

**THE PESTICIDE CONTAMINATION PREVENTION ACT:  
SETTING SPECIFIC NUMERICAL VALUES**

by

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## SUMMARY

The Pesticide Contamination Prevention Act (PCPA) (Food and Agricultural Code, Division 7, Chapter 2, Article 15, Section 13144) requires the California Department of Food and Agriculture (CDFA) to establish specific numerical values (SNVs) for water solubility, soil adsorption coefficient (Koc), hydrolysis half-life, aerobic and anaerobic soil metabolism and field dissipation of pesticides by December 1, 1986\*. Pesticides whose environmental fate properties exceed the SNVs must be reported to the State Legislature by December 1, 1987 and may be subject to further regulation if their agricultural use practices increase the probability that these pesticides will contaminate ground water.

SNVs were calculated using a method that is quantitative, reproducible and verifiable by historical detection data while adhering to PCPA requirements. The procedure for calculating SNVs was accomplished in two phases. In the initial phase, pesticide monitoring studies were performed to determine which pesticides had been detected in ground water as a result of agricultural use, and which pesticides have not yet been detected in ground water. Next, values for the environmental fate variables required by the PCPA were collected from published literature for over 200 active ingredients. The collected data were then entered into a data base management system for future statistical analysis.

The final phase involved evaluation and selection of mathematical and statistical methods that could be used to determine the most appropriate criteria for identifying potential ground water pollutants. The primary concern in setting values was that the final values should correctly classify pesticides according to their actual presence or absence in ground water. Therefore, a method of calculating SNVs was chosen based on a comparison of environmental fate values of common contaminants with those of non-contaminants. Comparison of environmental fate values of contaminant and non-contaminant pesticides revealed that while there are significant differences in the Koc and water solubility between the two

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\*While collecting values on environmental fate properties, it became apparent that sufficient data for independent values of aerobic and anaerobic metabolism or field dissipation did not exist. Consequently, these categories have been grouped together and represented by an SNV for soil degradation half-life.

pesticide groups, there are no significant differences between the hydrolysis and soil degradation half-lives of the two groups.

Based on available data, CDFA has determined that pesticides with the following average values may be classified as potential ground water contaminants:

- A. Soil adsorption coefficient (Koc) less than  $512 \text{ cm}^3/\text{gm}$  or water solubility greater than 7 parts per million, and
- B. Hydrolysis half-life greater than 13 days or soil degradation half-life greater than 11 days.

These values and the methods by which they were derived were reviewed by consultants from the University of California. The values are more stringent than criteria currently used by the U.S. Environmental Protection Agency for Koc ( $300\text{--}500 \text{ cm}^3/\text{gm}$ ), water solubility (30 ppm), hydrolysis half-life (25 weeks) or soil degradation half-life (2-3 weeks).

CDFA efforts to calculate SNVs were hampered by a lack of environmental fate data for many pesticides and by a general tendency to report the details of only positive detections when ground water surveys were conducted. More standardized data should be available after the PCPA environmental fate data collection process is completed. As provided for in the PCPA, the SNVs now proposed should be revised to improve their ability to identify ground water contaminants as additional data become available, and before the SNVs are used to prepare the annual lists of potential ground water contaminants.

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**THE PESTICIDE CONTAMINATION PREVENTION ACT:  
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**INTRODUCTION**

This report summarizes a procedure to set specific numerical values for certain pesticide properties as required by the Pesticide Contamination Prevention Act, Food and Agricultural Code, Division 7, Chapter 2, Article 15, Section 13144. Section 13144 requires that the California Department of Food and Agriculture (CDFA) establish specific numerical values (SNVs) for water solubility, soil adsorption coefficient (Koc), hydrolysis, aerobic and anaerobic soil metabolism, and field dissipation. Pesticides whose chemical properties exceed the SNVs will be reported to the State Legislature, and may later be placed upon a Ground Water Protection List depending upon whether their registered use practices present a risk of ground water contamination.

Three activities occurred in the initial phase of setting SNVs. First, a survey of ground water quality studies was conducted to identify pesticides and pesticide breakdown products which have been detected in ground water as a result of agricultural use in the United States, as well as those which have been monitored for, but not detected, in areas where use was known to occur. Secondly, data for environmental fate properties of over 200 pesticide active ingredients were collected from published literature. The third major activity of the initial work phase was to design a data base management structure where all of the collected data could be stored for future analysis.

The final phase in setting SNVs involved the evaluation of different mathematical and statistical methods that could be used to determine the most appropriate criteria for identifying potential ground water contaminants. By assigning pesticides into contrasting groups (contaminant vs. non-contaminant) based on their detection history, and through the application of statistical techniques to environmental fate data, we hoped to provide a suitable basis for the establishment and revision of SNVs.

**PROCEDURE**

**Environmental Fate Data**

Environmental fate data (Koc, water solubility, hydrolysis half-life and soil) was collected from published scientific literature. Water solubility and soil

adsorption coefficients were recorded along with the temperature or the percent organic carbon content and soil type at which measurements were made. Temperature, pH and type of aquatic media were included with hydrolysis data, when available. Soil degradation values included the soil type, percent soil moisture, and soil temperature when available. Soil degradation values were distinguished as aerobic or anaerobic metabolism, field dissipation studies, or studies performed under sterile laboratory conditions.

All of the data were entered into a computerized data base management system (DBMS) maintained on a PRIME 9650 minicomputer using SIR<sup>®</sup> software, at the California Department of Food and Agriculture. The data were edited for key entry errors and for accuracy.

### **Detection History Summary**

Results from several well water and ground water surveys for pesticide residues were compiled into a detection history summary. When available, the number of positive or negative detections for each pesticide, total number of samples collected and minimum detection limits were recorded, as well as whether or not pesticide use was confirmed in the immediate area of the site where the sample was taken. Positive detections arising from known point source or well contamination events were excluded from the summary. Two reports included in the summary were compilations of previous ground water monitoring activities (Cardozo *et al.* 1985, Cohen *et al.* 1985). In these reports, pesticide use was considered confirmed only in instances where the authors stated that their own analysis of the original studies, or personal knowledge, indicated that residues resulted from the routine application of specific pesticides. Individual studies on which these compilations were based were not independently reviewed by this author.

