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Study of the Fast Competitive Adsorption of Pesticides in Soils by Simultaneous Filtration and Solid-Phase Extraction with Subsequent GC-MS

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A simultaneous filtration-plus-solid phase extraction (SPE) with subsequent GC-MS method previously validated for the study of the adsorption equilibria of pesticides in an organic soil has been used to study samples with different physicochemical characteristics, i.e., a sandy soil and a sediment. The results of this study are consistent with those found for the organic soil. The online filtration-SPE procedure allows the determination of the amount of pesticide adsorbed in the insoluble soil (or sediment) particles and of that remaining in the aqueous phase by a single injection of the total slurry in the system. The standard deviations for the whole procedure were less than 6.5% (adsorbed) and 10% (solution) for all sorbents and for all test compounds. Comparison of the results found for the various samples showed the organic matter content as a key factor governing the partition equilibrium. The relative merits of different adsorption isotherms, including linear, Langmuir and Freundlich, for analyzing the organic soil fast adsorption data were examined. Results showed that fast adsorption of relatively polar compounds, with $\log K_{ow}$ values ranging from 1.51 to 3.74, on this soil was less ideal than simple partition and revealed the Freundlich coefficients n and K_f to be time-dependent. Interactions between the pesticides and specific sites on the soil are proposed as a plausible cause for this nonlinear behavior.

Introduction

The sorption/desorption mechanisms of pesticides and toxic chemicals in soils and their kinetics are important factors which determine their mobility in the environment. They affect the transport of pollutants in aquatic and terrestrial systems as well as their bioavailability and possible degradation. Hence, both should be considered in risk assessment of contaminants.

It is generally held that the principal sorbent for hydrophobic compounds in soils and sediments is the organic

matter (1, 2), except at very low organic contents ($<27 \text{ g kg}^{-1}$) (3, 4). Sorption of the analytes to the soil (or sediment) organic matter is then regarded as a simple partition process, i.e., as a simple uniform and concentration-independent dissolution of the analyte in this organic matter (5). In line with this assumption, the sorption/desorption process has been often simplified for modeling purposes by assuming instantaneous equilibrium conditions, isotherm linearity, and reversibility (6). However, examples of slow sorption (7), nonlinear isotherms (5, 7–9) and competitive effects (5, 9, 10) during the sorption of both low- and high-polar compounds as well as sorption/desorption hysteresis (7, 11, 12) can be found in the literature. All these results contradict the simple partition model and show that the sorption/desorption process is a much more complex mechanism which needs further study.

Much of the published sorption information refers to data collected after 1 day up to several months of equilibration (5, 9, 11, 12), because the main goal was to study how equilibrium is reached in the selected system. However, although in some cases a single day was found to be enough for some compounds to reach equilibrium (12), not much information can be found on the situation during the first few hours of equilibration. In this early stage, only so-called fast adsorption (5) of the compounds of interest to the soil (or sediment) particles occurs because additional processes such as slow sorption and desorption need longer times (13).

The first objective of this study was to evaluate a recently developed method (14) for obtaining adsorption equilibrium data of pesticides in samples with different physicochemical characteristics. The method is based on the online filtration-plus-solid phase extraction (SPE) procedure which provides information on the analyte concentrations in the particulate and the dissolved phase by a single sample injection of the total slurry in the system. This is a distinct advantage compared with previously published batch sorption techniques (3–5, 10, 11, 15, 16), which are more laborious and use large amounts of sample and solvents. The substantial improved limits of detection due to an online cleanup step and final MS detection are an additional advantage of the online method.

Second, the possible dependence of the generally assumed “fast sorption linearity” on time was studied. Previous studies have shown such a dependence for slow sorption, i.e., after contact times of several days (6, 8), which resulted in Freundlich isotherms with $n < 1$. However, it is widely accepted that fast adsorption is very close to linearity (5). In this paper, this assumption has been revised for the case of competitive adsorption by the simultaneous analysis of the two phases—the insoluble particles and the aqueous phase—of an organic soil slurry at different times during the first 2 days of equilibration. The feasibility of linear, Langmuir, and Freundlich adsorption isotherms for fitting the organic soil fast adsorption data is discussed.

For all experiments, pesticides ranging from relatively polar triazines to nonpolar organohalogen compounds were used.

