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Vertical Transport of Pesticides into Soil When Adsorbed on Suspended Particles

It is generally assumed that pesticides with very high K_D values are virtually immobile in the soil, though they may be transported laterally by erosion. Data presented in this paper show that vertical transport of [¹⁴C]DDT and [¹⁴C]paraquat adsorbed on suspended material can occur. Under favorable conditions for transport, 18% of the applied [¹⁴C]DDT was transported on solids in sewage effluent to a depth greater than 9 cm in a sandy loam soil. Dispersed Li-montmorillonite suspension transported over 50% of applied [¹⁴C]paraquat to a depth of 12 cm. The conditions required for such transport to occur are described.

It is observed in the literature that pesticides with high K_D values such as DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane] and paraquat (1,1'-dimethyl-4,4'-dipyridylum chloride) are so strongly adsorbed by soils as to be virtually immobile (Guenzi and Beard, 1967). Such pesticides may, however, be transported laterally in sediments removed by erosion [see Wauchope (1978) for a review] and in runoff water. Rao and Davidson (1982) point out that unless the K_D (partition coefficient) is greater than about 100 or the sediment load is high (>0.1%) most of the pesticide transported during lateral flow is in the aqueous phase because of the low concentration of solids in suspension. K_D is defined by the equation $X_e/n = K_D S_e$ where K_D = partition coefficient (mL/g), n = suspension concentration (g/mL), X_e = concentration of adsorbate on the adsorbed phase (g/mL), and S_e = concentration of adsorbate in the solution phase (g/mL). By contrast, during the flow of water through soil the contribution of pesticides in solution to vertical transport is always low if K_D is large and if the pesticide is rapidly transferred to adsorbing surfaces. Instantaneous equilibration is a good approximation of pesticide adsorption on the soil solid phase unless the flow rate is high (Davidson and Chang, 1972). Thus, only if the pesticide is complexed or adsorbed on mobile colloids will any significant vertical transport occur. Ballard (1971) had demonstrated the role of humic substances, dispersed by addition of urea to a forest soil, in complexing and transport of DDT. Guenzi and Beard (1967) postulated transport of DDT adsorbed on soil colloids as a mechanism of downward transport. The experiments reported here were part of two studies on the transport of suspended solids through soil. [¹⁴C]Paraquat adsorbed on Li-mont-

Table I. Characteristics of Soils

soils	% clay	% organic matter	% carbonates	pH	packing density, g/cm ³
[¹⁴ C]DDT Experiments					
Bet Dagan, sandy loam	13.7	0.68	2.3	7.9	1.30
Gilat, silty loam	23.1	0.95	12.9	7.8	1.59
Bene Darom, coarse sand	1.2	0.21	2.8	7.8	1.30
[¹⁴ C]Paraquat Experiments					
Begbroke, sandy loam	18	2.5	n.a. ^a	6.1	1.4

^a Not available.

morillonite in suspension was used in one study (Vinten, 1981) and [¹⁴C]DDT adsorbed on the organic suspended solids in sewage effluent was used in the other (Vinten et al., 1983). As a side shoot of these investigations these data show that under favorable conditions transport of pesticides with high K_D values on mobile colloids is feasible.

EXPERIMENTAL SECTION

Materials. [¹⁴C]Paraquat and [¹⁴C]DDT were obtained from Amersham International, Ltd., United Kingdom. They had specific activities of 425 and 80.8 mCi/g, respectively. Sewage effluent was obtained from Kibbutz Givat Brenner, Israel. It had a pH of 7.6, EC of 2.0 mmho/cm, COD of 316 mg/L, and a suspended solids concentration of 98 mg/L. Unaltered effluent (A) and effluent after filtration through a Whatman No. 92 filter (B) were used. Details of soils used in the experiments are given in Table I. Counting of samples was done on

Table II. Adsorption Data for Pesticides Studied

pesticide	adsorbent	K_D , mL/g	concn of suspended solids, ppm (w/v)	X_e/S_e^a
paraquat	Li-montmorillonite, <math><0.15 \mu\text{m}</math> esd	7.3×10^4	30	2.2
DDT	sewage effluent solids (fraction A) ^b	7.8×10^4	98 (84% organic) ^b	7.7
DDT	sewage effluent solids (fraction B) ^b	2.1×10^5	38 (100% organic) ^b	8.0

^a X_e = adsorbed label concentration at equilibrium.
 S_e = solution label concentration at equilibrium. ^b Determined by ignition at 600 °C.

Beckman (¹⁴C]paraquat) or Packard Prias (¹⁴C]DDT) liquid scintillation counters.

Procedure. (a) [¹⁴C]Paraquat was added to 30 ppm of Li-montmorillonite suspension at a rate of 15 nCi/mL (0.27 μ equiv/L) and shaken for 2 h. Supernatant activity was measured giving a K_D value (see Table II). Kinetics studies showed that desorption of pesticide from solids was of minor importance in the time course of experiments.

