

# **SETTING REVISED SPECIFIC NUMERICAL VALUES**

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Pursuant to the  
Pesticide Contamination Prevention Act

By  
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**ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM**



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## SETTING REVISED SPECIFIC NUMERICAL VALUES

### INTRODUCTION

The Pesticide Contamination Prevention Act requires the California Department of Food and Agriculture (CDFA) to set certain numeric 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 1990 of specific numeric values (SNVs) utilizing the 90th percentile of distributions of chemical properties. Throughout this report, the terms "leachers" and "non-leachers" refer to compounds, respectively, which have or have not been detected in ground water as a result of normal agricultural use. The primary hypothesized mechanism of transport is assumed to be leaching through the soil.

### SCOPE AND METHODS OF THE 1990 REPORT

The main effort for the 1990 report consisted of adding anaerobic soil metabolism (ANA) to the test types used to screen compounds. For all types, the normality of the log-transformed distributions was examined, the hypothesis structure was revised, and new significance levels were calculated. Aside from the addition of bentazon to the list of leachers for anaerobic metabolism half life, the remaining data were unaltered and the detection history for this 1990 report was not updated. Further methodological details may be found in previous reports (Johnson 1989, Johnson 1988, Wilkerson and Kim 1986).

Anaerobic soil metabolism half lives were estimated from open scientific literature and studies submitted to CDFA from chemical companies for the purpose of fulfilling the data-call-in requirements of the Pesticide Contamination Prevention Act.

Selected pesticide active ingredients were first categorized as either leacher or non-leacher based on their detection history. Then the normality of the data for each category was examined by calculating the Kolmogorov-Smirnov statistic in comparison to the cumulative normal distribution (Press et al. 1989), and by examining the 3rd (skewness) and 4th (kurtosis) moments in comparison to the normal distribution (Dixon 1988, Snedecor and Cochran 1980). The Kolmogorov-Smirnov statistic utilizes the maximum distance between the cumulative normal distribution and the cumulative empirical distribution of the group being tested. The Kolmogorov-Smirnov statistics were calculated using routines supplied by Press et al. (1989), and using their routine for the Students t-distribution with 5000 degrees of freedom to approximate the normal distribution. Skewness indicates the degree of asymmetry of the distribution about the mean. Kurtosis indicates how peaked or flat a distribution is about the mean. The skewness and kurtosis divided by their standard deviations ( $\sqrt{6/N}$  and  $\sqrt{24/N}$ , respectively) are approximately normally distributed with mean 0 and standard deviation of 1 (Dixon 1988). Snedecor and Cochran (1980), however, caution against using standard tables for kurtosis when sample sizes are less than 1000. Therefore, no significance level was estimated for kurtosis. The significance level for skewness was derived from a normal probability table using a 2-sided alternative hypothesis. A normal distribution would have a kurtosis of 0. The skewness and kurtosis calculations were obtained using BMDP version 1990 (Dixon 1988). For either the Kolmogorov-Smirnov or skewness/SD statistic, P values less than 0.05 were considered significant.

The underlying assumptions behind the screening model are that a compound will be more likely to leach to ground water if it exhibits a low Koc, a high solubility, and a long half life. Translating into statistical terms, these statements refer to a series of one-sided alternative hypotheses which

compare leachers to non-leachers. For example, the appropriate hypotheses to test for Koc are:

Null hypothesis: There is no difference in the mean Koc between leachers and non-leachers.

Alternative: Mean Koc of leachers is less than the mean Koc of non-leachers.

The remaining hypotheses are structured as follows:

Null hypothesis: There is no difference in the mean hydrolysis half life (aerobic metabolism half life, water solubility, anaerobic metabolism half life) between leachers and non-leachers.

Alternative: Mean hydrolysis half life (aerobic metabolism half life, water solubility, anaerobic metabolism half life) of leachers is greater than mean hydrolysis half life (aerobic metabolism half life, water solubility, anaerobic metabolism half life) of non-leachers.

In previous reports (Johnson 1989, Johnson 1988, Wilkerson and Kim 1986), a two-sided t-test was employed which only tested for inequality of mean values and did not impart any sense that any particular mean was greater or lesser than the other. In order to make the test consistent with the actual hypotheses used in the screening model, one-sided alternative tests were used. The significance levels (p-values) shown in Table 3 reflect one-sided t-tests.

