

**SETTING REVISED SPECIFIC NUMERICAL VALUES
OCTOBER, 1989**



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Environmental Hazards Assessment Program

**STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
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OCTOBER, 1989

**Pursuant to the
Pesticide Contamination Prevention Act**

By

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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INTRODUCTION

The Pesticide Contamination Prevention Act requires the Department of Food and Agriculture to set certain numeric threshold values for chemical properties of pesticides. Compounds which exceed these values may be placed on a Ground Water Protection List (Wilkerson and Kim, 1986). The current report details derivation for 1989 of specific numerical values utilizing the 90th percentile of distributions of chemical properties.

METHODS

The methodology in 1989 was similar to that in 1988 (Johnson, 1988). For the 1989 report, more ground water studies and more physicochemical parameter studies were available for use. In this report, the term contaminant refers to a compound which has demonstrated a propensity to leach into ground water as a result of normal agricultural use. The detection studies used were reviewed for consistency and accuracy and are listed in Appendix A. Based on these ground water studies, two lists of compounds were created. One list contained compounds which had been detected in ground water to a significant degree (contaminants), and the other list contained compounds which have not been detected to a significant degree in ground water (non-contaminants) as a result of agricultural non-point source contamination. The definition of 'significant degree' and the criteria used to judge the validity of a reported ground water find are discussed in Appendix B. Based on the review of detection studies and newly received studies since 1988, a few compounds were reclassified (see Tables 1 and 2). In addition, estimates were obtained for some properties for some compounds for which there were no data in 1988.

Table 1. List of contaminants. Units are Koc = cm³/gm, hydrolysis and aerobic metabolism = days (half life), water solubility = ppm. Data has been rounded to 2 significant figures. No data is indicated by -1.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism Half-Life	Water Solubility
Alachlor	150	720	18	200
Aldicarb	79	670	14	6000
Atrazine	180	160	190	33
Bromacil	60	110	300	820
Carbofuran	48	60	23	320
Chloramben	280	370	-1	700
Chlorothalonil (a)	2500	49	35	0.6
Chlorthal dimethyl	4000	36	24	3
Cyanazine	180	260	15	170
2,4-D (a)	53	4	8	230
DBCP	80	7100	180	1000
Dicamba	1.5	30	61	6100
Dieldrin	7100	1500	1000	0.12
Dinoseb	110	30	-1	75
Diuron	460	110	-1	42
EDB	44	7100 (b)	44	3400
Fonofos (a)	5100	110	120	16
Metolachlor	190	210	-1	530
Metribuzin	150	130	110	1100
Oxamyl	6	6	180	280000
Picloram	26	650	350	430
Prometon	79	1100	280	720
Propachlor	340	-1	-1	700
Propylene dichloride	49	-1	-1	2700
Simazine	220	110	110	4.9

(a) Compounds on non-contaminant list in 1988.

(b) Winsorized original value of 100,000,000 (see text).

Table 2. List of non-contaminants. Units are Koc = cm³/gm, hydrolysis and aerobic metabolism = days (half life), water solubility = ppm. Data has been rounded to 2 significant figures. No data is indicated by -1.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism Half-Life	Water Solubility
Aldrin	14000	-1	120	0.027
Ametryne	380	28	37	190
Carbaryl	360	5.2	8	110
Chlordane	33600	110	54	1.9
Chlorpyrifos (a)	17000	73	88	0.71
DDD	46000	-1	-1	-1
DDT	160000	-1	3800	0.003
Diazinon	1200	20	17	61
Dimethoate	17	62	2	25000
Disulfoton	940	320	2	14
1,3-D	150	7	13	1000
Endosulfan	2000	14	32	0.33
Ethroprop	180	-1	25	770
Fenamiphos	280	300	22	560
Heptachlor	16000	180	2000	0.06
Lindane	2500	310	790	10
Linuron	670	55	78	75
Malathion	1000	48	1	140
Methiocarb	490	24	-1	27
Methyl bromide	390	-1	35	9200
Naled (a)	167	0.68	3	2000
Pendimethalin	16000	60	1300	0.28
Phorate	2400	3.1	3	18
Prometryn (a)	680	75	150	48
Silvex (a)	-1	-1	16	160
Toxaphene	-1	110	-1	1.9
Trifluralin	9900	110	180	1.8

(a) Compound on contaminant list in 1988.

