The Need for Data Evaluation of Physical and Chemical Properties of Pesticides: The ARS Pesticide Properties Database

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Data evaluation of physical and chemical properties of information being entered into a database should be an integral part of the database development process. In the initial stages of developing a pesticide properties database, the issue of data quality quickly arose. An example of the range of reported solubility values for a commonly used insecticide, fenthion, is used to show the need for thorough data collection and the need for careful and objective data evaluation.

INTRODUCTION

The explosion of information over the past two to three decades has greatly strained our ability to store, retrieve, and digest the vast quantities of data available. Coupled with the fact that society relies heavily upon scientific studies to protect the environment, it is most important that the quality of the data being used for decision making be the best possible. For example, in examining possible groundwater contamination, a lawyer has recently noted that the "demand for scientifically accurate, yet legally appropriate, contaminant flow data modeling is mushrooming as hundreds of hazardous waste sites are added to the EPA Superfund National Priority List.... Modelers are being asked to answer such complex questions as how long will it take for chemicals to enter groundwater drinking supply, at what levels, and from which source(s)".[1] With the increased emphasis on the use of simulation and modeling, as well as environmental assessments, it is critical that accurate data be used. Without good data the results of such studies are likely to be successfully challenged in the many adversarial proceedings that are becoming a part of daily life. Failure to defend conclusions from scientific studies is likely to lead to adverse opinions of science by the public.

It appears on the surface that the need for accurate reference data should be known to everyone, and the information presented in this paper is not necessarily original or creative. However, from the actual state of handbook and literature data, it is clear that there is a very practical need to raise the level of awareness of actual data quality and to try to stimulate interest in the collection and dissemination of well-defined data that are as accurate as possible. The continued reporting of poor data, while original, and perhaps creative, is not considered a worthwhile scientific goal.

The use of pesticides to improve and sustain crops is basic to agricultural production and has increased dramatically over the past 40 years. At present, nearly a million tons of these chemicals are being applied annually by farmers in the U.S. This widespread use increases the potential for some of these materials to move through the soil into the groundwater[2] and to have other adverse environmental effects.

To provide the essential data on the chemical and physical properties of pesticides, the USDA Agricultural Research Service (ARS) has assumed the responsibility of creating, evaluating, and maintaining a pesticide properties database (PPD).[3] While there are several sources of information on the properties of pesticides,[4-11] including data collected over the years in an informal manner by ARS scientific staff,[12] no one has collected all the necessary data in one place at one time and defined their quality. A database of known accuracy and precision of physical and chemical properties is needed to support various environmental modeling and assessment activities. As Kollig has pointed out, "Data being used in the environmental and human risk assessment for regulatory purposes must be of known reliability for the assessment to have validity".[13] While many current models are crude and do not now require the most accurate data, at some point poor data will become the limiting step in developing better models.

LITERATURE SEARCHING AND DATA VARIATIONS

As part of the ARS PPD development, data have been obtained and evaluated from the literature. In addition, the National Agricultural Chemicals Association (NACA), as part of their Ground Water Protection Program, has requested their members provide ARS with the data they have submitted to the states of Arizona and California and any other data they may wish to make available.[14]

The bibliographic literature, as searched by using Chemical Abstracts Service Online, provided very little information. Rarely did we find that the bibliographic abstracts contained information that pointed to needed data. The few sources of actual data, found in such references as the *Agrochemical Handbook*,[5] *The Pesticide Manual*,[7] and *The Merck Index*,[11] both in hardcopy and computer-readable form, have no literature citations. Thus, when a question arises about the validity of a value, there is no way to resolve the matter.

For example, the solubility of the widely used pesticide Alachlor is reported as 242 mg/L at 25 °C in *The Agrochemical Handbook*.[14] This compares with the values of 140 mg/L at 23 °C in *The Merck Index*[16] and 148 mg/L at 25 °C in the Yalkowsky Arizona dATAbASE Solubility Database.[17] It would be logical to assume that a typographical error has occurred, but should the value 242 be 142, or should 140 be 240? Is 148 mg/L really another typographical error and the value should be 140 mg/L? When one of the editors of *The Agrochemical Handbook* was contacted about this matter, the response was that their published value (242 mg/L) was "also in the *Herbicide Handbook* of the Weed Society of America[4] and *The Pesticide Manual* published by BCPC".[18] But where did these publications obtain their values?