The purpose of collecting historical ground water monitoring data was to determine whether pesticides may be categorized as known contaminants or non-contaminants. Pesticides were divided into three groups: 1) pesticides reported consistently as positive detections (contaminants) in all studies where their use was confirmed (Table 1); 2) pesticides reported consistently as negative detections (non-contaminants) in all studies where their use was confirmed (Table 2); and 3) pesticides reported as positive or negative ('transition') in different studies where their use was confirmed (Table 3). Unfortunately, most monitoring studies emphasize or report only positive

Table 1. Average environmental fate values of pesticides and pesticide break-down products detected in ground water<sup>a</sup>.

Pesticide or pesticide break-down product	Koc	Hydrolysis half-life (days)	Soil Degradation half-life (days)	Solubility (ppm)
Aldicarb <sup>b</sup>	17	1800	7	6000
Atrazine <sup>b</sup>	107	72	74	52
Chlorthal dimethyl	ND	ND	100	3
Cyanazine	ND	ND	14	171
DBCP <sup>b</sup>	40	7050	ND	1000
Diuron <sup>b</sup>	389	113	188	41
EDB <sup>b</sup>	78	2100	ND	4300
Metolachlor	99	210	44	530
Metribuzin	ND	90	37	1200
Naled	133	14	ND	0.3
Oxamyl	26	6	8	269000
Picloram	26	ND	206	430
Prometon <sup>b</sup>	577	113	ND	750
Prometryn	614	75	94	48
Propylene dichloride <sup>b</sup>	955	ND	ND	2700
Simazine <sup>b</sup>	138	ND	56	4

Average for each pesticide is based on data remaining after all available values were restricted to temperatures between 20<sup>o</sup> and 25<sup>o</sup>C, and pH between 6.5 and 7.5.

a. ND = no data, or data did not meet restricted conditions.

b. Detected in California.

Table 2. Average environmental fate values of pesticides and pesticide breakdown products not detected in ground water<sup>a</sup>.

Pesticide or pesticide breakdown product	Koc	Hydrolysis half-life (days)	Soil Degradation half-life (days)	Solubility (ppm)
Aldrin	ND	ND	10	0.03
Chloramben	ND	ND	ND	700
Chlordane	19269	ND	37	2
Chlorothalenol	1380	ND	68	0.6
Chlorpyrifos	6085	44	54	1
2,4-D(amine)	53	ND	7	703
1,3-D	68	ND	ND	1425
DDD	45800	ND	ND	ND
DDT	213600	ND	38200	0.002
Dicamba	511	30	25	6150
Endosulfan	2040	14	120	ND
Endosulfan sulfate	ND	ND	ND	0.1
Endrin	11188	180	2240	0.3
Heptachlor	13330	180	109	0.06
Lindane	1727	113	569	11
Pendamethalin	ND	ND	ND	0.3
Phorate	1660	30	38	45
Propachlor	794	ND	4	660
Silvex	ND	ND	22	158
Toxaphene	95816	ND	9	3
Trifluralin	7950	ND	83	0.5

Average for each pesticide is based on data remaining after all available values were restricted to temperatures between 20<sup>o</sup> and 25<sup>o</sup>C, and pH between 6.5 and 7.5.

a. ND = no data, or data did not meet restricted conditions.

Table 3. Average environmental fate values of pesticides classified as both contaminants and non-contaminants based on qualified surveys of ground water<sup>a</sup>.

Pesticide or pesticide break-down product	Koc	Hydrolysis half-life (days)	Soil Degradation half-life (days)	Solubility (ppm)
Alachlor	161	ND	14	203
Carbaryl	423	5	19	120
Carbofuran <sup>b</sup>	55	28	37	700
Dieldrin	12100	ND	934	0.2
Dinoseb	5900	30	30	63
Ethoprop	26	ND	63	750
Fonofos	5105	ND	25	14

Average for each pesticide is based on data remaining after all available values were restricted to temperatures between 20<sup>o</sup> and 25<sup>o</sup>C, and pH between 6.5 and 7.5.

a. ND = no data, or data did not meet restricted conditions.

b. Detected in California.

detections. As a result, one study by the Iowa Department of Water, Air and Waste Management is the only qualified reference for most of the pesticides appearing in the non-contaminant group (Kelley and Wnuk, 1986).

In the initial categorization of pesticides into contaminant groups, azinphosmethyl, bromacil and terbufos were classified as contaminants, while lindane and heptachlor were included in the transition category. After review of the studies where these results were reported, azinphosmethyl, bromacil and terbufos were removed from the contaminant group, and lindane and heptachlor were moved into the non-contaminant group due to questions about the integrity of sampled wells, the existence of extreme conditions, or suspect analytical procedures (Appendix A).

Once a candidate list of contaminant and non-contaminant pesticides was developed from the detection history summary, the corresponding environmental fate data were extracted from the data base using a series of screening criteria.

Several screening criteria were applied to the environmental fate data during extraction from the data base. Duplicate values given by several authors were eliminated if cross referencing clearly occurred. Values were also restricted to a pH range of 6.5 to 7.5, and to temperatures between 20° and 25°C on the assumption that these represent general environmental conditions in California agricultural soils. Whenever pH or temperature data were missing, it was assumed that values fell within the acceptable range determined by the screening criteria as unusual experimental conditions are frequently specified, when they occur. Soil adsorption and soil degradation data were not restricted by soil type, unless the values had been obtained using sterile soil or activated sludge. Soil adsorption coefficients (Koc) were calculated from reported Kd values only when the percent organic carbon content was known<sup>1</sup>. No further calculation or estimation of missing values was attempted. An average value for each environmental fate variable was calculated after extraction from the database

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1.  $Koc = Kd / \text{organic carbon fraction}$ .