Four characteristics were determined for each compound: soil adsorption (Koc), hydrolysis half life, soil aerobic metabolism (SAM) half life, and solubility. Estimates of these properties were based on reviewed studies from the open literature and CDFA approved studies which fulfilled the data-call-in requirements of the Pesticide Contamination Prevention Act. More detailed information about the data values can be found in Johnson (1988, Appendix II).

Comparison of the distributions for these characteristics to expected normal distributions indicated that these physicochemical properties were extremely non-normally distributed. A log₁₀ transformation was used to normalize the distributions. All statistical calculations were performed on log₁₀ transformed data. The standard t-test, not assuming equal variances, was used to determine mean separation of contaminants versus non-contaminants for each chemical characteristic. The percentile calculations were based on the mean, standard deviation and appropriate t-value using 1 less than the number of observations for degrees of freedom. For Koc, the 90th percentile was the point below which 90% of the contaminant population fell. For hydrolysis and water solubility, the 90th percentile was the point above which 90% of the contaminant population fell. Aerobic metabolism lacked discriminatory power since the two means were not significantly different. Therefore its importance in the discrimination procedure was reduced by choosing the point above which only 10% of the combined contaminant and non-contaminant populations fell. For all parameters, estimates were then back-transformed to obtain final values.

One hydrolysis observation was 'winsorized' (Snedecor and Cochran, 1967) because of its extreme value. Hydrolysis half life studies typically last less than 365 days. Therefore the estimated half life for EDB of 100,000,000

was regarded as uncertain and reduced to the next highest value which was 7100 days for DBCP.

The language of the law provides for the following logic in testing each compound:

Classify as a potential contaminant if:

(A or B) and (C or D) are true,

where

A = 'Koc less than V1'

B = 'water solubility greater than V2'

C = 'hydrolysis half life greater than V3'

D = 'SAM half life greater than V4'

and V1, V2, V3, V4 are specific numerical values.

After determining the specific numeric values, this test was applied to the contaminant and non-contaminant compounds to determine an error rate for the classification procedure.

RESULTS

Contaminants and non-contaminants and their estimated Koc, hydrolysis, soil aerobic metabolism and water solubility properties are listed in Table 1 and Table 2, respectively. The statistics for the two groups are summarized in Table 3. Variances were not significantly different. However, testing power probably was reduced by moderately low sample sizes. Therefore non-equal variance t-tests were used to determine significance of mean separation. Means were significantly different between contaminants and non-contaminants except for soil aerobic metabolism.

Table 3. Statistics for log₁₀ transformed characteristics of contaminant and non-contaminant pesticides.

	Contaminants	Non-contaminants	P-values (a)
Koc	Mean 2.17	3.23	.001
	SD 0.84	0.95	.247
	N 25	25	
Hydro.	Mean 2.24	1.61	.009
	SD 0.83	0.70	.518
	N 23	21	
SAM	Mean 1.87	1.60	.251
	SD 0.58	0.97	.088
	N 19	24	
Solub.	Mean 2.34	1.29	.019
	SD 1.37	1.71	.189
	N 25	26	

(a) P-value for mean separation based on t test, not assuming equal variances. Separation for standard deviations (SD) based on Levene's test for equal variances. Values of p less than .05 are considered significant.

The 90th percentile calculations are shown in Table 4. The back-transformed 90th percentiles are Koc 1900 cm^3/gm , hydrolysis 14 days, soil aerobic metabolism 610 days and water solubility 3 parts per million (ppm).

The classification of contaminants and non-contaminants, using the logic detailed in the Methods Section in combination with the derived 90th percentiles, is shown in Tables 5 and 6, respectively. The errors associated with this technique are shown in Table 7. Three compounds contained insufficient information to classify. Of the remaining 49, 30.6% were misclassified. Most of the errors resulted from misclassification of non-contaminants. This error rate was an improvement over 1988, where the misclassification rate was 35.4% (Johnson, 1988).

