

ADSORPTION AND MOBILITY OF PESTICIDES IN SOIL

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THE DISTRIBUTION OF organic chemicals in the soil profile after irrigation or rainfall is important because: (1) the effectiveness of a given pesticide applied to the soil is dependent in part upon its position in the soil profile; and (2) persistent organic chemicals can build up in the surface soil if they are strongly adsorbed, or can be leached into the groundwater if they are very mobile.

In the course of a research project studying the adsorption and mobility of pesticides in soils, a mathematical model

has been developed to predict the distribution of pesticides in soil profiles. In this report this model is evaluated by comparing calculated results on the distribution of pesticides in soils with results obtained from laboratory experiments.

Theoretical considerations

The drawing included is a schematic diagram showing how pesticide molecules and soil particles interact when a pesticide solution is moving through a

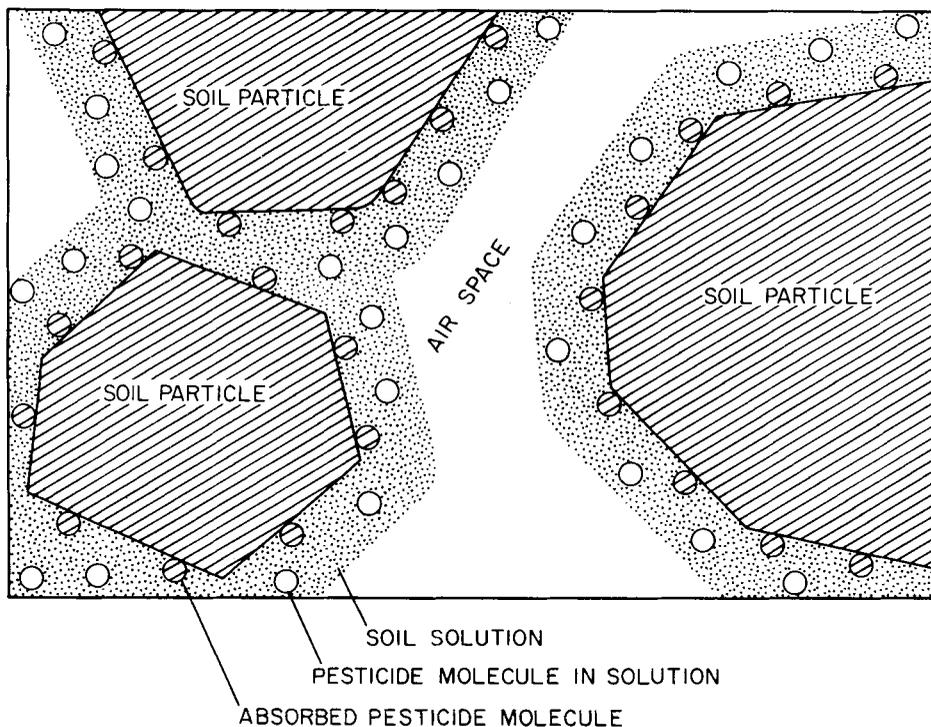
soil profile. As a pesticide solution moves through the soil profile a certain proportion of pesticide molecules is adsorbed on soil particles and therefore temporarily immobilized. What proportion of the pesticide molecules becomes adsorbed depends on the affinity between pesticide molecules and soil particles, and on geometrical relations between soil particles and the soil solution, and air in the pore space of the soil.

The affinity between pesticide molecules and soil particles is dependent on soil properties, and properties of the pesticide. A great proportion of pesticide molecules is adsorbed by soils high in organic matter content and/or high clay content. A low proportion of the pesticide molecules is adsorbed by sandy soils containing little organic matter. Pesticides with a high water solubility are generally adsorbed to a lesser degree than pesticides with low water solubility.