With the exception of aerobic metabolism, SNVs were set based on the mean and standard deviation of the log-transformed leacher population using a t-distribution. For adsorption, the SNV value was calculated as the partition

at which 90% of the leacher population was below the SNV. For solubility, hydrolysis, and anaerobic metabolism the SNV was calculated as the partition at which 90% of the leacher population was above the SNV. Because the leacher and non-leacher aerobic metabolism half life means did not separate statistically, a high value was set in order to reduce its influence on the screening procedure. Greater detail may be found in Johnson (1989, 1988) and Wilkerson and Kim (1986).

A final methodology note concerns the use of anaerobic metabolism in the screening procedure. The language of the law, with the addition of anaerobic metabolism, provides for the following logic in testing each compound:

Classify as a potential leacher if:

(A or B) and (C or D or E) is 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'
- E = 'ANA half life greater than V5'

and V1, V2, V3, V4, V5 are SNVs.

After setting SNVs, this logic was used to test each leacher and non-leacher compound to determine into which group it would be classified. The classification error rate was then computed by comparing the actual classification based on the detection history to the SNV procedure's classification based on the physicochemical properties.

## RESULTS

Estimated physicochemical properties, including an additional column for anaerobic metabolism for leachers and non-leachers are listed in Table 1 and Table 2, respectively. Statistical summary for each of the group characteristics is provided in Table 3. Variances were previously found to be not significantly different between groups (Johnson 1989) and employing a t-test assuming either equal or unequal variances made very little difference in the significance level. Significance levels shown assume unequal variances.

As in the previous report (Johnson 1989), aerobic metabolism means were not significantly different at the 5% level. Anaerobic soil metabolism rates, however, were significantly different ( $p < 3.3\%$ , Table 3), though exceptions were evident in the data. For example, chlordane on the non-leacher list had an estimated half life of 8200 days, and oxamyl and alachlor on the leacher list had estimated half lives of 3 and 5 days, respectively. A possible explanation for chlordane not leaching into ground water may lie with its high capacity to bind to the soil with a Koc of  $33600 \text{ cm}^3/\text{g}$ . Conversely, oxamyl has an extremely low Koc of  $6 \text{ cm}^3/\text{g}$  and a very high solubility of 280000 ppm, factors which would contribute to its leachability. Like oxamyl, alachlor has a moderately low Koc of  $150 \text{ cm}^3/\text{g}$ . Unlike oxamyl, however, alachlor has a moderately low solubility of 200 ppm. Perhaps a multivariate procedure would provide more distinction between leachers and non-leachers based on their physicochemical properties.

The relative importance of anaerobic compared to aerobic metabolism may relate to the general conditions under which pesticides leach to ground water. As compounds leach downward, at what point do the conditions become



Table 1. List of leachers. Units are Koc = cm<sup>3</sup>/gm, hydrolysis, aerobic metabolism, and anaerobic metabolism = days (half life), water solubility = ppm. Data has been rounded to 2 significant figures. No data is indicated by NA.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism Half-Life	Water Solubility	Anaerobic Metabolism Half-Life
Alachlor	150	720	18	200	5
Aldicarb	79	670	14	6000	41
Atrazine	180	160	190	33	3400
Bentazon	NA	NA	NA	NA	3500
Bromacil	60	110	300	820	170
Carbofuran	48	60	23	320	20
Chloramben	280	370	NA	700	59
Chlorothalonil	2500	49	35	0.6	8
Chlorthal dimethyl	4000	36	24	3	150
Cyanazine	180	260	15	170	110
2,4-D	53	4	8	230	60
DBCP	80	7100	180	1000	740
Dicamba	1.5	30	61	6100	88
Dieldrin	7100	1500	1000	0.12	270
Dinoseb	110	30	NA	75	NA
Diuron	460	110	NA	42	1000
EDB	44	7100 (a)	44	3400	230
Fonofos	5100	110	120	16	150
Metolachlor	190	210	NA	530	84
Metribuzin	150	130	110	1100	60
Oxamyl	6	6	180	280000	3
Picloram	26	650	350	430	5100
Prometon	79	1100	280	720	61
Propachlor	340	NA	NA	700	NA
Propylene dichloride	49	NA	NA	2700	NA
Simazine	220	110	110	4.9	58

(a) Winsorized original value of 100,000,000 .

