		no		140'
15S-21E-23	Metolachlor	31	Fresno	787	2/13/90		31		no		n/a
17S-20E-09	Metolachlor	19	Fresno	739	2/13/91		19		no		100'
02N-04E-31	Metolachlor	525	San Joaquin	235	2/15/91				no	adj sec 02N-04E-32 (1988=525lb)	190'
18S-06E-06	Metolachlor	292	Monterey	91	2/13/91	71	221		no		n/a
01N-04E-09	Metolachlor	840	San Joaquin	79	2/14/91	840			no		180'
14S-03E-19	Methiocarb	117	Monterey	1329	3/25/91		118		yes		210'
03S-04W-30	Methiocarb	224 & 541	Riverside	1311	3/27/91	541	224		yes		110'
03S-04W-31	Methiocarb	adj 541 & 224	Riverside	823	3/27/91	289	155		yes	adj sec 03S-04W-30 (1987=541lb, 1988=224lb)	100'
10N-35W-12	Methiocarb	32; adj 101	Santa Barba	1215	3/26/91	32			yes	adj sec 10N-34W-07 (1988=101lb)	n/a
10N-35W-22	Methiocarb	adj 144	Santa Barba	1287	3/26/91				yes	adj sec 10N-35W-21 (1988=144lb)	n/a
04S-05W-21	Methiocarb	adj 253 & 142	Riverside	1443	3/27/91				yes	adj sec 04S-05W-22 (1987=142lb, 1988=253lb)	180'
18S-25E-21	Metolachlor	107	Tulare	127	2/7/91	107			no		60'
13S-17E-32	Metolachlor	396	Fresno	157	2/6/91	198	198		no		n/a
17S-19E-26	Metolachlor	371	Fresno	283	2/5/91		371		no		n/a
17S-20E-19	Metolachlor	816	Fresno	697	2/5/91		816		no		105'
16S-24E-11	Metolachlor	99	Tulare	679	2/7/91		99		no		125'

SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
16S24E-25	Metolachlor	246	Tulare	667	2/7/91	246			no		72'
01S05E-18	Metribuzin	227	San Joaquin	883	2/19/91	227			yes		50'
01S06E-31	Metribuzin	106	San Joaquin	67	2020-91			106	yes		n/a
03S05E-01	Metribuzin	176	San Joaquin	97	2/19/91			176	yes		n/a
06S08E-05	Metribuzin	231	Stanislaus	661	2/20/91	118	114		yes		250'
06S08E-23	Metribuzin	80	Stanislaus	73	2/20/91	80			yes		n/a
06S08E-30	Metribuzin	94	Stanislaus	907	2/20/91		94		yes		219'
46N01W-30	Mocap	adj (west)	Siskiyou	1263	3/12/91				no	adj sec -29 (1987=755lb, 1988=900lb)	80'
46N01W-32	Mocap	adj (south)	Siskiyou	1029	3/12/91				no	adj sec-29 (1987=755lb, 1988=900lb)	n/a
46N01W-22	Mocap	adj (south)	Siskiyou	1005	3/14/91				no	adj sec-15 (1987=390lb)	n/a
47N01E-18	Mocap	360	Siskiyou	1197	3/13/91		360		no		n/a
47N01E-33	Mocap	adj (east)	Siskiyou	1431	3/13/91				no	adj sec-32 (1987=1365lb)	180'
47N01W-34	Mocap	1032	Siskiyou	1437	3/13/91		1032		no		n/a
18N02E-26	Molinate	4895	Butte	463	2/21/91		4895		yes	no ID numbers given, no sample date given	n/a
20N02E-17	Molinate	6225	Butte	469	2/20/91		6225		yes	no ID numbers given	n/a
20N02E-36	Molinate	4694	Butte	475	2/20/91		4694		yes	no ID numbers given	n/a
16N03W-22	Molinate	4244-4010-8254	Colusa	427	2/19/91				yes	adj sec 16N03W-27 (1987=4010lb, 1988=4244lb)	200'
17N03W-31	Molinate	4100-2565-6665	Colusa	433	2/20/91	2565	4100		yes	no ID numbers given	119-13
18N02W-13	Molinate	4780-3190-7970	Colusa	451	2/21/91				yes	no ID numbers given, adj sec 18N02W-24 (1987=3190lb, 1988=4780lb)	n/a
14S23E-36	Naled	315	Fresno	361	2/12/91		315		no		n/a
14S23E-36	Naled	315	Fresno	361	2/13/91		315		no		96'
15S23E-13	Naled	40	Fresno	391	2/12/91	40			no		110'
15S25E-31	Naled	453	Tulare	277	2/11/91	453			no		147'
20S25E-13	Naled	514	Tulare	175	2/12/91		514		no		400'
17S27E-35	Naled	185-463-648	Tulare	325	2/12/91	463	185		no		n/a
21N02W-10	Oxadiazon	adj 66	Glenn	115	3/21/91				no	adj sec 21N02W-15 (1990=66lb)	100'
21N02W-13	Oxadiazon	adj 50	Glenn	1191	3/20/91				no	adj sec 21N02W-14 (1990=50lb)	n/a
21N02W-36	Oxadiazon	66	Glenn	565	3/20/91			66	no		n/a
26S24E-36	Oxadiazon	106	Kern	1161	3/19/91			106	no		295'
27S24E-03	Oxadiazon		Kern	1338	3/19/91			43	no		400'
27S25E-18	Oxadiazon	179	Kern	223	3/19/91			179	no		300'
01N07E-26	Oxydementon-m	249 & 34	San Joaquin	1179	3/13/91	34	250		yes		n/a
01N08E-35	Oxydementon-m	184	San Joaquin	1245	3/13/91		184		yes		180'
02N06E-12	Oxydementon-m	74 & 112	San Joaquin	1185	3/13/91		73		yes		80'
18S25E-24	Oxydementon-m	80 & 86	Tulare	109	3/13/91	86	80		yes		339'
19S26E-17	Oxydementon-m	160	Tulare	265	3/12/91	160			yes		n/a