Experimental Section

Sampling. Two soils (an organic and a sandy soil) from Amsterdam (The Netherlands) and a Haringvliet river sediment (Den Bommel, The Netherlands) were used. The samples were air-dried and sieved to 270 mesh. This fraction was used for subsequent studies. Properties of this fraction for the soil and sediment samples investigated were determined by standard methods (Table 1). [Soils and sediment

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TABLE 1. Some Relevant Physico-Chemical Characteristics of the Selected Soil and Sediment Samples

| element | percent of the element in | | |
|----------------------|---------------------------|------------|----------|
| | organic soil | sandy soil | sediment |
| Si | 70 | 70 | 70 |
| Ca | 7 | 7 | 30 |
| Fe | 3 | | 35 |
| K | 3 | 3 | 10 |
| Al | 15 | | 20 |
| C ^a | 11.4 | 1.3 | 5.4 |
| H | 1.0 | 0.1 | 0.4 |
| N | 0.6 | 0.02 | 0.3 |
| pH _{soil} | 6.5 | 8.3 | 7.2 |
| pH _{slurry} | 7.2 | 8.2 | 8.1 |

^a C: percentage of organic matter.

TABLE 2. Molecular Weight, Quantification Masses, and Octanol/Water Partition Coefficients of the Selected Pesticides

| pesticide | mol. weight | m/z ^a | log K _{ow} ^b |
|-------------------|-------------|------------------|----------------------------------|
| desethylatrazine | 187.1 | 187/172 | 1.5 |
| atrazine | 215.0 | 215/200 | 2.2–2.8 |
| diazinon | 304.1 | 179/137 | 3.1–3.8 |
| terbutryn | 241.2 | 226/185 | 3.4–3.7 |
| trifluralin | 335.3 | 306/264 | 4.0 |
| fenchlorfos | 321.6 | 285/125 | 4.8–5.1 |
| chlorpyrifos | 350.6 | 197/97 | 5.0–5.3 |
| hexachlorobenzene | 283.9 | 284/249 | 5.4–6.2 |
| bromophos-ethyl | 330.9 | 303/97 | 5.7–6.2 |

^a Two most abundant ions. ^b Log octanol/water partition coefficient (27).

pHs were determined (744 pH meter, Metrohm, Switzerland) after stirring for 1 min every 15 min during 1 h a sediment: quartz-distilled water (1:2, w/v) mixture (16). The elemental analysis was carried out on a Scintag (Scintag Inc., Pasadena, CA) XDS 2000 X-ray diffractometer using Cu–K alpha radiation. The percentage of organic matter was determined by using an element analyzer (Carlo Erba NA 1500, Milan, Italy) after removal of the carbonates with HCl.]

Chemicals. All pesticides (desethylatrazine, atrazine, diazinon, terbutryn, trifluralin, fenchlorphos, chlorpyrifos, hexachlorobenzene (HCB), and bromophos-ethyl) were from Riedel de Haen (Seelze, Germany). A working stock solution containing 111 µg mL⁻¹ of each compound was prepared and used for further dilution and for spiking of the samples. Table 2 summarizes some of the more relevant physico-chemical properties of the selected pesticides. Pesticide-residue-grade methanol and methyl acetate were obtained from J. T. Baker (Deventer, The Netherlands). Methyl acetate was freshly distilled prior to use. Quartz-distilled water was used in all experiments.

Batch Methodology. A 0.34 g subsample of the air-dried and sieved soil (or sediment) of interest was used for each adsorption measurement (14). The soil (or sediment) sample was presoaked with 50 mL of quartz-distilled water and homogenized by magnetically stirring during 30 min to release the organic colloids and to break down the possible sorbent aggregates before spiking (17). Some additional slurries to which 0.08 mg mL⁻¹ of bactericide (thimerosal) was added were prepared according to the same procedure. The typical spiking level for samples involved in this first part of the study, i.e., both soils and the sediment, was 0.36 µg mL⁻¹ of each pesticide. Each sample was analyzed in 4-fold after 24 h of equilibration. Total recoveries of the test compounds by using the online procedure were compared with those obtained by 5 min liquid–liquid extraction of the

total slurry (1 mL) with methyl acetate (1:1, v/v). Besides, pesticides adsorbed in the soil/sediment particles were determined by 5 min shaking with methyl acetate (0.5 mL) after separation by 30 min centrifugation (Ittettich Rotixa KS, Depex, de Bilt, The Netherlands) at 2500g.

