The Relationship of Insecticide Solubility in Water to Toxicity in Soil[1,2]

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ABSTRACT

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The toxicity of 11 insecticides, varying in solubility in water from <1 to >8000 ppm, was determined by using crickets, *Acheta pennsylvanicus* (Burmeister) (24–48h old) as test insects. LD_{50}values were determined for the insecticides applied by direct contact and by incorporation into Bondhead sandy loam containing 20 and 2.5% water. Analysis of the results indicated that, despite the diverse chemical structures of the compounds tested, there was a significant negative correlation between water solubilities of insecticides and their respective toxicities in soil, i.e., insecticide toxicity in soil decreased with increasing solubility of the insecticides in water.

It is well known that the toxicity of an insecticide in soil is influenced by many factors. Soil and climatic conditions, e.g., clay and organic matter content, moisture, and temperature, influence insecticide activity. In addition, the physicochemical properties of the insecticide, e.g., volatility and stability to chemical and microbial degradation, play an important role (Harris 1972). When screening experimental compounds to determine their potential as soil insecticides (e.g., Harris and Mazurek 1966, Harris and Turnbull 1977), we noted that, in general, insecticides known to be very soluble in water tended to be less insecticidal in soil. A more quantitative assessment of the relationship between the water solubility of an insecticide and its activity in soil has been hampered by the scarcity of data on water solubility and the large discrepancies reported in some instances, depending on the techniques and experimental conditions used. Recognizing the need for reliable information on insecticide solubility in water, we recently began to accumulate such data in our laboratory (Bowman and Sans 1979). We report here results of a subsequent study done to determine if there is a relationship between water solubility of an insecticide and its toxicity in soil.

Materials and Methods

Twenty-four to 48 h old 1st-stage crickets, *Acheta pennsylvanicus* (Burmeister), reared as described by Harris and Svec (1964) were used as test insects. Insecticides were all >98% purity. Direct contact toxicity was determined as described by Harris and Mazurek (1964). The insecticides, dissolved in 19:1 acetone:olive oil, were applied to the crickets with a Potter spray tower, after which the treated insects were transferred to clean containers and provided with food and water. Soil bioassays were conducted in a manner similar to that described by Harris and Mazurek (1966). Insecticides were dissolved in chromatographed (2:1 activated charcoal: florisil), distilled n-pentane or pentane-acetone, and appropriate amounts of insecticide solution were pipetted onto Bondhead sandy loam. The mineral fraction of the soil comprised 77% sand, 15% silt, and 8% clay. Cation exchange capacity was 30.7 meq/100 g, organic matter was 3.9% using the Walkley-Black procedure, and the pH was 6.4. Tests were done on soil containing 20 and 2.5% (air-dry) water. Following evaporation of the solvent, the treated soil was weighed into containers, the crickets were introduced, and food was provided.

Each bioassay comprised a minimum of 6 insecticide concentrations with 2 replicates of 10 crickets at each concentration. Solvent controls were included with all tests. Posttreatment conditions were: 27º±1ºC, 60±5% RH, and 24 h light. Mortality counts were made after 18 h. Each assay was done 3 times and results were pooled. Mortality values were corrected for natural mortality by using Abbott's formula and the results were analysed by probit analysis (Finney 1952). LD_{50} values were reported in percent solution for direct contact applications and ppm (based on the oven-dry wt) for soil treatments.

Results and Discussion

Initially we selected fensulfothion, carbofuran, diazinon, fonofos, and chlorpyrifos, which varied widely in terms of their solubilities in water, i.e., from <1 ppm for chlorpyrifos to 2000 ppm for fensulfothion (Table I). The susceptibility of the crickets to direct contact applications of the insecticides varied considerably, with carbofuran being most toxic > fensulfothion = chlorpyrifos > diazinon > fonofos (Table 1). Even with such wide differences in the susceptibility of the test insects to the insecticides, the soil bioassays showed a trend for the less water soluble insecticides to be the most toxic ones in the moist soil, a trend which was obviously not present in air-dry soil (Table 1). At first glance, it would appear that fonofos did not follow the general pattern, i.e., although less soluble in water (15.7 ppm) than diazinon (69 ppm), it was also less toxic in moist soil. This anomaly can be explained by the fact that fonofos was inherently less toxic to the test insects than were the other insecticides, e.g., diazinon was >5 times more toxic by direct contact to crickets than was fonofos.