Table 2. List of non-leachers. Units are Koc = cm<sup>3</sup>/gm, hydrolysis, aerobic metabolism and anaerobic metabolism = days (half life), water solubility = ppm. Data has been rounded to 2 significant figures. No data is indicated by NA.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabolism Half-Life	Water Solubility	Anaerobic Metabolism Half-Life
Aldrin	14000	NA	120	0.027	130
Ametryne	380	28	37	190	320
Carbaryl	360	5.2	8	110	76
Chlordane	33600	110	54	1.9	8200
Chlorpyrifos	17000	73	88	0.71	140
DDD	46000	NA	NA	NA	160
DDT	160000	NA	3800	0.003	53
Diazinon	1200	20	17	61	35
Dimethoate	17	62	2	25000	1
Disulfoton	940	320	2	14	2.4
1,3-D	150	7	13	1000	16
Endosulfan	2000	14	32	0.33	150
Ethoprop	180	NA	25	770	130
Fenamiphos	280	300	22	560	120
Heptachlor	16000	180	2000	0.06	39
Lindane	2500	310	790	10	37
Linuron	670	55	78	75	15
Malathion	1000	48	1	140	30
Methiocarb	490	24	NA	27	64
Methyl bromide	390	NA	35	9200	6
Naled	167	0.68	3	2000	2
Pendimethalin	16000	60	1300	0.28	50
Phorate	2400	3.1	3	18	7
Prometryn	680	75	150	48	360
Silvex	NA	NA	16	160	32
Toxaphene	NA	110	NA	1.9	25
Trifluralin	9900	110	180	1.8	37

Table 3. Statistics for log<sub>10</sub> transformed characteristics of leacher and non-leacher pesticides.

		Leachers	Non-leachers	P-values (a)
Koc	Mean	2.17	3.23	p<.001
	SD	0.84	0.95	p<.247
	N	25	25	
Hydro.	Mean	2.24	1.61	p<.004
	SD	0.83	0.70	p<.518
	N	23	21	
SAM	Mean	1.87	1.60	p<.126
	SD	0.58	0.97	p<.088
	N	19	24	
Solub.	Mean	2.34	1.29	p<.009
	SD	1.37	1.71	p<.189
	N	25	26	
Anaer.	Mean	2.08	1.64	p<.033
	SD	0.85	0.79	p<.673
	N	23	27	

(a) P-values based on 1-sided t test, assuming unequal variances. Separation for standard deviations (SD) based on Levene's test for equal variances. Values of p less than .05 are considered significant.

anaerobic? It is not possible to specify a particular depth below the surface at which the soil atmosphere becomes anaerobic. In general, conditions become more anaerobic with depth, finer textured soils, and increasing soil moisture (Ball 1981ab, Campbell 1985, Grundman and Rolston 1987, Lund et al. 1974, Rolston 1981, Stolzy and Fluehler 1978). Temperature and microbial activity can also affect oxygen conditions in the soil. The relative statistical importance of anaerobic half lives suggest that anaerobic conditions may be more important than aerobic in determining whether or not pesticides will eventually leach into ground water. For example, the subcommittee examining scientific evidence about the presence of bentazon in ground water concluded that "...because of the long persistence of bentazon in anaerobic conditions, there is a high likelihood of movement of bentazon through non-gravelly soils under flooded rice growing practices." (Hawkins et al. 1990 p. 3) The means of the log-transformed data for leacher and non-leacher anaerobic metabolism rates were 2.08 and 1.64, respectively. Backtransforming these means results in 120 and 44 day half lives, respectively. This would imply, for example, that if all other conditions were equal and if downwardly leaching solute required 2 years to reach ground water, the concentrations reaching ground water would be reduced by 2 vs 5 orders of magnitude (.01 vs .00001) of the surface concentrations for the 120 and 44 day half lives, respectively.

Use of the t-test, both in assessing the significance of differences in group means, and to derive the specific numerical values, requires an underlying assumption of normality in the data. All data were log-transformed prior to analysis due to significant non-normality in the untransformed data. The log base 10 transformation apparently normalized all the data. Neither the Kolmogorov-Smirnov test, nor skewness or kurtosis calculations indicated significant departure from normality (Table 4), with

Table 4. Statistical indicators of non-normality for log<sub>10</sub>-transformed data for leachers (L) and non-leachers (NL) for each physicochemical test type: soil adsorption (Koc), hydrolysis (Hyd), soil aerobic metabolism (SAM), water solubility (WS), and soil anaerobic metabolism (ANA). The Kolmogorov-Smirnov statistic, D, is the maximum distance between the cumulative normal distribution and the cumulative empirical distribution of the group being tested. Significance levels, P, were calculated as described in Methods. P values less than 0.05 are considered significant.

