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Adsorption of Fenitrothion and 3-Methyl-4-nitrophenol on Soils and Sediment

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Adsorption of pesticides and their degradation products on soils and sediments plays a major role in the environmental fate of such chemicals. Fenitrothion is an insecticide of economic significance in Canada (ANON. 1975). Its major degradation product, 3-methyl-4-nitrophenol, was shown to be more toxic to microorganisms than the parent compound (BAARSCHERS *et al.* 1980). Of the extensive literature on pesticide adsorption, few reports on fenitrothion adsorption are available (ZITKO & CUNNINGHAM 1974; BOWMAN & SANS 1977). Therefore the adsorption characteristics of fenitrothion and 3-methyl-4-nitrophenol on several soils were studied, and the results of this study are reported here.

EXPERIMENTAL

Soils and Chemicals - Four soils and a Lake Superior sediment were used as adsorbents. The Northwestern Ontario soils (Cg, Ah and Ae) were obtained from the Lakehead University School of Forestry soils chemistry laboratory. The Lake Superior sediment (S75) was a gift from Dr. J.S. Mothersill, Lakehead University, Department of Geology, and the soil Ps was a commercially available, blended potting soil. The characteristics of the soils are summarized in Table 1. Soil samples were oven-dried (110^{o}C, 24 h), and the fractions passing through a 100-mesh sieve were used.

Fenitrothion was a gift from Sumitomo Shoji, Canada Ltd. and was purified by the method of KOVACICOVA *et al.* (1971). 3-Methyl-4-nitrophenol was obtained from Aldrich Chemical Co. and was recrystallized from ethanol.

Adsorption Measurements - Freundlich adsorption isotherms were measured according to a protocol proposed by the U.S. Environmental Protection Agency (ANON. 1979). Thus, suspensions of soil in a solution of the pesticide were prepared (for fenitrothion 1 g soil in 20 mL pesticide solution, for the methylnitrophenol 0.5 g soil in 10 mL pesticide solution) in triplicate for each of a series of concentrations (4 - 23 ppm for fenitrothion and 10 - 350 ppm for the methylnitrophenol). These suspensions were equilibrated in a constant temperature bath (20^{o}C) by slow stirring (magnetic stirrer) for 24 h. With each triplicate set one blank suspension (soil in distilled water) was equilibrated.

After equilibration the suspensions were centrifuged (15,000 rpm, 10 min), and the supernatant was extracted with ethyl acetate (2 x 10 mL). The extracts were concentrated on a flash evaporator at room temperature and made up to 1 mL with a solution of a suitable internal standard for gas chromatographic analysis. The extractions of the blanks ensured that no compounds were leached from the soils which could interfere with the analyses. At each concentration level, duplicate control extractions of the pesticide solution used ensured that the pesticide was recovered quantitatively. All extracts were analyzed by quantitative gas chromatography. Soil pellets resulting from centrifugation were extracted with methanol (25 mL) by stirring for 24 h at room temperature, and the extracts were concentrated and prepared for analysis as above.

Adsorption Capacities - Suspensions of some of the soils in 20 ppm pesticide solutions were prepared in the same proportions as above, equilibrated, centrifuged, and the amount of pesticide in the supernatant determined as above. The pellets were resuspended in fresh pesticide solution (1:20) of the same concentration, equilibrated again, centrifuged, and the second supernatant extracted and analyzed as above. Soil pellets were resuspended and equilibrated with fresh pesticide solutions until analysis of the supernatant indicated that no further adsorption took place. Usually three, sometimes four, equilibrations were required.

At that point, the soil pellets were extracted with methanol, and the methanol extracts were concentrated and analyzed by gas chromatography.

Gas Chromatography - A dual column gas chromatograph with flame ionization detectors was used with either silicone rubber gum (SE-30, 5%) for fenitrothion, or Dexsil 300 (3%) for the methylnitrophenol on Gas-Chrom Q in 1.8 m glass columns. Nitrogen was the carrier gas (25 mL/min) at column temperatures from 175 to 200°C. Extracts, obtained as above, were made up to 1 mL with ethyl acetate containing an appropriate amount of diethyl sebacate as an internal standard (TAKIMOTO *et al.* 1976). Calibration curves, derived from analyses of solutions of the internal standard containing a range of known concentrations of the pesticide, then allowed for the quantitative analysis of all extracts.