In the second part of the study, four initial analyte concentrations in solution were used for the organic soil sorption kinetic experiments: 0.71, 0.36, 0.20, and 0.09 µg mL⁻¹ of each pesticide. In these experiments, the first slurry subsample was taken 5 min after spiking and then every 90 min. Measurements were made in duplicate and continued for a minimum of 24 h.

In all cases, the soil (or sediment) slurry was magnetically equilibrated during the whole experiment to ensure sample homogeneity and kept at room temperature (25 ± 1 °C).

Blank samples were analyzed to check any contamination throughout the analytical procedure. Blanks were prepared following the same procedure as for batch soil experiments, however, without spiking. No background interference was found to be introduced by the proposed methodology.

In all cases, brown glass containers were used as vessels. Vessels were kept closed during the whole experiment to prevent analyte losses due to volatilization.

Simultaneous Filtration-Plus-SPE System. The simultaneous filtration and SPE of the samples was carried out according to a general method previously described in detail (14). Briefly, a 500-µL sample out of the stirred bottle mentioned above was injected to rinse and fill a 100-µL loop mounted on a valve referred to as valve No. 1. The sample was pumped (flow, 2 mL min⁻¹) for 5 min through a system with three Valco six-port valves with quartz-distilled water as transport solvent. On valve No. 2 a 10 mm × 3.0 mm I.D. stainless steel hollow holder manufactured in the laboratory and on valve No. 3 a 10 mm × 2.0 mm I.D. SPE cartridge packed with 15–25 µm PLRP-S (a polystyrene-divinylbenzene copolymer; Polymer Laboratories, Church Stretton, U.K.) were mounted. A 0.5-µm frit (Sigma, Zwijndrecht, The Netherlands) was placed at the bottom of the hollow holder to retain the injected particles and prevent that they reached the SPE cartridge. A single injection of the total slurry (particles plus dissolved phase) provided information about the two phases involved in the equilibrium, the insoluble solid particles, and the aqueous solution. Once both phases were separated, particles retained in the filter were dried by 30 min purging with nitrogen gas at 3 bar, and subsequently extracted with 100 µL of methyl acetate at a flow rate of 125 µL min⁻¹; the organic solvent was collected in microvials. Then, the frit was replaced by a clean one. Simultaneously, the SPE cartridge which retained the analytes from the aqueous phase was also dried by 30 min purging with nitrogen gas at 3 bar. Desorption was carried out with 100 µL of methyl acetate at a flow rate of 125 µL min⁻¹. The desorption solvent was collected in microvials. Next, the system was reconditioned by flushing with 10 mL of quartz-distilled water.

A Gilson (Villiers-le-Bel, France) Model 302 pump was used to transport the sample into the microfilter and the SPE cartridge. A Phoenix 20 CU syringe pump (Carlo Erba Strumentazione, Milan, Italy) was used to deliver the desorption solvent.

Prior to use, the SPE cartridge was conditioned with 5 mL of methanol and, next, 5 mL of quartz-distilled water.

GC-MS. The pesticides in the collected extracts were determined by capillary gas chromatography (HP 6890 Series, Hewlett-Packard, Palo Alto, CA) with MS (HP 6890 Series) detection in the selected ion monitoring (SIM) mode. One microliter amounts of the extracts were injected in the splitless mode (splitless time, 1.0 min) on a capillary Restek XTI-5 column (30 m × 0.25 mm I.D., 0.25 µm film thickness). The column temperature was programmed linearly from 69 °C (3.5 min) to 280 °C at 15 °C min⁻¹. The final temperature was