(Tables 1,2 and 3). Average values were then converted to logarithmic equivalents both to normalize the variable distributions, and to aid data processing.

### Statistical Analysis

Distributions of the transformed values for each variable in contaminant and non-contaminant groups were tested for normality, and analysis of variance (ANOVA) was conducted to determine if significant differences were present in the distribution of variables between contaminant and non-contaminant pesticide groups. Then least significant difference (LSD) tests of each variable, as well as standard deviations from group means and ninetieth percentile intervals, were calculated to determine potential specific numerical values. Transition pesticides which had been reported as both contaminants and non-contaminants in qualified studies were not included in the statistical analyses. All analyses were performed using SAS® software (SAS, 1978).

The LSD between means of two distributions, or treatments, is a type of t-test based upon the combined standard errors of each treatment multiplied by a t value reflecting a chosen level of significance:

$$\text{LSD} = t_{,05} (S_1^2/r_1 + S_2^2/r_2), \quad (\text{Equation 1})$$

where  $S_x^2$  = estimated variance of treatment x, x = number of observations in treatment x, and  $t_{,05}$  = tabular t value for degrees of freedom. (Little and Hill, 1978.) When using the LSD test, contaminant ( $x_c$ ) and non-contaminant ( $x_{nc}$ ) group means are considered to be significantly different if the absolute distance between them is greater than the calculated LSD ( $|x_c - x_{nc}| > \text{LSD}$ ). The LSD can be used as a measure of the maximum difference between the values of a group mean and an independent observation, in order for the observation to be considered a member of the group represented by the mean. The SNV for Koc was calculated by subtracting the LSD from the mean of the contaminant group ( $\text{SNV} = x_c - \text{LSD}$ ). The SNVs for water solubility, hydrolysis half-life and soil degradation half-life were calculated by adding the LSD to the positive group means ( $\text{SNV} = x_c + \text{LSD}$ ). SNVs calculated in this manner represent the largest or smallest values that statistically fall within the 95% confidence limit of the contaminant group mean.

Strictly speaking, SNVs should not be determined for hydrolysis or soil degradation half life using this method, as the LSD test is invalid when there are no significant differences between group means (Table 5).

Two other statistics of the environmental fate variable distributions were used to calculate potential SNVs. The standard deviation and 90th percentile are statistics which measure the dispersion of normally distributed populations. One standard deviation from the contaminant group means of water solubility and Koc, and one standard deviation from the combined contaminant and non-contaminant means of the hydrolysis half-life and soil degradation half-life distributions were used to determine potential SNVs. Combined contaminant and non-contaminant distribution of hydrolysis and soil degradation half life were used since there were no significant differences between contaminant and non-contaminant groups for these two variables according to the ANOVA (Table 5). Approximately 84% of the contaminant pesticides have values exceeding an SNV determined by one standard deviation from the contaminant or combined group means, based on the normal probability distribution<sup>2</sup>. Similarly, SNVs based on the 90th percentile of the contaminant or combined distributions represent values which approximately 90% of the contaminant pesticides will exceed. SNVs based on the 90th percentile are slightly more conservative than SNVs based on one standard deviation from the mean, because there is a higher probability that a pesticide will exceed an SNV based on 90% of a normal distribution.

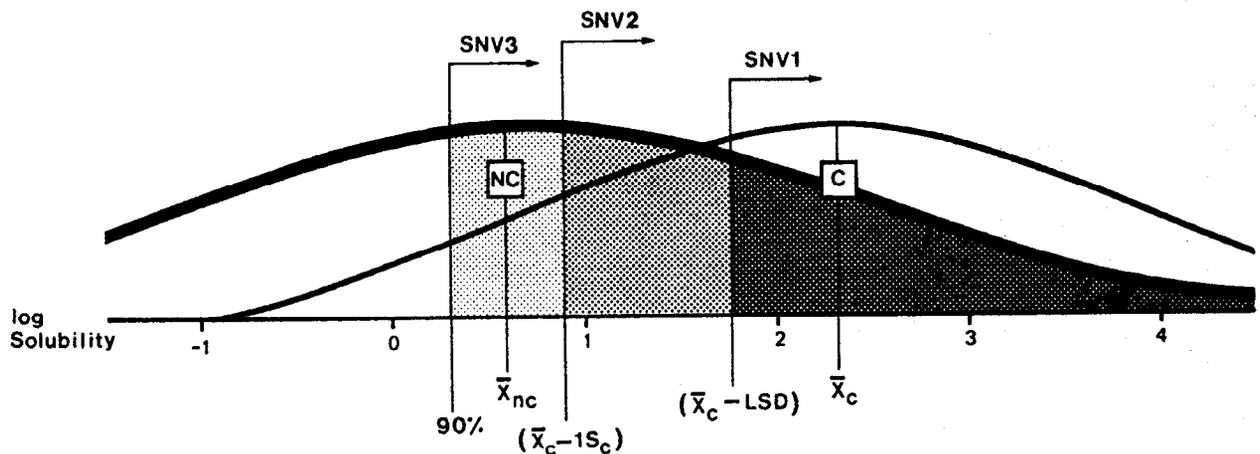
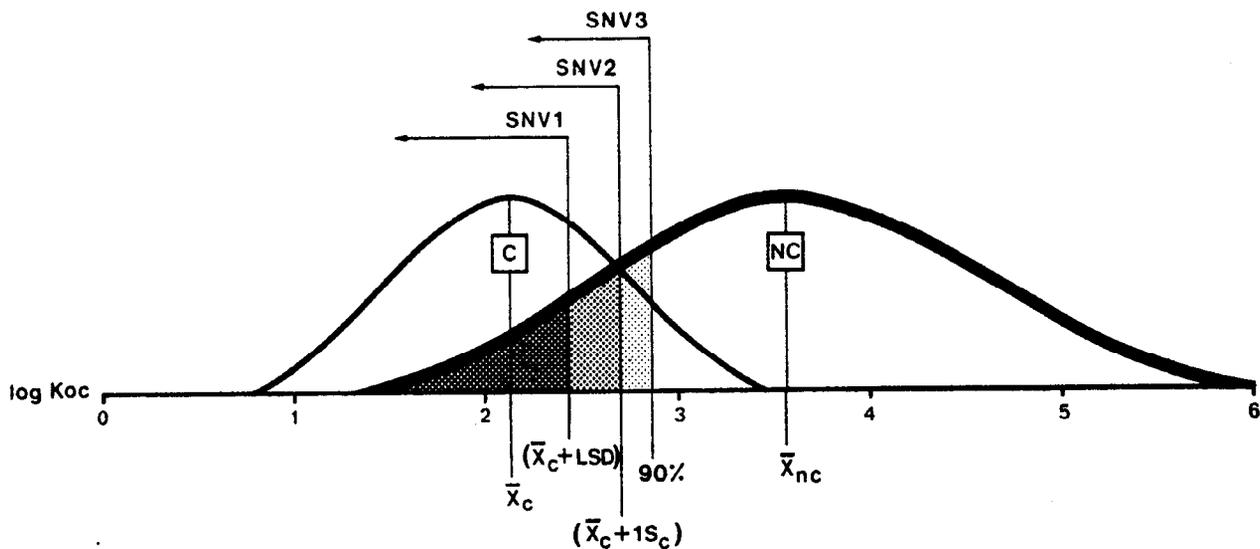
## RESULTS