Table 1. Chemical-Physical Properties of the Soils Used

Soil Code	Soil Type	% Organic Matter^a)	pH^b)
Cg	Gleysol	0.9	5.5
S75^c)	Sediment	2.9	7.1
Ac	Luvisol	5.5	4.7
Ah	Gleysol	6.1	4.7
Ps	Commercial blend	33.1	5.3

a) By chemical oxidation with chromic acid

b) Aqueous slurry and pH-meter

c) Sample taken from central area of Batchawana Bay, Lake Superior

RESULTS AND DISCUSSION

Freundlich Isotherms - Analyses of single equilibrations allowed the plotting of isotherms according to the equation

$$\log \frac{x}{m} = N \log C_e + \log K \qquad (1)$$

where $\frac{x}{m}$ = weight of adsorbate/weight of adsorbent (μg/g)

C_e = equilibrium concentration of adsorbate (μg/mL)

and N and K are constants.

The isotherms were determined by linear regression from an average 7 datapoints (with a minimum of 4 in two cases) per isotherm. Correlation coefficients were generally 0.95 or better (see Table 2, columns 4 and 7).

According to the protocol used (ANON.1979), the major practical significance of determining these isotherms is a suggested correlation between the value of the soil/solution partition coefficient K and the mobility of the pesticide in the soil. This mobility can also be determined directly by soil thin layer chromatography (HELLING 1971), but this has the disadvantage of requiring radioactively labelled pesticides. Since toxicity measurements (BAARSCHERS *et al.* 1980) demonstrated the need for investigating *known derivatives* as well as the parent pesticide, the requirement for several labelled derivatives could lead to much time-consuming and expensive synthetic chemistry. Thus, notwithstanding criticism of the stirring method (GREEN & COREY 1971), the measurement of adsorption isotherms appeared to be a more convenient method for estimating pesticide adsorption and mobility. Table 2 summarises K-values, N-values (slope) and correlation coefficients of the isotherms measured for fenitrothion and 3-methyl-4-nitrophenol in this way.

Two conclusions may be drawn from these results. Firstly, the mobility of both compounds decreases (K increases) with increasing percentage organic matter in the adsorbents. This is in agreement with earlier observations (*e.g.*, SALTZMAN *et al.* 1972; UPCHURCH & PIERCE 1958). The objective of confirming this effect of organic matter content was the reason for including the soil Ps with the adsorbents studied.

Secondly, in all soils studied, the more water soluble 3-methyl-4-nitrophenol is more mobile (lower K-values) than fenitrothion itself. This finding also agrees with earlier reports (*e.g.*, BAILEY & WHITE 1964), but probably would not extend to strongly alkaline soils which would interact chemically with the acidic methylnitrophenol.

Relative adsorption of the two compounds on each soil may be expressed as the ratio $R = K_f/K_p$ of the K-values as given in column 8 of Table 2. The significance of these ratios is discussed below.

Table 2. Freundlich Constants for Adsorption of Fenitrothion and 3-Methyl-4-nitrophenol on Five Soils.

Soil	(% o.m. - pH)[a)]	K_p[b)]	N_f	r_f	K_p	N_p	r_p	$R = K_f/K_p$
Cg	(0.9 - 4.9)	17.0	0.98	0.99	2.1	1.07	0.98	8.1
S75	(2.9 - 7.1)	15.5	1.20	0.97	3.0	1.10	1.0	5.1
Ae	(5.5 - 4.5)	100.0	0.63	0.99	43.7	0.51	0.98	2.3
Ah	(6.1 - 4.4)	57.5	0.89	0.92	39.8	0.80	1.00	1.4
Ps	(33.1 - 5.3)	354.8	1.82	0.97	147.8	0.56	0.92	2.4

a) Figures in parentheses refer to % organic matter and pH resp.
b) Subscripts f and p refer to data for fenitrothion and the phenol resp.