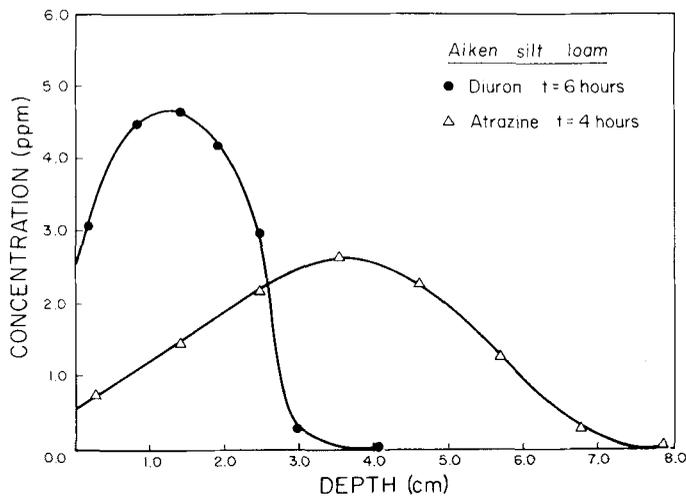
The geometrical factors influencing the adsorption of the pesticide molecules can be explained as follows: the higher the volumetric solution content in the soil profile the more of the space between the soil particles is filled with pesticide solution. From the drawing, it can be visualized that at a higher volumetric solution content, proportionately fewer pesticide molecules are likely to come in contact with soil particles, and have therefore a chance to get adsorbed. The ratio between the number of pesticide molecules adsorbed and the number of pesticide molecules in solution is therefore expected to decrease with increasing volumetric solution content.

It can also be seen from the drawing

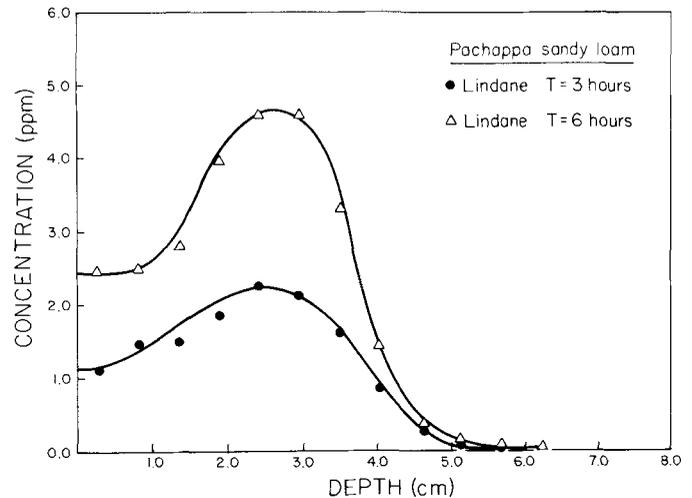
SCHEMATIC DIAGRAM SHOWING HOW PESTICIDE MOLECULES AND SOIL PARTICLES INTERACT WHEN A PESTICIDE SOLUTION IS MOVING THROUGH A SOIL PROFILE



GRAPH 1. DISTRIBUTION OF DIURON AND ATRAZINE
(T = 3 HOURS, v = 0.8 cm/HOUR).



GRAPH 2. DISTRIBUTION OF LINDANE WITH DIFFERENT AMOUNTS
OF LINDANE ADDED (t = 27 HOURS AND v = 0.8 cm/HOUR).



that as the space between the soil particles gets smaller—that is, as the bulk density of the soil profile increases—the greater the chance for a pesticide molecule to come in contact with a soil particle. Therefore, the higher the bulk density, the greater the ratio between the number of pesticide molecules adsorbed and in solution. In a given soil pesticide system with uniform volumetric solution content and bulk density, the ratio (K) between adsorbed pesticide molecules and pesticide molecules in solution has been found to be constant over a wide range of pesticide concentrations in the soil solution at equilibrium. K is also referred to as effective adsorption coefficient because it is a measure of the proportion of the pesticide molecules adsorbed in a given soil pesticide system.