The values of the contaminant and non-contaminant group means, LSDs, standard deviations and 90th percentiles used to calculate the numerical thresholds of the environmental fate variables using transformed data are shown in Table 4. SNVs calculated by the LSD method were least conservative, while SNVs based on the 90th percentile were most conservative (Figures 1 and 2). Separate SNVs could not be set for aerobic and anaerobic metabolism or field dissipation because of insufficient data. For the present, the SNVs for these degradation

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2. In this discussion, values 'exceeding' the proposed SNVs refer to water solubility, hydrolysis and soil degradation half-lives greater than the numerical value of the corresponding SNV. Koc values 'exceeding' the proposed SNV are less than the numerical value of the SNV.

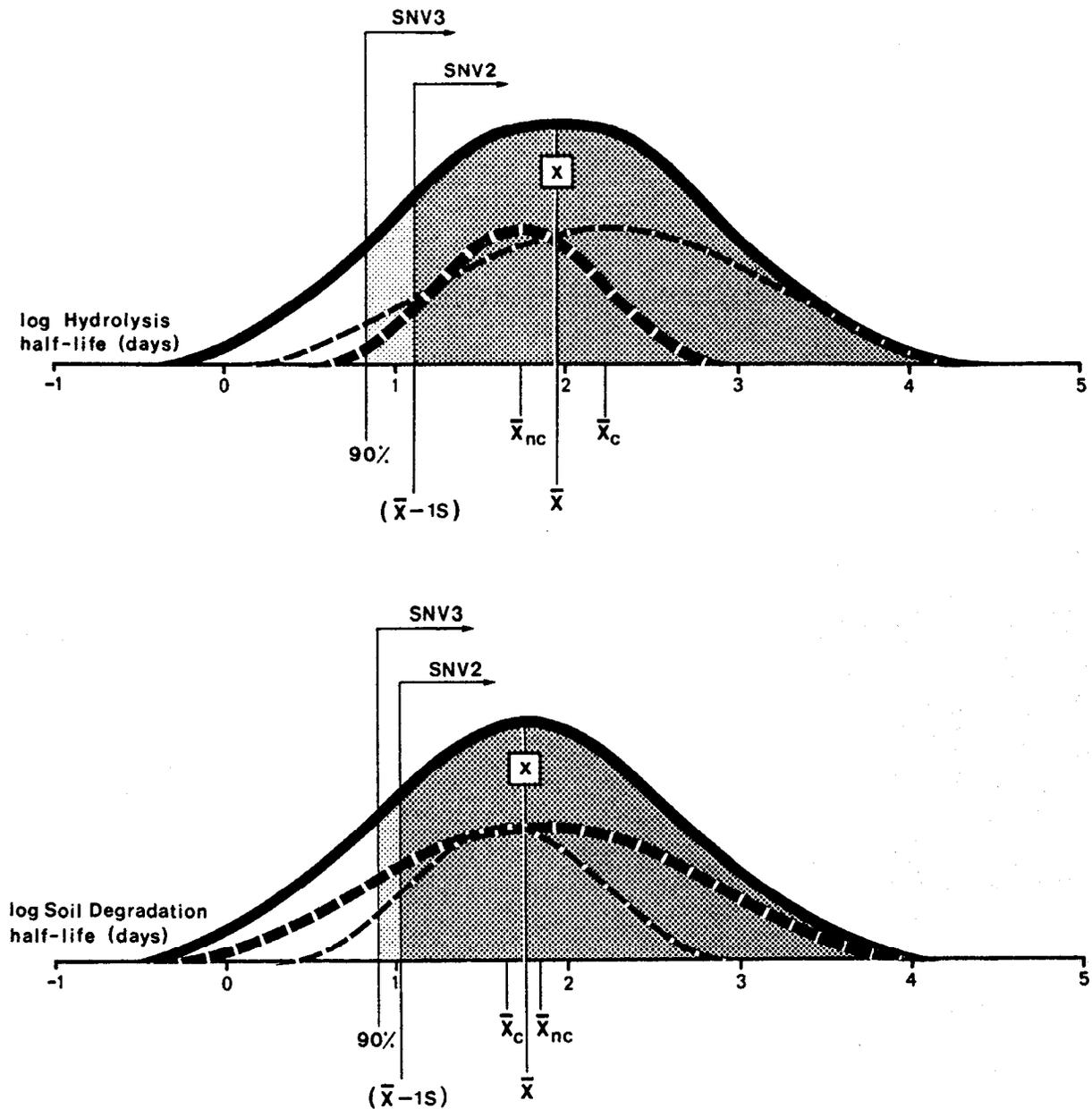
Figure 1. Stylized distributions of log Koc and log solubility of contaminant (C) and non-contaminant (NC) pesticide groups based on group means and standard deviations.