The Modified Freundlich Equation - In the conventional Freundlich equation (Eq. 1), the units of K can be shown to be a function of the slope N, which makes it difficult to compare K-values of isotherms having different slopes. For this reason, it has been proposed (BOWMAN 1981) to modify the log Freundlich equation to

$$\log \frac{x}{m} = N \log Z + \log K \qquad (2)$$

where $\frac{x}{m}$ = wght. of adsorbate/wght. of adsorbent (nanomoles/g)

Z = mole fraction (approximated as moles of solute/moles of solvent) at equilibrium in solution

and K and N are constants.

In this case, the value of K, evaluated at $\log Z = 0$ ($Z = 1$, i.e., no solvent) becomes meaningless, and relative adsorption must be evaluated at a Z-value where there is adsorption data for both compounds. When the data obtained in the present study are expressed in terms of Eq. 2, a series of isotherms are obtained for which $\log Z = -6.5$ appears to be a suitable value for comparing adsorption. This value represents the high end of the concentration range used for fenitrothion (≈20 ppm) and the lower end of that used for the methylnitrophenol (≈15 ppm). The resulting values for x/m in nanomoles/g are given in Table 3, together with K-values obtained from Eq. 2. (N repeated for convenience). Again relative adsorption of the two compounds on each adsorbent may be expressed as the ratio $R = (x/m)_f/(x/m)_p$ at $\log Z = -6.5$.

The ratio R in both systems is of similar magnitude for all adsorbents except in the case of soil Ps. The widely different R-values for this adsorbent in the two systems dramatically shows the effect of a slope N that is substantially different from unity. At the same time, the x/m value for fenitrothion at $\log Z = -6$ (40738 nanomoles/g = 11292 µg/g) is quite clearly outside the meaningful area of the isotherm, since it would require more than 12 mg of fenitrothion in 20 mL water. This exceeds the water solubility of fenitrothion (23 ppm) by a factor of 25. For the fenitrothion-Ps combination even an evaluation of x/m at log Z = – 7 would still be meaningless for the same reason.

It thus becomes clear that, while the modified Freundlich equation may have advantages when data expressed in different units are compared (BOWMAN 1981), it fails when relative adsorptions are compared on the basis of isotherms with a slope N greatly in excess of unity.

In this respect it may be noted that adsorption from solution in most cases gives isotherms with slope N equal to or smaller than unity (BOWMAN 1981; WU *et al.* 1975; MURRAY *et al.* 1975). A value of N substantially greater than unity may mean that multilayer adsorption or chemical interaction is taking place.

Table 3. Constants for Adsorption of Fenitrothion and 3-Methyl-4-nitrophenol Derived from the Modified Freundlich Equation.

Soil	$(x/m)_f$ a)	K_p	N_f	$(x/m)_p$	K_p	N_p	$R = \frac{(x/m)_f}{(x/m)_p}$
Cg	292.3	8.8	0.98	44.7	8.5	1.07	6.5
S75	376.0	10.4	1.20	57.6	8.9	1.10	6.7
Ae	970.5	7.3	0.63	484.2	6.0	0.51	2.0
Ah	851.1	8.6	0.89	562.3	8.0	0.81	1.5
Ps	40738.0	16.4	1.82	1717.9	6.9	0.56	23.7

a) x/m values in nanomoles/g at log Z = – 6.5

Adsorption Capacities - Figures obtained for relative mobility, in terms of K-values, or for relative adsorption, in terms of x/m values at a chosen log Z, can be useful for comparing adsorption behaviour per se of the two compounds. These figures do not, however, give a complete picture of the environmental significance of adsorption. Particularly in view of toxicity to microorganisms (BAARSCHERS *et al.* 1980) the question arises how much pesticide can be adsorbed when a soil is repeatedly (or continuously) exposed to fresh pesticide solution.