CONCLUSION

A list of 26 contaminant and 26 non-contaminant pesticides were analyzed to determine specific numeric values. Significant mean separation of log₁₀ transformed values occurred for Koc, water solubility and hydrolysis, but not for aerobic metabolism. Based on the log₁₀ transformed means, 90th percentiles were computed. Back-transformed 90th percentiles were Koc 1900 cm^3/gm , hydrolysis 14 days, soil aerobic metabolism 610 days and solubility 3 ppm. The compounds were classified as potential contaminants if (Koc < 1900 or water solubility > 3.0) and (hydrolysis half life > 14 or soil aerobic metabolism half life > 610). This procedure resulted in a 30.6% misclassification rate, which compared favorably to the 35.4% error rate in 1988.

Table 4. 90th percentile calculations based on log10 transformed contaminant data. The formula is 90th percentile = mean + (SD)(T), where + was used for Koc and SAM and - for hydrolysis and solubility, SD is standard deviation, and T is the appropriate T value (value where 90% of the distribution is lower for Koc and SAM and higher for hydrolysis and solubility with N-1 degrees of freedom).

	Mean of log10 values	SD	N	T	Log10 90th percentile	Back- transform
Koc	2.17	0.84	25	1.32	3.28	1900 cm ³ /gm
Hydro.	2.24	0.83	23	1.32	1.14	14 days
SAM	1.72(a)	0.82(a)	43	1.30	2.79	610 days
Solub.	2.34	1.37	25	1.32	0.53	3 ppm

Note: Back-transformed values may not agree exactly with computations using values in this table due to greater precision in original calculations and round-off differences. Back-transformed values were rounded off to nearest integer or 2 significant places.

(a) Based on pooled contaminant and non-contaminant data since no significant differences were detected between the 2 group means.

Table 5. Classification of contaminant compounds based on specific numerical values. See Table 1 for further notes.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism	Water Solubility	Class
Alachlor	150*	720*	18	200*	C
Aldicarb	79*	670*	14	6000*	C
Atrazine	180*	160*	190	33*	C
Bromacil	60*	110*	300	820*	C
Carbofuran	48*	60*	23	320*	C
Chloramben	280*	370*	-1	700*	C
Chlorothalonil	2500	49*	35	0.6	N
Chlorthal dimethyl	4000	36*	24	3	N
Cyanazine	180*	260*	15	170*	C
2,4-D	53*	4	8	230*	N
DBCP	80*	7100*	180	1000*	C
Dicamba	1.5*	30*	61	6100*	C
Dieldrin	7100	1500*	1000*	0.12	N
Dinoseb	110*	30*	-1	75*	C
Diuron	460*	110*	-1	42*	C
EDB	44*	7100*	44	3400*	C
Fonofos	5100	110*	120	16*	C
Metolachlor	190*	210*	-1	530*	C
Metribuzin	150*	130*	110	1100*	C
Oxamyl	6*	6	180	280000*	N
Picloram	26*	650*	350	430*	C
Prometon	79*	1100*	280	720*	C
Propachlor	340	-1	-1	700	I
Propylene dichloride	49	-1	-1	2700	I
Simazine	220*	110*	110	4.9*	C

* Indicates value which exceeds specific numeric value.

C Indicates classified as contaminant.

N Indicates classified as non-contaminant.

I Indicates insufficient information to classify.