- Cumulative portion of non-contaminant distribution exceeding SNV1
- ▨ Cumulative portion of non-contaminant distribution exceeding SNV2
- ▩ Cumulative portion of non-contaminant distribution exceeding SNV3

SNV1: specific numerical value based on LSD.  
 SNV2: specific numerical value based on standard deviation.  
 SNV3: specific numerical value based on 90th percentile.  
 $\bar{x}_c$  : contaminant group mean.  
 $\bar{x}_{nc}$  : non-contaminant group mean.  
 LSD : least significant difference.  
 S : standard deviation.  
 90% : 90th percentile.

Figure 2. Stylized distributions of log hydrolysis half-life and log soil degradation half-life of contaminant (—), non-contaminant (---) and combined (X) pesticide groups based on group means and standard deviations.



- Proportion of combined contaminant and non-contaminant distributions exceeding SNV3
- Proportion of combined contaminant and non-contaminant distributions exceeding SNV2

SNV2: specific numerical value based on standard deviation.  
 SNV3: specific numerical value based on 90th percentile.  
 $\bar{x}_c$  : contaminant group mean.  
 $\bar{x}_{nc}$  : non-contaminant group mean.  
 $\bar{x}$  : combined contaminant and non-contaminant group mean.  
 S : standard deviation.  
 90% : 90th percentile.

Table 4. Descriptive statistics of environmental fate variables of contaminant and non-contaminant pesticides used to calculate specific numerical values.

Environmental fate variables	$\bar{x}_{nc}$	$\bar{x}_c$	$\bar{x}_{nc,c}$	LSD	S	90%tile
log Koc	3.5740 (n=16)	2.1250 (n=14)	na	0.3306	0.5846 <sup>a</sup>	2.8948 <sup>a</sup>
log solubility (ppm)	1.8403 (n=19)	2.3167 (n=17)	na	0.5449	1.4512 <sup>a</sup>	0.2911 <sup>a</sup>
log hydrolysis half-life (days)	na	na	1.9233 <sup>c</sup> (n=21)	ns <sup>b</sup>	0.7988 <sup>c</sup>	0.8518 <sup>c</sup>
log soil degradation half-life (days)	na	na	1.7445 <sup>c</sup> (n=35)	ns <sup>b</sup>	0.7130 <sup>c</sup>	0.9006 <sup>c</sup>

na = not applicable to calculation of SNV's;  $x_{nc}$  = non-contaminant mean;  $x_c$  = contaminant mean;  $x_{nc,c}$  = combined contaminant and non-contaminant mean; s = standard deviation; 90%tile = 90th percentile.

- a. statistic of contaminant group.
- b. not significant ( $p > 0.05$ ).
- c. statistic of combined contaminant and non-contaminant groups.

Table 5. Analysis of variance (ANOVA) of contaminant, non-contaminant and transient pesticide groups.

	F value	pr>	DF
log Koc	9.96 *	0.0004	34
log solubility (ppm)	4.64 *	0.0154	40
log hydrolysis half-life (days)	2.42	0.1173	18
log soil degradation half-life (days)	0.33	0.7239	32

Comparisons significant at the 0.05 level are indicated by '\*'. Significant differences were between contaminant and non-contaminant groups only.

Table 6. Specific numerical values calculated using univariate statistical methods.

method	environmental <sup>a</sup> fate variable	proposed <sup>b</sup> SNV	misclassified <sup>c</sup> contaminants	misclassified <sup>d</sup> non-contaminants
least significant difference (LSD) from contaminant mean.	Koc	$\leq 285$	naled, oxamyl	(carbofuran), (ethoprop)
	water solubility	$\geq 59$		
	hydrolysis half-life	$\geq 70$		
	soil degradation half-life	$\geq 23$		
one standard deviation from contaminant mean.	Koc	$\leq 512$	oxamyl	dicamba, (alachlor), (carbaryl),
	water solubility	$\geq 7$		
one standard deviation from combined contaminant and non-contaminant mean.	hydrolysis half-life	$\geq 13$		(carbofuran), (ethoprop)
	soil degradation half-life	$\geq 11$		
90th percentile of contaminant distribution.	Koc	$\leq 785$	oxamyl	dicamba, (alachlor), (carbaryl), (carbofuran), (ethoprop)
	water solubility	$\geq 2$		
90th percentile of combined contaminant and non-contaminant distribution.	hydrolysis half-life	$\geq 7$		
	soil degradation half-life	$\geq 8$		

Solubility in parts per million (ppm), hydrolysis half-life and soil degradation half life in days.

- a. Soil degradation half-life includes aerobic and anaerobic metabolism, and field dissipation half-life.
- b. SNV signifies 'specific numerical value'.
- c. Pesticides from contaminant group not classified as contaminants using SNV's.
- d. Pesticides from non-contaminant groups, transition pesticides (shown in parentheses), which were classified as contaminants using SNV's.

variables will be represented by the SNV for soil degradation half-life. Specific numerical values calculated by each method are shown in Table 6.