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SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified	Comments	Depth
21S26E-24	Oxydemeton-m.	146 & 164	Tulare	1149	3/12/91	164	146		yes		n/a
12S21E-19	Parathion	2211	Fresno	673	2/8/91	1136	1075		yes		n/a
14S23E-34	Parathion	1504	Fresno	49	2/7/91				yes	adj sec 14S23E-33 (1987=778lb, 1988=726lb)	n/a
17S21E-05	Parathion	1653	Fresno	25	2/6/91	864	789		yes		180'
16S23E-10	Parathion	2444	Tulare	709	2/5/91	783	1661		yes		140'
16S23E-22	Parathion	1364	Tulare	649	2/5/91	761	603		yes		97'
16S24E-14	Parathion	1610	Tulare	139	2/5/91	757	853		yes		70'
14S17E-16	Phosmet	adj to 936	Fresno	1083	2/26/91				yes	adj sec 14S17E-21 (1987=936lb), no ID number given	190'
16S19E-21	Phosmet	240; 1 1/2 mi e 700	Fresno	607	2/26/91	240			yes		225'
16S20E-11	Phosmet	407	Fresno	841	2/26/91	225	182		yes	no ID numbers given	n/a
07S14E-23	Phosmet	420	Merced	619	2/26/91		420		yes		160'
07S15E-20	Phosmet	280	Merced	901	2/25/91	280			yes		n/a
08S14E-12	Phosmet	250	Merced	553	2/25/91		250		yes		n/a
05S11E-22	Prometon	Railroad	Merced	199	2/13/91				no		50'
07S14E-26	Prometon	Railroad	Merced	55	2/12/91				no		150-20'
08S16E-21	Prometon	Railroad	Merced	151	2/12/91				no		n/a
03N06E-18	Prometon		San Joaquin	295	2/14/91				no	no pounds recorded	n/a
03N07E-05	Prometon		San Joaquin	745	2/14/91				no	no pounds recorded	192'
04N06E-14	Prometon		San Joaquin	721	2/14/91				no	no pounds recorded	n/a
14S17E-10	Prometryn	102, 40	Fresno	397	2/12/91	40	102		no		n/a
14S17E-13	Prometryn	239	Fresno	409	2/12/91		239		no		n/a
14S18E-08	Prometryn	80, 54	Fresno	403	1/11/91	54	80		no		n/a
15S04E-29	Prometryn	92	Monterey	193	2/12/91				no	adj sec 15S04E-32 (1988=92lb)	80'
16S05E-19	Prometryn	56	Monterey	241	2/13/91		56		no		650'
19S07E-04	Prometryn	198	Monterey	85	2/13/91	110	89		no		120'
15S16E-10	Propargite	1397	Fresno	643	2/6/91		1397		no		200'
16S17E-17	Propargite	2080	Fresno	187	2/6/91	2080			no	no ID numbers given	n/a
17S18E-16	Propargite	1301	Fresno	145	2/6/91	1301			no	no ID numbers given	155'
18S24E-13	Propargite	2930	Tulare	349	2/5/91	1447	1483		no		n/a
19S25E-14	Propargite	2422	Tulare	313	2/5/91	1508	924		no	ID numbers: P-313, B1-314, B3-316, B4-317, FB-318	n/a
21S26E-13	Propargite	1693	Tulare	337	2/5/91		1693		no		145'
14S19E-19	Simazine	1393	Fresno	715	2/5/91				no	no ID numbers given; adj sec 14S19E-20 (1988=1393lb)	120'
14S21E-34	Simazine	536	Fresno	36	2/7/91	300	236		no	positive	150'
15S24E-01	Simazine	584	Fresno	48	2/7/91	170	414		no	no ID number given	n/a
17S26E-19	Simazine	451	Tulare	6	2/6/91		451		no	positive	n/a
19S26E-01	Simazine	527	Tulare	348	2/6/91		527		no	positive	75'

SAMPLING LOCATIONS AND USE INFORMATION

T/R-S	Chemical	Pounds	County	Id	Sample Date	1987 use	1988 use	1990 use	Acidified Comments	Depth
22S/27E-15	Simazine	643	Tulare	18	2/6/91	355	288		no	400'

Appendix 3. Results of supplementary analysis of positive samples for atrazine, bromacil, diuron, prometon and simazine.

7/24/91

To confirm a positive result, a second sample was analyzed using a method which detects atrazine, bromacil, diuron, prometon and simazine at 0.1 parts per billion. Additional analytical results are listed below. Since these additional results are unconfirmed, single samples, these additional results were not used in any analysis or interpretation in this report.

<u>Chemical</u> <u>Sampled For</u>	<u>Concentration (ppb)</u>	<u>Sample</u> <u>#</u>	<u>Additional Chemicals</u> <u>Sampled For</u>	<u>Concentration (ppb)</u>
Simazine	0.48/0.33	0002	Diuron Atrazine, Bromacil, and Prometon	0.10 None Detected ^a
Simazine	0.19/0.27	0044	Bromacil Diuron Atrazine, Prometon	0.19 0.65 None Detected
Simazine	0.29/0.45	0344	Bromacil Diuron Atrazine, Prometon	0.45 0.21 None Detected
Bromacil	0.17/0.16	0866	Diuron Simazine Atrazine, Prometon	0.33 0.44 None Detected
b		1101	Diuron Atrazine, Bromacil, Prometon, Simazine	0.17, 0.25 None Detected

a. None detected at the minimum detection limit of 0.1 parts per billion for these compounds.

b. This well was targeted for fonofos sampling; however, since enough wells were sampled for that compound we sampled for these herbicides as a courtesy to the well owner.