Table 6. Classification of non-contaminant compounds based on specific numerical values. See Table 2 for further notes.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism	Water Solubility	Class
Aldrin	14000	-1	120	0.027	N
Ametryne	380*	28*	37	190*	C
Carbaryl	360*	5.2	8	110*	N
Chlordane	33600	110*	54	1.9	N
Chlorpyrifos	17000	73*	88	0.71	N
DDD	46000	-1	-1	-1	I
DDT	160000	-1	3800*	0.003	N
Diazinon	1200*	20*	17	61*	C
Dimethoate	17*	62*	2	25000*	C
Disulfoton	940*	320*	2	14*	C
1,3-D	150*	7	13	1000*	N
Endosulfan	2000	14	32	0.33	N
Ethoprop	180*	-1	25	770*	N
Fenamiphos	280*	300*	22	560*	C
Heptachlor	16000	180*	2000*	0.06	N
Lindane	2500	310*	790*	10*	C
Linuron	670*	55*	78	75*	C
Malathion	1000*	48*	1	140*	C
Methiocarb	490*	24*	-1	27*	C
Methyl bromide	390*	-1	35	9200*	N
Naled	167*	0.68	3	2000*	N
Pendimethalin	16000	60*	1300*	0.28	N
Phorate	2400	3.1	3	18*	N
Prometryn	680*	75*	150	48*	C
Silvex	-1	-1	16	160*	N
Toxaphene	-1	110*	-1	1.9	N
Trifluralin	9900	110*	180	1.8	N

* Indicates value which exceeds specific numeric value.

C Indicates classified as contaminant.

N Indicates classified as non-contaminant.

I Indicates insufficient information to classify.

Table 7. Classification errors using 90th percentile statistics.

Number of Compounds				
		Classified as		
		<u>non-contam</u>	<u>contam</u>	
<u>Actual</u>	non-contam	16	10	26
<u>Class</u>	contam	5	18	23
Total				49
Number misclassified				15

Fraction of Compounds				
		Classified as		
		<u>non-contam</u>	<u>contam</u>	
<u>Actual</u>	non-contam	.327	.204	.531
<u>Class</u>	Contam	.102	.367	.469
Total				1.000
Fraction misclassified				.306

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A P P E N D I X B

CRITERIA FOR INCLUSION OF COMPOUND AS 'CONTAMINANT'

To classify a compound as a contaminant for the purposes of determining the specific numerical values, ground water studies are required which document the presence of the compound in ground water due to legal agricultural use. The ideal study would include the following attributes: good chemical analytical quality control such as spike recoveries conducted near the proposed lower limit of detection and field blanks; adequate confirmation of all positive detections; low temperature storage and clean handling of samples; sufficient description of wells to discern if the casing were cracked; sufficient site descriptions to determine if point sources such as leaky pesticide containers in mixer/loader operations, or direct entry mechanisms like dry wells may have caused the positive detection; surveys to insure that the detected compound was in normal agricultural use; and verification chemical sampling that may include reanalysis of the same positive sample and/or analysis of a second replicate sample obtained from the same location.

In practice, few studies fulfill all of these requirements. Studies vary in how much sampling and surveying was conducted, and in how much of what was conducted is reported. Several studies reviewed present detailed questionnaires, but fail to present the data from the questionnaires. Alternatively, in many instances the survey data is summarized so that it is not possible to link the actual well in which a pesticide was found to the particular site description for the well. Consequently, judgments are required in order to classify a compound as a contaminant. For the purposes of eventual statistical analysis, these judgments should be made independently

of whatever knowledge may exist about the physicochemical characteristics of a compound. Otherwise the analysis becomes biased.

As a practical matter, the general conduct of the studies is evaluated. The sampling and laboratory methods are evaluated for analytical quality and the reviewer looks for hints or direct statements as to possible point source contamination. Recognizing the uncertainty and possible inability to determine the source of contamination, three out-of-state studies with positive ground water detections are required for a compound to be considered a contaminant. This will constitute evidence that a compound has leached into ground water to a significant degree. Studies are not used which fail to report on methods, are poorly written, or present reasons for doubting the validity of the methods. Alternatively, compounds detected in California, which have been found in ground water may be considered contaminants if samples are confirmed and subsequent investigation indicates that the compound reached ground water through leaching and not from a point source or other extenuating condition. Also, a compound may be classified as a contaminant if it is shown to leach by column studies or soil coring studies, even though ground water sampling may not be involved.

When metabolites are found, they must be reported as metabolites, not as the parent compound because the SNV process depends on the characteristics of the actual compounds which leached or did not leach. Unfortunately, in some cases, there is no information available on adsorption, hydrolysis, etc. for metabolites.