To be classified as a potential ground water contaminant according to the Pesticide Contamination Prevention Act, a pesticide must exceed SNVs set for either solubility or Koc, and either soil or hydrolysis half-life. Specific numerical values were applied to average values of the contaminant, non-contaminant and transition pesticide groups to evaluate the accuracy of pesticide classification by each of the univariate methods. Two known contaminants, naled and oxamyl (Table 1), were not classified as contaminants using SNVs calculated from the LSD test, and only two of the possible seven contaminants in the transition group (Table 3) were classified as contaminants using the same SNVs. Application of the SNVs calculated using the standard deviation of variable distribution classified all known contaminants except oxamyl as contaminants, and classified a substantial portion of the transition pesticides as contaminants (Table 6). One non-contaminant pesticide, dicamba, was classified as a contaminant. Classification of pesticides using SNVs based on the 90th percentile were not different from the classification obtained using SNVs based on one standard deviation. Considering their relative performance, the SNVs calculated using one standard deviation of environmental fate distributions are acceptable indicators of potential contaminants and are more conservative than criteria for environmental fate variables proposed by the US EPA (Creeger, 1986).

#### DISCUSSION

Methods other than univariate statistics were considered for determining SNVs, including simple transport models and multivariate statistical analyses. Each of the methods present different advantages and disadvantages to pesticide classification.

The univariate methods for setting specific numerical values were based on two critical assumptions. First, we assumed that pesticides may be classified correctly as contaminants or non-contaminants based on historical monitoring data. Several problems are involved with this assumption: incidences of contamination were reported from widely different geographical settings throughout the United States, and most individual monitoring efforts were

relatively limited in the number of pesticides sampled and in the spatial extent of well sampling. Therefore, pesticides which were classified as contaminants because they were detected in one location may not be contaminants in less vulnerable agricultural settings when appropriate use practices are followed. Conversely, the classification of a pesticide as a non-contaminant does not preclude the possibility that it will move through soil to ground water depths under extreme environmental conditions, or that it does not already occur in ground waters which have not been surveyed. The classification of pesticides into contaminant and non-contaminant groups is perhaps the most critical step in setting SNVs by any statistical method. Changes in the classification of pesticides from non-contaminant to contaminant based on future surveys, or the addition of new pesticides to these groups, will probably require the revision of the SNVs proposed here.

The second assumption for setting SNVs concerns the treatment of data collected for each pesticide. We assumed that average values of solubility, Koc, hydrolysis and soil degradation half-life adequately represent the characteristic properties of pesticides, despite the enormous amount of variability that is frequently reported for these variables; values ranging over one or two orders of magnitude are not uncommon, even when measurements are made under controlled conditions. We did not attempt to identify single 'best' values to represent the environmental fate characteristics of each pesticide from the data that were available, but accepted all values falling within a limited range of temperature (20°-25°C) and pH (6.5-7.5). In fact, there are no standard conditions or standard media established for the measurement of the environmentally sensitive variables: Koc, hydrolysis half-life and soil degradation half-life. The decision to calculate SNVs with data obtained under the two assumptions discussed above was based on the belief that the amount of variation 'built-in' to average environmental fate values obtained from different experimental conditions complements the uncertainty in the classification of pesticides as contaminants or non-contaminants, resulting in the broadest possible description of relative pesticide behavior in the environment.

Multivariate statistical analysis is another approach that could be used to identify potential contaminant pesticides. A multivariate treatment such as principal components analysis would identify combinations of variables that

could be tested for their predictive capability. Like univariate analysis, multivariate combinations of environmental fate variables would not presume the quantitative relationship of variables theoretically involved in pesticide transport, or the conditions of pesticide use and geographical setting. In this type of analysis, additional environmental fate and chemical properties could be included to more fully describe pesticide chemistry and establish classes of pesticides. For example, physico-chemical properties such as vapor pressure, molecular mass, boiling point, melting point and others could be included in the statistical analysis. A multivariate combination of many chemical properties would lessen the overriding influence of any one property on the predicted result, increasing the flexibility and accuracy of the statistical model. A multivariate analysis may require more data, but this disadvantage would be partially offset by the use of basic chemical measurements which are more generally available and standardized. The application of this method would also require a departure from the screening mechanism currently prescribed by Section 13144(b)[2] of the PCPA.

Several mathematical screening models which simulate pesticide transport through soil have been formulated in recent years (Jury, et al, 1984, Enfield, 1985, Carsel et al, 1985). These models are usually based on variations of the advection-dispersion equation, and assume linear, reversible and instantaneous equilibrium adsorption and first order degradation rates of pesticides moving through uniform soil matrices. Within a given soil matrix, pesticide velocity in solution is calculated as a function of the soil adsorption coefficient (Koc). Pesticide concentration over time is a function of the quantity of pesticide initially available to the system, minus the quantity lost through degradation processes. Thus, the models attempt to estimate both the time required for a pesticide to arrive at a certain point in the soil profile, and the concentration expected at the time of arrival. The relative mobility and persistence of pesticides may be ranked within a given soil matrix by comparing their environmental fate properties (Koc and soil degradation). Screening models facilitate the comparison of pesticide transport through different soil matrices by altering the values of bulk density, organic carbon content and volumetric water content and water flux, allowing changes in velocity of a pesticide through the soil to be related to different environmental conditions. While there are some apparent advantages in using screening models to identify potential ground water contaminants, there are also some significant drawbacks.

The use of a screening model to set SNVs based on theoretical equations governing solute transport, is appealing because this approach appears to include the effect of different environmental settings, and considers quantitative relationships between chemical and soil properties rather than arbitrary, independent threshold values established by statistical comparison. However, several underlying assumptions on which transport models are based have come under increasing scrutiny. More importantly, the predicted behavior of large numbers of pesticides have not been verified by field observation. Increasingly, field observation of pesticide mobility indicates that transport models may underestimate pollutant velocities by as much as 60 percent (Bowman and Rice, 1986 and Rice et al, 1986). Accelerated movement through preferential flow pathways, changes in adsorption kinetics and other interactions between environmental fate properties and physical soil properties have been implicated as possible mechanisms to account for the discrepancy between field observation and predicted behavior, but as yet these processes have not been sufficiently described or incorporated into models of pesticide behavior.