Columns of Begbroke sandy loam, varying from 2.1 to 12 cm in length, were packed to a bulk density of about 1.3 g/cm³, saturated and leached with [¹⁴C]paraquat-labeled Li-montmorillonite suspended in distilled water or 1 mM CaCl₂. Leachate activity and volume were monitored. A constant activity was achieved after 2–5 pore volumes, depending on column length.

(b) [¹⁴C]DDT was adsorbed on suspended solids in sewage effluent by adding 300 nCi to 300 mL of effluent and gently stirring for 1 h. Supernatant activity gave the K_D value (Table II). Desorption kinetics were measured by monitoring the rate of partitioning of [¹⁴C]DDT into a hexane phase in the presence of effluent and from distilled water. These again showed that release of DDT from the adsorbed phase was not important in the time course of experiments, though a correction needs to be made for DDT present in the equilibrium solution. Further details of experimental methods are given in Vinten et al. (1982) for DDT and Vinten (1981) for paraquat.

Columns of Gilat (silt loam), Bet Dagan (sandy loam), and Bene Darom (coarse sand) soils were leached with [¹⁴C]DDT-labeled effluent. Following leaching of the soils, columns were sectioned and the [¹⁴C]DDT was extracted by shaking with a 1:1 hexane–acetone mixture for 1 h. The distribution of solids deposited in the soil with depth was thus determined. Activity in the leachate was also measured. By assuming that the rate of deposition of particles is a function of depth through the column only (and not of time) for a given run, it is possible from the distribution in the column to calculate the concentration of pesticide remaining in the mobile phase as a function of depth. Thus, if half the pesticide used in the experiment is located in the soil in the top 5 cm, then it is assumed that the concentration of pesticide in suspension at that depth is half that of the input suspension and that this remains constant.

RESULTS AND DISCUSSION

Figure 1A shows the vertical transport of [¹⁴C]paraquat adsorbed on Li-montmorillonite suspension through columns 2.1–12-cm in length. Data on experimental conditions in columns are presented in Table III. When distilled water is the suspension medium, 50% of the pesticide penetrates beyond 12 cm. However, in 1 mM CaCl₂ only 5% of the pesticide penetrates deeper than 1 cm. The high [Ca²⁺] results in rapid immobilization of the clay in the soil through flocculation and straining or through adsorption

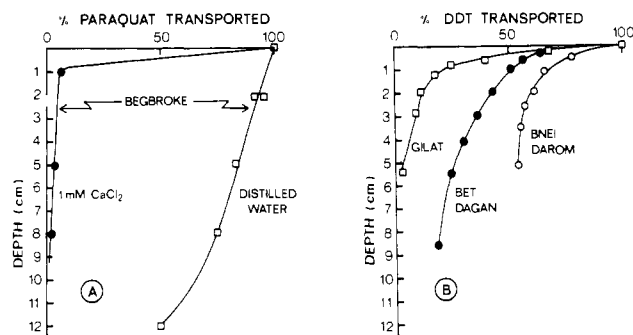


Figure 1. Vertical transport of DDT and paraquat adsorbed on suspended particles (in percent of total applied). (A) [¹⁴C]Paraquat adsorbed on Li-montmorillonite. (B) [¹⁴C]DDT adsorbed on suspended solids in sewage effluent.

Table III. Data on Column Experiments

[¹⁴ C]Paraquat Experiments			
column length, cm	suspension medium	initial flow rate, cm/s	leachate vol, cm
2	distilled water	3.5×10^{-4}	30
2	distilled water	2.6×10^{-3}	23
5	distilled water	1.1×10^{-3}	24
8	distilled water	5.4×10^{-3}	35
12	distilled water	1.2×10^{-2}	45
1	1 mM CaCl ₂	4.3×10^{-3}	32
2	1 mM CaCl ₂	1.1×10^{-2}	35
8	1 mM CaCl ₂	3.1×10^{-3}	38

[¹⁴ C]DDT Experiments			
soil	effluent	initial flow rate, cm/s	leachate vol, cm
Bene Darom	A	9.4×10^{-2}	20
Bet Dagan	A	1.2×10^{-2}	54
Gilat	B	8.9×10^{-4}	36

on pore surfaces, and consequently little pesticide transport occurs. Under conditions when the clay is dispersed there is no flocculation and little interaction with the soil solid phase, so the pesticide is readily transported through the soil.