Subsequently, we tested 2 other groups of insecticides: phorate, which at 17.9 ppm was relatively insoluble in water, and its much more water soluble sulfone (860 ppm) and sulfoxide (>8000 ppm); and terbufos, and its respective sulfone

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Table 1. **Toxicity of 11 insecticides applied as direct contact applications or incorporated into moist (20% water) or air-dry (2.5% water) sandy loam to 24-48 h 1st stage crickets.**

Insecticide	Direct contact toxicity		Solubility in water at 20ºC [a] (ppm)	Toxicity in soil			
				Moist		Air-dry	
	LD50 (% sol.)	95% F.L.		LD_{50} (ppm)	95% F.L.	LD_{50} (ppm)	95% F.L.
Fensulfothion	0.00141	0.00135, 0.00147	2000	13.4	13.0, 13.7	38.0	36.3, 39.7
Carbofuran	.000364	.000336, .000393	320	4.89	4.67, 5.13	26.2	24.9, 27.6
Diazinon	.00453	.00407, .00498	69	1.17	1.13, 1.22	37.6	36.1, 39.1
Fonofos	.0246	.0237, .0255	15.7	2.73	2.64, 2.82	49.8	48.0, 51.5
Chlorpyrifos	.00148	.00142, .00154	0.7	0.305	0.297, 0.314	8.12	7.78, 8.47
Phorate sulfoxide	.00255	.00241, .00272	>8000	22.8	22.0, 23.6	76.6	74.0, 80.0
Phorate sulfone	.00407	.00387, .00429	860	20.3	19.6, 21.0	87.8	83.9 , 93.2
Phorate	.00437	.00413, .00460	17.9	1.21	1.17, 1.25	9.1	8.73, 9.58
Terbufos	.00105	.00101, .00109	>1100	5.94	5.73, 6.17	28.5	27.1, 29.9
Terbufos sulfone	.00187	.00180 , .00196	408	4.93	4.78, 5.07	27.8	26.8, 28.7
Terbufos	.00303	.00293, .00315	5.5	.304	.293, .315	8.81	8.46, 9.19

[a] as reported by Bowman and Sans (1979).

and sulfoxide, which exhibited a similar relative solubility pattern (Table 1). The direct contact toxicity of the insecticides varied with the sulfoxides being most toxic > the sulfones > the sulfides. However, in moist soil, insecticide toxicity decreased with increasing solubility of the insecticides in water, i.e., the sulfides were most toxic > the sulfones > the sulfoxides.

Despite the fact that there were marked differences in the inherent toxicity of the insecticides to the test insect, there was a significant relationship (0.01 level, 9 df) between insecticide toxicity in moist soil and insecticide solubility in water (correlation coefficient, r = 0.769). To improve on this relationship, the moist soil LD_{50} values were corrected for the inherent differences in susceptibility of the crickets to each insecticide by calculating a "normalized LD_{50} value," R, (LD_{50} on moist soil/LD_{50} by direct contact). This process created a curvilinear relationship between solubility (S) and R, producing a nonsignificant correlation coefficient (0.477). However, there was excellent correlation (r = 0.877) for Log S vs. Log R, and the relationship could be represented by the linear regression equation, log S = -1.832+ 1.269 log R, (Fig. 1). Analysis of variance showed significant regression and no lack of fit (P≤ 0.005). Terbufos sulfoxide and phorate sulfoxide were included in the statistical analysis despite the fact that their actual solubilities were greater than the values given in Table 1. These values are the best data currently available for these compounds and were situated above the regression line, thus exerting a corrective effect on the line toward their actual solubility values. The broad scatter of data points in Fig. I was not unexpected considering the diverse chemical structure of the compounds tested, the ca. 70-fold range in direct contact toxicity within this group of insecticides, and the complex interactions which occur in soil. Nevertheless, there was a definite relationship between water solubility of the insecticide and its toxicity in moist soil.

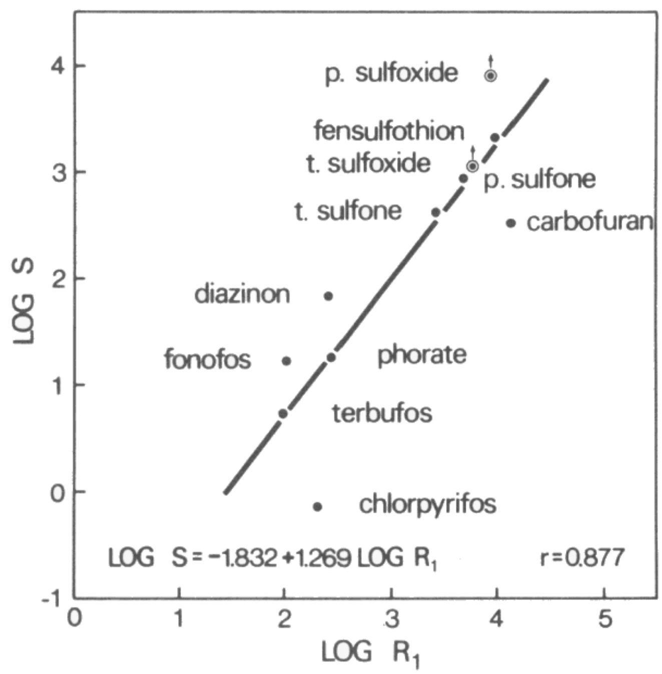

FIG. 1. - Relationship between insecticide solubility (S) in water and the ratio of the LD_{50} on moist soil/ LD_{50} by direct contact (R_1) using crickets as test insects.