#### CONCLUSION

A univariate statistical procedure based on the comparison of designated contaminant and non-contaminant pesticides was used to determine specific numerical values (SNVs) for four environmental fate variables in accordance with Section 13144 of the Pesticide Contamination Prevention Act. Comparison of the environmental fate data of known contaminant and non-contaminant pesticides indicated that pesticides with soil adsorption coefficient (Koc) values less than 512 cm<sup>3</sup>/gm or water solubility greater than 7 ppm, and hydrolysis half-life greater than 13 days or soil degradation half-life greater than 11 days, may be classified as potential ground water contaminants. The calculation of SNVs using univariate statistics, and the mechanism for applying the SNVs as set forth in AB 2021, implies that single values of environmental fate variables exist which would identify potential ground water contaminants, and that these 'threshold' values are successful regardless of the conditions of pesticide use or geographical setting. The method on which the present calculation of SNVs was based offers an advantage over other contaminant screening methods because it uses environmental fate data in a manner that is quantitative, reproducible and verifiable by historical detection data while adhering to a strict interpretation of the requirements of Section 13144.

While the proposed SNVs satisfactorily classify certain pesticides as contaminants or non-contaminants based on available data, other methods of identifying potential contaminants may be developed which make more comprehensive uses of pesticide characteristics and specific environmental conditions. In this case, it is recommended that the implementation of Section 13144 be expanded to allow pesticide classification using a series of threshold values, or mathematical equations.

Environmental fate data for many of the pesticides used in the analysis were not available, or did not meet specific criteria restricting data to a range of standard conditions. For this reason, the proposed SNVs should be revised after standardized environmental fate data are submitted to the Department of Food and Agriculture as required by the data call-in portion (Section 13143) of the PCPA. SNVs based on comparative statistical methods may also require revision as new pesticide detections occur in ground water.

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APPENDIX A



COLLEGE OF NATURAL AND AGRICULTURAL SCIENCES  
CITRUS RESEARCH CENTER AND  
AGRICULTURAL EXPERIMENT STATION  
DEPARTMENT OF SOIL AND ENVIRONMENTAL SCIENCES

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January 7, 1987

Ms. Muffet Wilkerson  
Environmental Monitoring, Room A-149  
Department of Food and Agriculture  
1220 "N" Street  
Sacramento, CA 95814

Dear Muffet:

I have reviewed the draft copy of your report entitled *The Pesticide Groundwater Prevention Act: Setting Specific Numerical Values* which I received on approximately 12-11-86.

The use of a statistical approach as you describe in your report to establish the specific numerical values for pesticides is understandable given the framework of the regulation and the need to provide a quantifiable and varifiable method. However, I fully support your recommendation that additional procedures including the use of mathematical models for predicting pollution potential of groundwater be pursued. As an example of one of the benefits to be derived, the use of such a model would allow combinations of environmental factors to be used to predict pollution potential rather than relying on a specific numerical value. For example, as the property of soil adsorption coefficient decreases, and a compound becomes more mobile in soil, compounds of shorter half-life would be more likely to reach groundwater. On the other hand, compounds with high soil adsorption would require a longer half-life in order to reach groundwater. Such combinations of two properties whose values vary depending on each other cannot be easily attained with single specific numerical values.

As we have discussed in the past, there are several advantages and disadvantages to the use of the statistical approach many of which you have presented. One of the advantages of the

statistical approach is that it allows a testing of previous investigations into the factors controlling the movement of pesticides in soil. Presumably the pesticide properties of soil adsorption coefficient, water solubility, hydrolysis, aerobic and anaerobic soil metabolism, and field dissipation became a part of the present regulation because of the extensive evidence existing in the pesticide literature based on laboratory and field studies and on mathematical modelling which showed these properties as prime indicators of the leaching potential of a pesticide. Now that pesticides are being detected in the groundwaters of this state and of the country, it is possible to apply statistical approaches such as you have used to evaluate these properties and determine if there is a relation between the specific numerical values of these pesticide properties and the detection of pesticides in groundwater. As you pursue your investigation of predictive models, perhaps more of these relationships will become evident.

One of the unavoidable disadvantages of the use of a statistical approach at this time is the lack of sufficient data. This lack is evident both in the number of pesticides present in both the contaminant and noncontaminant groups and in the lack of environmental fate data for the pesticides. As monitoring for pesticides in groundwater continues, the data base will doubtlessly increase thereby improving the potential usefulness of the statistical approach. In this regard, it is my opinion that the list you show in your report as the transient group should be included in the contaminant list. Currently there is a tendency for investigators to report only positive but not negative results in groundwater monitoring. As the reporting of negative results becomes more common place, I think many of the compounds on the contaminant list would be shifted to the transient group using the present criteria.

The lack of environmental fate data for the individual compounds is the most serious drawback to the present use of the statistical approach. As you state, this situation will improve as the data call in phase of this regulation begins. However,

there will always be uncertainties in the data such as in soil adsorption and field dissipation rates due to influences of such variables as soil type, temperature, and moisture.

One of the possible results of the lack of sufficient data is what appears to be the low value you report for the specific numerical values. These values are considerably more conservative than the values suggested by EPA and could result in a large number of compounds targeted as potential groundwater contaminants. As the data base improves, this may change. That is, when the list of compounds is small as it now is, a few pesticides with unusual properties can have a large influence on the final outcome. As the number of pesticides and pesticide properties in the set increases, the result should become more representative.

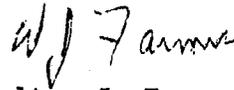
The use of the soil degradation half-life value for aldicarb shown in Table 1 would contribute to a low specific numerical value for this property. The aldicarb value is probably not representative of the groundwater pollution problems that have been associated with the use of this compound. It would be better to use the half-life value for the toxic degradation products of aldicarb. It is usually the total toxic residues for a pesticide that are reported in groundwater. For aldicarb this would include aldicarb and its toxic degradation products, the sulfoxide and sulfone.