In the second case a range of behavior of [¹⁴C]DDT is observed in three soils (Figure 1B). In the Gilat soil—a silt loam—the flow rate is slow, the pore structure is fine, and little transport of pesticide occurs (only 3% reaches 5.4 cm). This is a result of efficient removal of suspended solids by the soil, despite the use of the finer effluent fraction B. Fraction B, the effluent filtered through a Whatman No. 92 paper, was used to prevent sedimentation of coarse suspended solids at the soil surface. This occurred because of the low flow rates occurring in the Gilat soil. In the case of the Bet Dagan soil—a sandy loam—there is considerable pesticide transport as the flow rate is higher and the organic colloids are more mobile. Eighteen percent of the pesticide is transported to a depth greater than 9 cm. In the case of the Bene Darom coarse sand, still more transport of pesticide occurs, with 54% penetrating deeper than 5 cm. Again these differences are due to the differences in mobility of the solids which is directly related to soil type and flow rate.

Some qualification of the assumption of the steady rate deposition of suspended particles (see Experimental Section) is needed here. As deposited solids accumulate in the soil, clogging of soil pores may occur, reducing flow rate. This may result in increased particle deposition and, hence, pesticide removal near the soil surface. Data presented in Figure 1B thus give the time-averaged concentration of pesticide in the mobile phase at any depth. This simplification was valid for the experimental conditions used here as the leachate activity was nearly con-

stant with time, despite the reduction in the flow rate that occurred.

Having demonstrated the feasibility of transport of strongly adsorbed pesticides on mobile colloids during leaching, it is important to indicate under what field conditions such transport might occur and contribute to edge-of-field loss. DDT or paraquat may reach the soil following foliar application and will be strongly adsorbed close to the soil surface. Other soil-applied herbicides such as the s-triazine group and other organochlorine pesticides have high K_D values and will not be transported much in solution. Hartley and Graham-Bryce (1980) point out the potential hazard in lateral runoff for such pesticides but consider vertical transport unimportant. However, if soils are leached with rainwater, or with sodic water and subsequently with low EC water, dispersion and release of clay can occur [e.g., Shainberg et al. (1981)]. Under such conditions, when release of soil colloids occurs, pesticides adsorbed in the surface soil may be transported to drainage water. Pesticides applied as wettable powders may also be transported in suspension form if leaching conditions occur soon after application.

The extent to which this type of transport occurs depends on the amount of clay or organic matter released by the surface soil on dispersion, the mobility of these colloids in the soil profile, the rate at which soil clogging occurs, the K_D value, and the kinetics of desorption of pesticide from the mobile colloids.

Registry No. Paraquat, 4685-14-7; Li-montmorillonite, 67034-72-4; DDT, 50-29-3.

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Further Investigations on "Polysugars" Derived from Poly(vinyl alcohol)

"Polysugars" derived from poly(vinyl alcohol) have recently been reported in the literature. The organoleptic properties of these polysugars ranged from sweet to extremely bitter. The syntheses of both sweet and bitter polysugars were repeated. The resultant polysugars were found by high-performance liquid chromatography analyses of reaction mixtures and by ¹H NMR and ¹³C NMR analyses of separated reaction products to be unreacted mixtures of poly(vinyl alcohol) and sucrose.

Recently two papers have appeared in the scientific literature (Usmani and Salyer, 1979, 1981) reporting the preparation of "polysugars" by heating sucrose with poly(vinyl alcohol) in the presence of 3A molecular sieves in dimethyl sulfoxide. Since the authors, without supporting data, went on to speculate that these polysugars "may prevent caries formation and function as noncaloric artificial sweeteners", these reports have received considerable attention in the lay press.

We were intrigued by several aspects of these reports. First, the authors claimed intermolecular etherification between sucrose and poly(vinyl alcohol), but the only data presented on the possible extent of etherification are titrimetric hydroxyl determinations. Aside from the removal of the molecular sieves and dimethyl sulfoxide the "slightly syrupy reaction products" were not further characterized. Second, the authors reported that the polysugars possessed organoleptic properties ranging from sweet to extremely bitter. Introduction of sweetness into a polymeric structure has been a long sought goal (DuBois and Crosby, 1977;

Brown et al., 1978; Wingard et al., 1978). So it is somewhat surprising that simple ethers of sucrose and poly(vinyl alcohol) were found to be sweet.

With these issues in mind the most favorable experiment for the generation of a sweet polysugar described by Usmani and Salyer [polysugar sample 204249, in Usmani and Salyer (1979)] was repeated several times as closely as the published experimental description allowed. A 1:1 weight ratio of sucrose and poly(vinyl alcohol), 37-42% residual poly(vinyl acetate), was heated in dimethyl sulfoxide with 3A molecular sieves at 100 °C for 7 h. The reaction mixture was worked up as reported by Usmani and Salyer and the crude reaction product was subjected to analysis. High-performance liquid chromatography (HPLC) of the reaction mixture showed only a mixture of poly(vinyl alcohol), sucrose, and dimethyl sulfoxide, Figure 1. Within the experimental error, the poly(vinyl alcohol) and sucrose were present in the same 1:1 weight ratio as the starting materials, Figure 2. Preparative gel permeation chromatography separated the poly(vinyl alcohol) and sucrose.