Therefore some of the soils were equilibrated repeatedly with fresh aliquots of the same pesticide solution at approx. 20 ppm as as described. Total amounts adsorbed after 3 or 4 equilibrations are given in Table 4. As might be expected, amounts adsorbed show the same relationships with organic matter content of the adsorbent and water solubility of the adsorbate. Observed amounts are probably higher than those that would occur under field conditions, where actual concentrations, at least of fenitrothion, would be lower (LOCKHART *et al.* 1977). It is clear, however, that amounts adsorbed could reach *potentially* fungitoxic concentrations (BAARSCHERS *et al.* 1980), particularly so in the case of accidental spills of pesticide formulations.

Table 4. Adsorption of Fenitrothion and 3-Methyl-4-nitrophenol on Three Soils after Repeated Equilibration with 20 ppm Solutions.

	Quantities adsorbed (μg/g)	
Soil Code	Fenitrothion	3-Methyl-4-nitrophenol
S75	740	100
Ae	913	347
Ps	1120	480

Material Balance - The protocol proposed (ANON. 1979) for the measurement of adsorption isotherms includes a requirement for extraction of pesticide from the soil samples so as to provide a material balance for each analysis. In the present study, soil samples were extracted with methanol for that purpose. The amounts of pesticide recovered varied greatly; in several cases less than 30% of the pesticide adsorbed was recovered, in others the amount recovered greatly exceeded the amounts adsorbed. The latter may be caused by the extraction of other compounds from the soil which interfere with gas chromatographic analysis. It thus appears that these attempts to recover the adsorbed pesticide serve no useful purpose.

Conclusions - It was found that fenitrothion and its hydrolysis product 3-methyl-4-nitrophenol are adsorbed on sediment and soils in amounts that increase with increasing organic matter content of the adsorbate. Whereas the use of K-values derived from the Freundlich equation (Eq. 1) has limitations, the use of a modified Freundlich equation presents problems when the slope of the isotherm is appreciably larger than unity. Both compounds can be adsorbed on soils so as to reach concentrations that are fungitoxic on agar plates. Since compounds adsorbed on soil (and on the organic litter of the forest floor) would not be readily subject to photodegradation, the results of this study show that it is essential that attention be given to further studies on the microbial degradation of these compounds.

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REFERENCES

ANON.: Fenitrothion: The effects of its use on environmental quality and its chemistry. National Research Council of Canada, Report No. 14104, Ottawa, 1975.
ANON.: U.S. Federal Register. March 16, 1979. Part IV
BAARSCHERS, W.H., A.I. BHARATH, M. HAZENBERG, J.E. TODD: Canad. J. Bot, 58,426 (1980).
BAILEY, G.W. and J.L. WHITE: J. Agric. Food Chem. 12,324 (1964)
BOWMAN, B.T. and W.W. SANS: Soil Sci. Soc. Amer. J. 41, 514 (1977).
BOWMAN, B.T.: J. Environ. Sci. Health B16,113 (1981).

CHU-HUANG WU, N. BUEHRING, J.M. DAVIDSON, P.W. SANTELMANN: Weed Sci. 23, 454 (1975).

GREEN, R.E. and J.C. COREY: Soil Sci. Soc. Amer. Proc. 35, 561 (1971).

HELLING, C.S.: Soil Sci. Soc. Amer. Proc. 35, 743 (1971).

KOVACICOVA, J., Z. MAZUD, V. BATORA, J. KOVAC, S. TRUCHLIK:Pestic. Sci. 4, 759 (1973).

LOCKHART, W.L., J.F. FLANNAGAN, R.P. MOODY, P. WEINBERGER, R. GREENHALGH: Proc. of Symposium on fenitrothion, National Research Council of Canada, Publication No. 16073, 1977.

MURRAY, D.S., P.W. SANTELMANN, J.M. DAVIDSON: J. Agric. Food Chem. 23,578 (1975).

SALTZMAN, S., L. KLIGER, B. YARON: J. Agric. Food Chem. 20,1224 (1972).

TAKOMOTO, Y., A. MURANO, J. MIYAMOTO: Residu Rev. 60, 11 (1976).

UPCHURCH, R.P., and W.C. PIERCE: Weeds 6, 24 (1958).

ZITKO, V., and T.D. CUNNINGHAM: Environment Canada, Fisheries and Marine Service, Technical Report No. 458, 1974.

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