As a result of this and many other inconsistencies encountered (see Table I for additional examples), we decided that every value must be subjected to rigorous and objective scrutiny. To do this we require two things: (1) a data evaluation scheme that is as consistent and as objective as possible and (2) a thorough report of the experimental procedure and conditions. Literature citations of experimental procedures needed for this evaluation are difficult to obtain. An evaluation scheme is now being developed[19] that will result in a PC-based expert system to quickly evaluate the quality of the data on the basis of criteria developed by experts in the field. The first property being examined is the aqueous solubility of pesticides.

While it would be desirable to have an estimation technique available for checking the reported solubility or for checking the consistency of the solubility with a series of similar compounds, such methods have not yet been developed for the

Table I. Examples of Solubility Data Variability

aqueous solubility, mg/L	temp, °C	aqueous solubility, mg/L	temp, °C
Alachlor		Atrazine	
148	unknown	70	21
150	unknown	70	22
200	20	29.9	25
140	23	33	25
148	25	70	25
242	25	33	27
Aldicarb		320	85
4000	unknown	Bromacil	
6000	unknown	800	unknown
6000	25	820	unknown
7800	26.5	815	25
Atrazine		1024	25
70	unknown	Carbofuran	
85	unknown	291	10
22	0	320	19
107.8	2	350	25
28	20	415	25
29	20	700	25
30	20	375	30

classes of compounds commonly encountered in pesticide products. The few reported estimation techniques are too crude and cover too limited a scope of classes of chemicals to be of use for multifunctional group compounds as are found in the structures of most pesticides. In a handbook on property estimation, Lyman states, "the available estimation techniques usually yield values that are, on the average, uncertain by less than one order of magnitude, but errors of over two orders of magnitude occur in about 10% of the cases with some equations".[20] Furthermore, Lyman asserts that "few (estimation techniques) can handle complex structures or uncommon functional groups". In addition, there are generally too few data for one to adequately test the validity of an estimation technique.[21]

CASE STUDY USING FENTHION

As a result of the cooperation of the NACA, data on fenthion were received from Mobay Corp. Fenthion is the common name for *O,O*-dimethyl *O*-[3-methyl-4-(methylthio)-phenyl] phosphorothioate. Fenthion was introduced in 1957 and is used as an insecticide, primarily for ornamental flowers. The data for fenthion from Mobay are the same as those provided to the states of Arizona and California under the laws of those states relating to pesticides. The Mobay data and other data found from literature searching are given in Table II.

Most of the citations appear to refer to the original work of Schrader[23] reported in 1960, although there are some minor variations in the value [e.g., a range (54–56) vs a single value (55)] and the temperature may differ slightly or is not reported at all. We have also checked the U.S., Canadian, and German patents[24] issued to Schegk and Schrader and found no solubility value in these publications. Rather, the data in these patents referred primarily to toxicity and other biological data, with values for boiling point, melting point, density, and refractive index.

As we continued our investigation it appeared that transcription errors are probably responsible for most of the differences reported for the values shown in Table I. The exception is that *The Pesticide Manual*[28] reports the solubility of fenthion as 54–56 mg/L in the 5th and 6th editions, but then changes it to 2 mg/kg (=2 mg/L) in the 7th and 8th editions[33] without any explanation. A change of a factor of nearly 30 does seem to us to merit some explanation.

Experimental conditions were reported for the data in Table I from only two sources, Mobay[36] and Bowman and Sans.[32,34]

Table II. Chronological Order of Reported Solubility Values (mg/L) for Fenthion

value	SD	temp,[a] °C	exptl cond	ref
54–56		room	no	Schrader[23]
54–56		room	no	Gunther[25]
54–56		room	no	Spencer[26]
55		room	no	Verschueren[27]
54–56		room	no	Worthing/6th[28]
56		22	no	Khan[29]
54		none stated	no	Eto[30]
55		none stated	no	Merck Index[31]
7.51	0.31	20	yes	Bowman and Sans[32]
2		20	no	Worthing/7th[33]
6.4		10	yes	Bowman and Sans[34]
9.3		20	yes	Bowman and Sans[34]
11.3		30	yes	Bowman and Sans[34]
54–56		room	no	*Agrochemicals Handbook*[35]
4.2	0.19	20	yes	Mobay report[36]
50		20	no	Suntis et al.[37]
50		20	no	*Farm Chemicals Handbook*[38]

[a] Room temperature was not defined in any reference, but is usually assumed to be 15–25 °C.