As plain water enters the soil profile, after the initial pesticide application, the pesticide concentration in the soil solution initially drops to zero. To maintain the ratio K between adsorbed pesticide molecules and pesticide molecules in solution, pesticide molecules adsorbed on soil particles go back into solution as equilibrium is approached. Consequently pesticide molecules are removed from soil particles in the top portion of the soil profile, move down while in solution and become re-adsorbed in the lower portions of the profile, where fewer pesticide molecules have yet penetrated. This process continues as long as water is applied at the soil surface.

Desorption near the top, and adsorption in the lower portion of the soil profile results in a wavelike distribution of

the pesticides as shown in graphs 1 and 2. In most cases, however, a certain number of pesticide molecules are adsorbed irreversibly to the soil particles. Even after prolonged water infiltration, a residual number of pesticide molecules remains in the top portion of the soil columns and the distribution curves of the pesticides tend therefore to be asymmetrical.

Calculated results indicate that the lower the effective adsorption coefficient K in the soil profile, the broader the pesticide distribution curve. As K increases, the distribution becomes narrower. The calculated position of the maximum concentration is also dependent upon K . The position of the maximum concentration is equal to the depth of water penetration divided by K . Calculations have also shown that application of a greater amount of the pesticides to the soil surface increased the concentration of the pesticides but did not influence the depth of penetration of the pesticides under leaching conditions.

Experimental results

The proportion of the pesticides adsorbed on the soils used in these experiments has been determined by shaking a suspension of soil in pesticide solutions of various concentrations. The ratio between the pesticide adsorbed and in solution at equilibrium has been found to be constant over the concentration range which occurs under field conditions. This ratio, as determined in these adsorption experiments, is designated by k .

Experimental data on the distribution of the pesticides have been obtained from vertical infiltration experiments into initially dry soil columns in the laboratory. First, pesticide solutions were applied to the top of the soil columns. Subsequently, water was applied to the soil columns at the same application rate. The columns were sectioned after completion of the experiments and the concentration of the pesticides determined in each section. The depth of the wetting front at the end of each experiment, the average volumetric water content (θ) and the bulk density (β) of the soil columns were recorded for each experiment. The effective adsorption coefficient K in the soil columns was obtained from the relationship $K = k\beta/\theta$. This is consistent with the previous discussion of the geometrical factors influencing the proportion of pesticide molecules adsorbed by soil particles in a soil profile. In all experiments radioactive labeled pesticides were used.

Experimental conditions and results from infiltration experiments together with the appropriate k and K values are given in the table. Graph 1 shows that, as predicted by the theory, increasing the effective adsorption coefficient from 7.8 for atrazine on Aiken silt loam to 26.1 for diuron on the same soil has the effect of narrowing the distribution curves. Even though three times as much water has been applied in the experiment with diuron than in the experiment with atrazine, the diuron distribution curve is much narrower than the atrazine distribution curve.

ADSORPTION COEFFICIENTS AND RESULTS FROM INFILTRATION EXPERIMENTS

Pesticides and adsorbents	Time of pesticide application (hrs)	Total time of infiltration (hrs)	Application rate (cm/hr)	Adsorption coefficient	Effective adsorption coefficient	Depth of water penetration (cm)	Calculated depth of max. concentration (cm)	Observed depth of maximum concentration (cm)	% error *
	(T)	(t)	(v)	(k)	(K)				
LINDANE									
Gila silt loam	24	36	0.2	2.88	11.0	21.5	2.0	1.7	1.4
Pachappa sandy loam	12	60	0.2	5.14	28.3	41.8	1.5	1.4	0.2
Pachappa sandy loam	3	27	0.8	5.14	22.6	66.1	2.9	2.6	0.5
Pachappa sandy loam	6	27	0.8	5.14	22.8	66.7	2.9	2.7	0.3
Kentwood sandy loam	12	84	0.2	10.51	55.4	53.5	1.0	1.3	-0.6
DIURON									
Pachappa sandy loam	3	6	0.8	1.59	8.7	18.2	2.1	2.0	0.5
Kentwood sandy loam	3	6	0.8	3.34	16.1	15.9	1.0	1.2	-1.3
Aiken silt loam	3	24	0.8	11.49	26.1	39.7	1.5	1.2	0.8
ATRAZINE									
Pachappa sandy loam	3	4	0.8	0.33	1.9	13.2	6.9	3.1	28.8
Kentwood sandy loam	3	4	0.8	0.88	4.5	12.5	2.8	1.5	10.4
Aiken silt loam	3	12	0.8	3.15	7.8	22.1	2.8	3.6	-3.6