Traditionally, water has been regarded as a competitive factor in the adsorption of nonionic organic molecules by soil colloids, e.g., in the case of insecticides, adding moisture to dry soil appears to desorb some insecticide molecules rendering them more available to the target organism. (Harris 1972) Fig. 2 shows the relationship of insecticide solubility (S) to the ratio of the LD_{50} on air-dry soil/LD_{50}on moist soil (R_2). The regression line for the 11 data points was: log S = 4.590-2.650log R_2. The correlation coefficient, 0.854, was significant at the 0.01 level (9 df). Analysis of variance similar to that performed earlier also yielded a significant F value (P -0.005).The range of R_2values on the abcissa of Fig. 2 demonstrates the effect of moisture on the toxicity of insecticides in a sandy loam soil. When R_2= 1.0 (i.e., log R_2 = 0), the toxicity of the insecticide would be the same on both moist and air-dry soil. When R_2= 100 (i.e., log R_2= 2.0), the toxicity of a given insecticide would

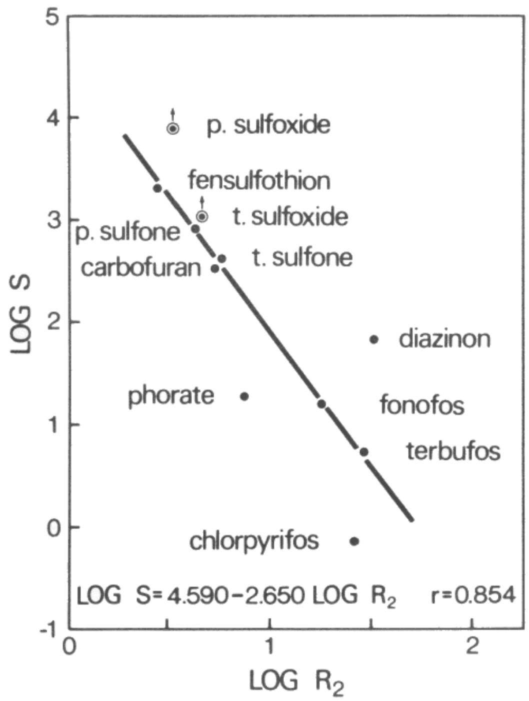

FIG. 2. - Relationship between insecticide solubility (S) in water and the ratio of the LD_{50} on air-dry soil/LD_{50} on moist soil (R_2) using crickets as test insects.

be 100 times greater in moist soil than in dry soil. R_2 values for these insecticides ranged from 2.84 for fensulfothion to 32.1 for diazinon. The data clearly show that the more water soluble an insecticide is, the less its relative toxicity will be increased by adding moisture to a treated air-dry soil. Conversely, the toxicity of the more insoluble insecticides would be affected to a greater extent by wetting and drying cycles in the soil.

These results indicate that there is a significant negative correlation between insecticide solubility in water and toxicity in soil but do not indicate the mechanisms involved. The effect of the water on insecticide toxicity in soil may be related to both the traditional theory of competitive adsorption of the insecticide and water, and, for the more water soluble materials, the partitioning of the insecticide between the soil organic matter and the soil solution. The latter theory has been suggested by Chiou et al. (1979) to explain their observations on the relationship between water solubility and adsorption behavior. If so, this partitioning must affect the availability of the insecticide to the target organism, with the more water soluble insecticides being less available to the insects.

In addition to defining another major factor influencing insecticide activity in soil, these results could be of practical importance in the design of soil insecticide screening programs, which can be time consuming and expensive. In the early stages of their screening pro-grams, most chemical companies obtain contact toxicity data on several species of insects and data on solubility of a compound in several solvents including water. These 2 parameters should provide an indication of experimental insecticides meriting evaluation as soil insecticides, e.g., a moderately to highly toxic contact insecticide which is relatively insoluble in water would merit immediate evaluation for soil activity; a very water soluble insecticide would merit evaluation only if it was so highly toxic to insects, as occurs with carbofuran, that the inherent toxicity of the insecticide is great enough to overcome the negative effect of its high solubility in water.

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REFERENCES CITED

Bowman, B. T., and W.W. Sans. 1979. The aqueous solubility of twenty-seven insecticides and related compounds. J. Environ. Sci. Health B14: 625-34.

Chiou, C. T., L.J. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206: 831-2.

Finney, D.J. 1952. Probit Analysis. A Statistical Treatment of the Sigmond Response Curve. Cambridge Univ. Press, Cambridge, England 318 pp.

Harris, C.R. 1972. Factors influencing the effectiveness of soil insecticides. Annu. Rev. Entomol. 17: 177-98.

Harris, C.R., and J.H. Mazurek. 1964. Comparison of the toxicity to insects of certain insecticides applied by contact and in the soil. J. Econ. Entomol. 57: 698-702.
1966. Laboratory evaluation of candidate materials as potential insecticides. Ibid. 59: 1215-21.

Harris, C.R., and H.J. Svec. 1964. Mass rearing of the common field cricket, *Gryllus pennsylvanicus* Burmeister (Orthoptera, Gryllidae), for use as a test insect in toxicological studies. Bull. Entomol. Res. 54: 805-9.

Harris, C.R., and S.A. Turnbull. 1977. Laboratory assessment of the potential of 16 experimental compounds as soil insecticides. Can. Entomol. 109: 1109-14.