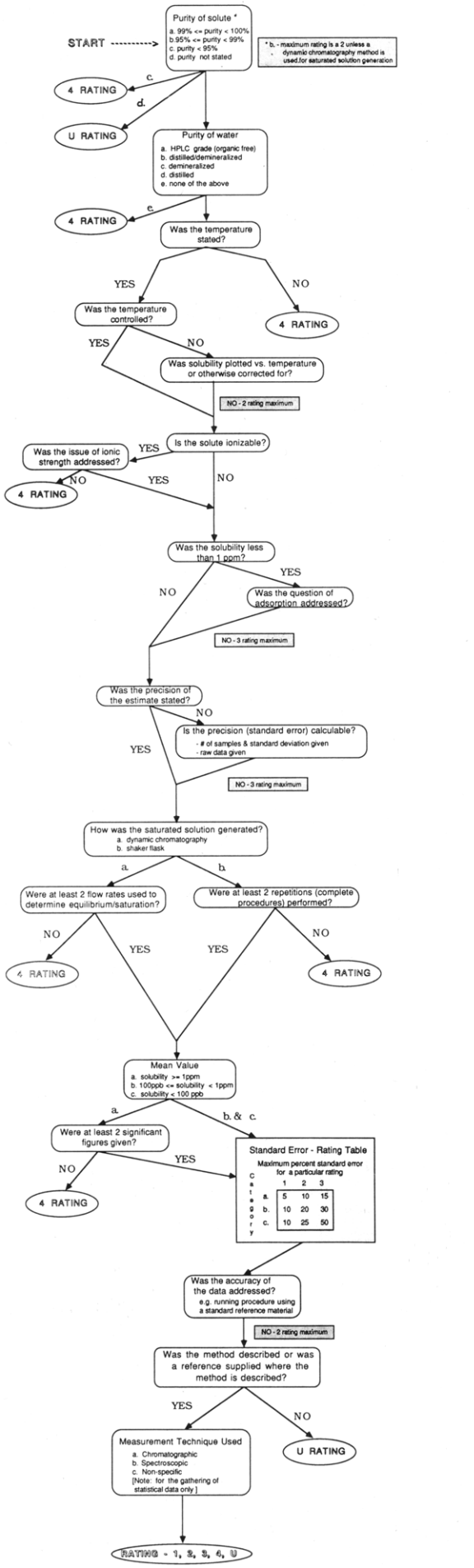
On the basis of our evaluation procedure[19] we have come to the conclusion that the solubility data from the internal Mobay Chemical Corp. report (4.2 mg/L) is likely to be the most accurate value available. The quality control expert system evaluation procedure elicits answers to a number of questions about the data reported, in a manner similar to that used in the SELEX expert system described previously.[22] The main questions asked are the following: (1) Is there a citation with an analytical procedure described? (2) What type of method was used (chromatographic, spectroscopic, or nonspecific)? (3) What is the purity of chemicals used? (4) What is the purity of water used? (5) How was the temperature of the experiment controlled? (6) How many repetitions were performed, and what was the standard error? The overall scheme of this expert system, called SOL, is shown in Table III.

Briefly, after putting the experimental data for the solubility of fenthion through the SOL expert system, we conclude that the Mobay data were superior on the basis of the following distinctions: (1) Of the two studies where experimental procedures were reported, a dynamic chromatographic technique was used for the measurement, and only the Mobay study[36] used more than one gas chromatographic flow rate (10 and 20 mL/h). (2) The data from Mobay stated the purity of fenthion was 99.7%, whereas the data from Bowman and Sans[32,34] indicated the purity of fenthion was only 97.1%.

SUMMARY

The computer-based models for estimating potential groundwater contamination[39-42] and environmental assessments require the best available data for input. These data must be accurate if the user community (scientists, government regulators, industrial groups, and environmental groups) is to have confidence in the predictions of these models or the results of assessments, so that decisions based on these results will be acceptable. Data in current literature citations, from journal publications to widely used and cited handbooks, have not undergone sufficient evaluation to assure their accuracy. We have shown a number of examples of the proliferation of errors and the lack of evaluation that has spanned a period of more than 20 years and have analyzed one example, fenthion, in detail. We hope that the development of the ARS PPD will be a first step in improving this situation. The ARS PPD is expected to be used in two main ways, besides being a reference for pesticide chemical and physical properties. The first is for the current modeling efforts in looking into what happens to

Table III. ARS/NIST Aqueous Solubility Data Evaluation Scheme Flow Diagram



a pesticide when it enters the soil and the possible contamination of the groundwater that makes its way into drinking water supplies. The second is to help in regulatory assessments of pesticides. Predictive models are needed because time and cost make it impossible to run actual experiments in the field to determine the impact of chemicals on groundwater quality. Accurate and reliable predictions will be a considerable benefit over the coming years, but these are only possible with accurate physical and chemical property data.

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