The lack of any significant differences between the means of the contaminant and noncontaminant groups for the properties of hydrolysis and soil degradation is noteworthy and doubtlessly illustrative of the lack of sufficient data points. Soil degradation is known to be a significant factor influencing the potential for movement in soil.

The use of a depth variable soil degradation rate may prove to be a significant improvement in assessing movement to groundwater. Field dissipation rates for pesticides generally decrease with soil depth due to a number of factors such as reduced

volatilization to the atmosphere, reduced photodecomposition, reduced aeration and a significant reduction in the number of soil microorganisms. Data on the variation in the rate of degradation with soil depth is beginning to accumulate in the literature and should prove useful in future evaluations of the specific numerical values.

Sincerely,



Walter J. Farmer  
Professor of Soil  
Chemistry

WJF:mds

cc: J. N. Seiber  
W. F. Spencer  
W. A. Jury



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December 2, 1986

Ms. Muffet Wilkerson  
Environmental Monitoring, Rom A-149  
Department of Food and Agriculture  
1220 "N" Street  
Sacramento, CA 95814

Dear Muffet:

I read over your draft of November 6, 1986, on "Setting Specific Numerical Values."

In Table 1 and 2, I question the water solubility of naled (0.33 ppm) which seems low even considering the 2 bromine atoms. Also question for aldicarb whether entries should be made for sulfoxide and sulfone, because these are usually the products found in groundwater. Units should be specified for the last 3 columns. We have to keep an eye on the soil degradation half lives because if they are determined from field data the more volatile surface applied chemicals such as toxaphene (and perhaps oxamyl) will show relatively short half-lives, because of volatilization, where in fact they could have very long half-lives if volatilization were not pronounced. Similarly, aldicarb soil half-life (7 days) may be for the parent rather than the sulfoxide/sulfone.

In Table 5, you calculated an average only, without a confidence interval. Perhaps the averages should be given as e.g.  $Koc = < 360 \pm 50$  (95% confidence), and thus Koc in Table 6 would be set at 310 to reflect the lower (more conservative) range of Koc. (I estimated the  $\pm 50$  -- needs to be calculated accurately.) If you did it that way, diuron would then become a 'potential yes' although you would still miss on oxamyl.

The oxamyl case is interesting, because it tends to argue in favor of the Jury-Focht-Farmer approach for considering an interaction between numerical values. Oxamyls exceptionally high water solubility can apparently compensate for its low half-lives in soil and water, particularly when applied to a porous soil under high moisture penetration conditions (and coupled with groundwater analysis taking place relatively soon after application!).

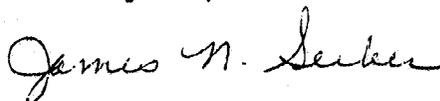
I question the finding of carbaryl in groundwater. The LaFluer reference used UV spectrophotometry at 222 nm to detect carbaryl. This is a very non-specific method, and even the authors themselves admitted that 1-naphthol and methyl isocyanate (degradation products of carbaryl) could have contributed to

the absorbance. (In fact, all of the absorbance could have been due to naphthol!). Although they did not specify their detection limit, it probably was 0.1  $\mu\text{Mole/liter}$  (the lowest 'positive' finding) and the maximum observed was 0.3  $\mu\text{Mole/liter}$ . Not very convincing! In my opinion, this report should not be given much weight.

Ethoprop, from its structure and properties, looks like a good candidate for groundwater contamination. I believe that it is also used as a soil nematicide. Thus, I was pleased to see that you predicted positive for it. The negative finding by Marti et al., which is based on very convincing analytical data, may be due to the depth of the wells (150 ft) which penetrated the Ocala limestone aquifer. I could not find any information in this article on the soil type or depth to groundwater. Thus, I feel ethoprop does indeed carry potential, at least for shallow wells under sandy soils.

I would be pleased to review any of the references an analytical finding (positive or negative) if you point me in the right direction.

Best regards,



James N. Seiber  
Professor

JNS:gm

cc: Walt Farmer



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October 6, 1986

Ms. Muffet Wilkerson  
Environmental Monitoring  
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California Department of Food and Agriculture  
1220 N Street  
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Dear Muffet:

Following are my observations on the reported finding of azinphosmethyl in a well located within a treated blueberry field [Bull. Environ. Contamin. Toxicol. 28, 341 (1982)].

1. Azinphosmethyl was determined to be present in samples collected 7/9 (1.9 ppb), 7/14 (11.2 ppb), 7/23 (24 ppb) from a single well.
2. Azinphosmethyl was not detected (i.e. < 0.23 ppb) on 8/11 in a sample(s) from the same well.
3. The type of well was not described, except that it was a household well, nor was its configuration in the treated field or its depth presented.
4. No information on the number of samples, or standard deviation of replicates, was given.
5. No azinphosmethyl was found in surface runoff from any fields in the study.
6. The fields are described as glaciomarine deltas--gravel and sand.

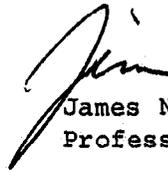
I don't believe that this study should be given much weight as indicative of a tendency of azinphosmethyl to move into groundwater. If the positive well samples were the result of azinphosmethyl leaching through the "soil", it is surprising that the levels would have declined so dramatically from the 7/23 to 8/11 samples, because pesticides rarely leach through soil as a quick-moving, quick-clearing plug of material. If azinphosmethyl did behave this way, it seems likely it would have been found in surface water runoff, too.

I think that the results are consistent with direct introduction of material to the well water during application and subsequently by rain washing more material from the well covering into the well.

Even if the well contamination were due to leaching, the unusual soil characteristics (sand and gravel) preclude any generalizations.

Unless this finding is corroborated by other investigators in other locations, I do not believe that this study should be included in defining those pesticides found in groundwater in connection with the AB 2021 data call-in.

Best regards,



James N. Seiber  
Professor

JNS:jls