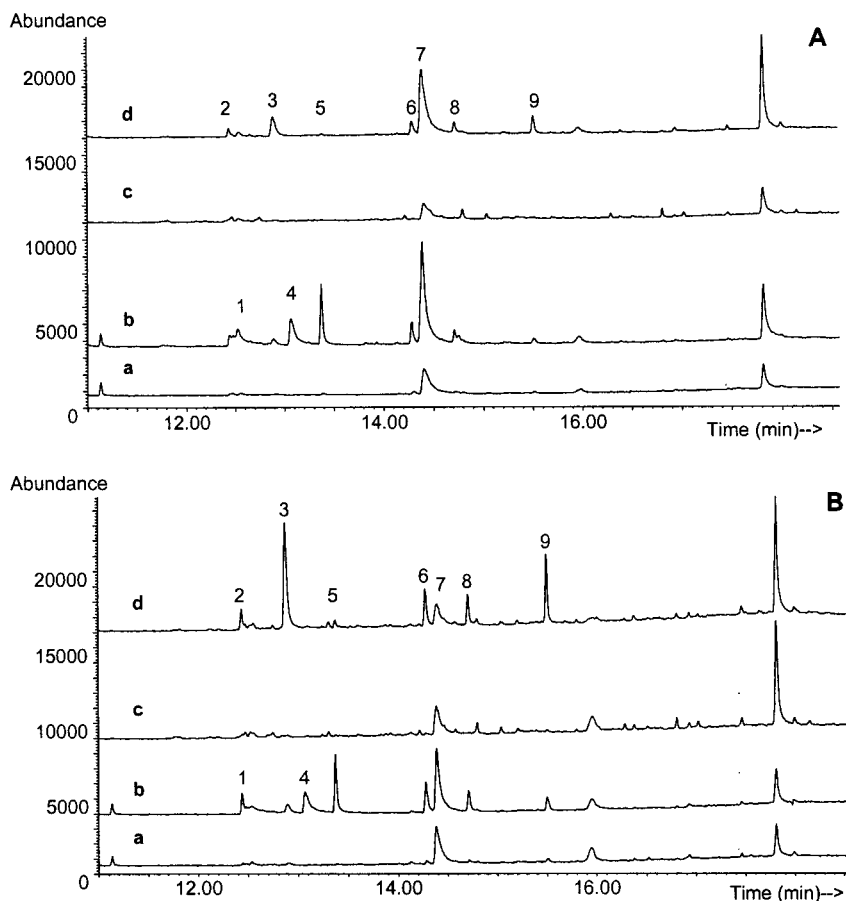


FIGURE 1. GC-MS chromatograms of the dissolved (a, b) and soil (c, d) phases obtained after online filtration-plus-SPE of (A) a sandy soil and (B) a sediment without (a, c) spiking and with (b, d) spiking at the $0.36 \mu\text{g mL}^{-1}$ level. Pesticides: 1. desethylatrazine, 2. trifluralin, 3. HCB, 4. atrazine, 5. diazinon, 6. fenclorfen, 7. terbutryn, 8. chlorpyrifos, and 9. bromophos-ethyl.

held for 1 min. Helium was used as the carrier gas at a column head pressure of 97 KPa. For each compound, the two most abundant ions were monitored (Table 2).

Results and Discussion

Application of Online Filtration-Plus-SPE to Samples with Different Physicochemical Characteristics. The methodology of online filtration of the insoluble soil particles and SPE of the aqueous phase with subsequent determination of the analyte concentrations in both phases has successfully been used to predict the soil-water partition coefficients of pesticides in an organic soil slurry equilibrated for 24 h (apparent equilibrium conditions) (14). To demonstrate the feasibility of this procedure for the analysis of samples with other physicochemical characteristics, the earlier results were compared with those obtained when analyzing a sandy soil and a river sediment slurry presoaked in quartz-distilled water, spiked at the $0.36 \mu\text{g mL}^{-1}$ level and equilibrated during 24 h. Figure 1 shows typical chromatograms obtained after the simultaneous filtration and SPE of a sandy soil and a sediment slurry, respectively. Chromatograms obtained for control samples, i.e., soils and sediment without spiking, revealed that none of the investigated pesticides was present in the samples.

The percentages of each analyte adsorbed in the soil/sediment particles and remaining in solution were calculated after 24 h of equilibration (apparent equilibrium conditions). The results, the standard deviations (SD as %; $n = 4$), and the total recoveries calculated by adding those found for the two analyzed phases are summarized in Table 3. The proposed online procedure showed a good repeatability for the different sample types, organic and sandy soils and

sediments. The SD values of the recoveries, of less than 7–8%, were in the range of those previously found (14). As expected, for all the investigated matrices, the percentage of pesticides found to be adsorbed on the insoluble soil/sediment particles increased with the hydrophobicity of the selected compound. Following the implications of this result, and in agreement with previously published data (7, 10), it can be concluded that the polarity of the analytes is an important parameter affecting their fast adsorption in soils and sediments. The high percentages of the most polar pesticides, such as desethylatrazine and atrazine, found in the aqueous phase at this contact time contribute to support this idea. (Despite their importance (8), this study was not designed to identify trends in adsorption depending on either the molecular geometry or the electronic properties of the sorbate).