* The per cent error is obtained by dividing the difference between predicted and observed depths of maximum concentration by the depth of water penetration.

In Graph 2 the total time of infiltration was maintained at 27 hours for both infiltration experiments shown. In the experiment which resulted in the steeper distribution curve, twice as much pesticide was applied to the soil surface before leaching as in the experiment with the shallower distribution curve. In agreement with calculated results, the addition of greater amounts of lindane has therefore increased the concentration of the pesticide at each point in the soil column but has not influenced the depth of maximum concentration, and the depth of lindane penetration. It should be noted that the solid lines in Graphs 1 and 2 are interpolations between data points and do not represent calculated distribution curves.

Results in the table show that dividing the depth of water penetration by K predicts the depth of maximum concentration of lindane and diuron with good accuracy for the experimental conditions of this study. The error in predicting the depth of maximum concentration of atrazine in the soil columns has been considerable, however, namely for the two soils with low adsorption coefficients—Pachappa and Kentwood. The reason for this discrepancy is not clear. It could be argued that in soil pesticide systems with low adsorption the adsorption coefficient k as determined in adsorption experiments and the effective adsorption coefficient K in the soil columns are not related by the simple relationship $K = k\beta/\theta$ as assumed earlier.

The fact that the adsorption of atrazine is influenced by the pH of the soil could also be a factor contributing to the discrepancy between observed and calculated depths of maximum concentration. The pH of the soils studied decreases in the order Pachappa, Kentwood, Aiken.

The adsorption of atrazine increases with decreasing pH. The mobility of atrazine is therefore expected to decrease with decreasing pH. For the higher pH soils Pachappa and Kentwood, the mobility of atrazine was over-estimated. For the lower pH soil, Aiken, the mobility was under-estimated. The effect of the pH on the adsorption would then appear to be greater in the adsorption experiments than in the soil columns.

Despite the failure to predict the depth of maximum concentration of atrazine, the following can still be observed: Increasing the adsorption coefficient reduced the depth of maximum concentration if the same amount of water has been applied to the soil columns (experiments with Pachappa and Kentwood). When increasing the adsorption coefficient by a factor of 9.5, it took 9 times as much water to move the depth of maximum concentration to approximately the same depth (experiments with Pachappa and Aiken).

This study therefore supports important results obtained from theoretical considerations experimentally. It can also be concluded that the adsorption coefficient as used in this study is a valuable parameter for predicting the mobility of organic chemicals in soils. Even though it is not always possible to predict the depth of the maximum concentration of the pesticides accurately, the adsorption coefficient gives at least a qualitative indication of the relative mobility of the pesticides in soils.

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AMMONIA AND RELATE EMANATING FROM A LAR DAIRY AREA

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VOLATILIZATION OF NITROGEN from animal wastes in combined form, principally ammonia, has recently received attention because of the high concentration of large numbers of animals in some production operations. One constituent of animal waste that is a potential pollutant to surface and ground water is combined nitrogen. Small amounts of nitrogen in animal wastes are also apparently volatilized in the form of amines which are ammonia derived compounds. Amines are one group of compounds that contribute to the objectionable odors emanating from confined animal operations.

One-half of the nitrogen excreted by cattle is estimated to be in the urine. Urea, the principal nitrogen form in animal urine, is readily hydrolyzed to ammonia and, under the alkaline conditions of corral surfaces, this ammonia is volatilized. Ammonia is also formed and vola-