Group	Kolmogorov-Smirnov		Asymmetry			Flatness	
	<u>D</u>	<u>P</u>	<u>Skewness</u>	<u>Skewness/SD</u>	<u>P</u>	<u>Kurtosis</u>	<u>Kurtosis/SD</u>
KOC							
L	0.15	0.67	0.11	0.22	0.82	0.18	0.19
NL	0.12	0.85	0.20	0.40	0.69	-0.74	-0.76
Hyd							
L	0.10	0.98	0.10	0.19	0.84	-0.41	-0.41
NL	0.16	0.64	-0.79	-1.48	0.14	-0.05	-0.04
SAM							
L	0.14	0.85	0.04	0.07	0.94	-1.18	-1.05
NL	0.10	0.98	0.33	0.66	0.51	-0.73	-0.73
L+NL <sup>a</sup>	0.07	0.99	0.09	0.25	0.80	-0.39	-0.53
WS							
L	0.15	0.64	-0.38	-0.78	0.44	0.26	0.26
NL	0.10	0.98	-0.30	-0.63	0.52	-0.62	-0.65
ANA							
L	0.14	0.77	0.20	0.39	0.70	-0.49	-0.48
NL	0.13	0.78	0.29	0.61	0.54	0.98	1.04

<sup>a</sup> Provided because there was no significant statistical separation between leacher and non-leacher aerobic metabolism means.

the possible exception of hydrolysis for non-leachers. Snedecor and Cochran (1980, Table A20) provide an estimate of significance for skewness at a 2% two-tailed significance level of 1.061 for a sample size of 25. This probably would be exceeded by the calculated value of -1.48 for a sample size of 21 found for the data in this report. As this primarily relates to the comparison of the leacher and non-leacher means, the significance of this comparison was recalculated on transformed values using the Mann-Whitney non-parametric test, which does not assume normality. The result was  $W=624.5$ ,  $p<.012$  ( $p<1.2\%$ ). Therefore, the possible non-normality of hydrolysis for non-leachers did not affect the significant difference between mean hydrolysis half lives for leachers and non-leachers. While larger sample sizes are required to evaluate the significance of the kurtosis calculations (Snedecor and Cochran 1980), the kurtosis/SD values do not appear to be extreme.

The 90th percentile calculations indicate that the anaerobic metabolism SNV is 9 days (Table 5). Taken together with the logic outlined in the methods section, a pesticide would be classified as a leacher if either water solubility is greater than 3 ppm or Koc is less than  $1900 \text{ cm}^3/\text{g}$ , and either hydrolysis half life is greater than 14 days or aerobic metabolism is greater than 610 days or anaerobic metabolism is greater than 9 days.

The results of using this screening procedure on the physicochemical data are shown in Tables 6 and 7. Three of the compounds were not classifiable. Of the remaining compounds, 33 were classified as leachers and 17 were classified as non-leachers. Table 8 summarizes the errors produced by the screening model. Of the 18 misclassifications, 14 non-leachers were erroneously classified as leachers. A total of 36% of the compounds were misclassified. This represents a minor increase in the error rate over the

Table 5. 90th percentile calculations based on log10 transformed leacher data. The formula is 90th percentile = mean + (SD)(T), where + was used for Koc and SAM and - for hydrolysis, solubility and anaerobic metabolism, 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, solubility and anaerobic metabolism with N-1 degress 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 <sup>3</sup> /gm
Hydro.	2.24	0.83	23	1.32	1.14	14 days
SAM	1.72 <sup>a</sup>	0.82 <sup>a</sup>	43	1.30	2.79	610 days
Solub.	2.34	1.37	25	1.32	0.53	3 ppm
Anaer.	2.08	0.85	23	1.32	0.96	9 days

Note: Back-transformed values many 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.

<sup>a</sup>Based on pooled leacher and non-leacher data since no significant differences were detected between the 2 group means.

Table 6. Classification of leacher compounds based on specific numerical values. See Table 1 for further notes.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabol.	Water Solub.	Anaer. Metab.	Class
Alachlor	150*	720*	18	200*	5	L
Aldicarb	79*	670*	14	6000*	41*	L
Atrazine	180*	160*	190	33*	3400*	L
Bentazon	NA	NA	NA	NA	3500*	I
Bromacil	60*	110*	300	820*	170*	L
Carbofuran	48*	60*	23	320*	20*	L
Chloramben	280*	370*	NA	700*	59*	L
Chlorothalonil	2500	49*	35	0.6	8	N
Chlorthal dimethyl	4000	36*	24	3	150*	N
Cyanazine	180*	260*	15	170*	110*	L
2,4-D	53*	4	8	230*	60*	L
DBCP	80*	7100*	180	1000*	740*	L
Dicamba	1.5*	30*	61	6100*	88*	L
Dieldrin	7100	1500*	1000*	0.12	270*	N
Dinoseb	110*	30*	NA	75*	NA	L
Diuron	460*	110*	NA	42*	1000*	L
EDB	44*	7100*	44	3400*	230*	L
Fonofos	5100	110*	120	16*	150*	L
Metolachlor	190*	210*	NA	530*	84*	L
Metribuzin	150*	130*	110	1100*	60*	L
Oxamyl	6*	6	180	280000*	3	N
Picloram	26*	650*	350	430*	5100*	L
Prometon	79*	1100*	280	720*	61*	L
Propachlor	340*	NA	NA	700*	NA*	I
Propylene dichloride	49*	NA	NA	2700*	NA*	I
Simazine	220*	110*	110	4.9*	58*	L

\* Indicates value which exceeds specific numeric value.

L Indicates classified as leacher.

N Indicates classified as non-leacher.

I Indicates insufficient information to classify.



Table 7. Classification of non-leacher compounds based on specific numerical values. See Table 2 for further notes.

Pesticide	Koc	Hydrolysis Half-Life	Aerobic Metabol.	Water Solub.	Anaer. Metab.	Class
Aldrin	14000	NA	120	0.027	130*	N
Ametryne	380*	28*	37	190*	320*	L
Carbaryl	360*	5.2	8	110*	76*	L
Chlordane	33600	110*	54	1.9	8200*	N
Chlorpyrifos	17000	73*	88	0.71	140*	N
DDD	46000	NA	NA	NA	160*	N
DDT	160000	NA	3800*	0.003	53*	N
Diazinon	1200*	20*	17	61*	35*	L
Dimethoate	17*	62*	2	25000*	1	L
Disulfoton	940*	320*	2	14*	2.4	L
1,3-D	150*	7	13	1000*	16*	L
Endosulfan	2000	14	32	0.33	150*	N
Ethoprop	180*	NA	25	770*	130*	L
Fenamiphos	280*	300*	22	560*	120*	L
Heptachlor	16000	180*	2000*	0.06	39*	N
Lindane	2500	310*	790*	10*	37*	L
Linuron	670*	55*	78	75*	15*	L
Malathion	1000*	48*	1	140*	30*	L
Methiocarb	490*	24*	NA	27*	64*	L
Methyl bromide	390*	NA	35	9200*	6	N
Naled	167*	0.68	3	2000*	2	N
Pendimethalin	16000	60*	1300*	0.28	50*	N
Phorate	2400	3.1	3	18*	7	N
Prometryn	680*	75*	150	48*	360*	L
Silvex	NA	NA	16	160*	32*	L
Toxaphene	NA	110*	NA	1.9	25*	N
Trifluralin	9900	110*	180	1.8	37*	N

\* Indicates value which exceeds specific numeric value.

L Indicates classified as leacher.

N Indicates classified as non-leacher.

I Indicates insufficient information to classify.

Table 8. Classification errors using 90th percentile statistics.

Number of Compounds				
		Classified as		
		non-leacher	leacher	
Actual non-leacher		13	14	27
Class leacher		4	19	23
Total				50
Number misclassified				18

  

Fraction of Compounds				
		Classified as		
		non-leacher	leacher	
Actual non-leacher		.260	.280	.540
Class leacher		.080	.380	.460
Total				1.000
Fraction misclassified				.360

previous year. It should be noted that the error rate is based on the data which was used to derive the SNVs and therefore, may understate the error rate which might occur for compounds not used to derive the SNVs.

Further research should be initiated to determine if other screening procedures might lower the error rate. A multivariate approach such as discriminant analysis, for example, might have an advantage over the current univariate approach by simultaneously accounting for varying physicochemical parameters.

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