The results of Table 3 also show that, for soils, the calculated total recoveries of the least polar compounds were distinctly lower than those of the most polar ones. This trend was not observed in the case of the sediment. An additional set of experiments showed that a general good agreement existed between the total recoveries summarized in Table 3 for the sandy soil as well as the sediment and those calculated by 5-min liquid-liquid extraction of the total slurry with methyl acetate. The SDs ($n = 3$) for the total recoveries determined by liquid-liquid extraction were below 7% (sandy soil) and 9% (sediment). The differences between the liquid-liquid extraction yields and those calculated for the online procedure were less than 10% for the sandy soil and less than 5% for the sediment, except for bromophos-ethyl (15%). Similar results were obtained for all analytes when the bactericide thimerosal was added during preparation of the slurries. That is, no microbial degradation of the pesticides

TABLE 3. Typical Sorption/Solution Data for Partition Studies of Selected Pesticides in the Different Soils and Sediment Investigated

| pesticide | organic soil | | | sandy soil | | | sediment | | |
|-------------------|------------------------------------|------------------------------------|-------|------------|----------|-------|----------|----------|-------|
| | ads ^a (SD) ^b | sol ^a (SD) ^b | total | ads (SD) | sol (SD) | total | ads (SD) | sol (SD) | total |
| desethylatrazine | | 97 (10) | 97 | | 78 (8) | 78 | | 71 (7) | 71 |
| atrazine | | 95 (10) | 95 | 7 (0.2) | 72 (8) | 79 | 7 (1) | 68 (6) | 75 |
| diazinon | 14 (3) | 62 (7) | 76 | 9 (1) | 63 (8) | 72 | 16 (2) | 56 (5) | 72 |
| terbutryn | 14 (4) | 52 (5) | 66 | 9 (1) | 74 (8) | 83 | 16 (2) | 63 (6) | 79 |
| trifluralin | 29 (1) | 32 (0.1) | 61 | 25 (4) | 30 (5) | 55 | 42 (4) | 45 (3) | 87 |
| fenchlorfos | 18 (2) | 24 (3) | 42 | 20 (3) | 33 (6) | 53 | 40 (3) | 35 (5) | 75 |
| chlorpyrifos | 23 (1) | 27 (0.9) | 50 | 23 (1) | 29 (4) | 52 | 42 (2) | 39 (0.8) | 81 |
| hexachlorobenzene | 28 (6) | 9 (0.4) | 37 | 20 (4) | 8 (1) | 28 | 84 (6) | 11 (2) | 95 |
| bromophos-ethyl | 29 (6) | 25 (9) | 54 | 28 (4) | 21 (4) | 49 | 79 (7) | 34 (4) | 113 |

^a Percent adsorbed (ads) and percent remaining in solution (sol). ^b Standard deviation (as percent), $n = 4$; separate analyses of the investigated soil or sediment spiked at $0.36 \mu\text{g mL}^{-1}$ level.

TABLE 4. Adsorption Coefficients Calculated for the Selected Pesticides after 24 h of Equilibration of the Different Soils and Sediment Investigated

| pesticide | organic soil | | sandy soil | | sediment | |
|-------------------|--------------|-------------|------------|-----------|----------|-----------|
| | K_d^a | K_{dOC}^b | K_d | K_{dOC} | K_d | K_{dOC} |
| desethylatrazine | 0.0 | 0 | 0.0 | 0 | 0.0 | 0 |
| atrazine | 0.0 | 0 | 13 | 1000 | 15 | 300 |
| diazinon | 33 | 300 | 20 | 1500 | 42 | 800 |
| terbutryn | 40 | 400 | 17 | 1200 | 37 | 700 |
| trifluralin | 130 | 1200 | 130 | 9900 | 140 | 2600 |
| fenchlorfos | 110 | 1000 | 95 | 7100 | 170 | 3100 |
| chlorpyrifos | 130 | 1100 | 110 | 8200 | 160 | 3000 |
| hexachlorobenzene | 450 | 4000 | 370 | 28000 | 1120 | 21000 |
| bromophos-ethyl | 170 | 1500 | 230 | 18000 | 340 | 6400 |

^a K_d (L kg^{-1}) on the basis of amounts of pesticide adsorbed on insoluble soil particles and remaining in solution. ^b K_{dOC} (L kg^{-1}): K_d corrected for the organic content (OC, g kg^{-1}).

occurred during the short contact times used in the present study. As no organic modifier was added to the water used to equilibrate the samples (18, 19), the low total recoveries reported for some compounds obviously were, at least partly, due to sorption to the walls of the equilibration vessel. This fact was especially evident for the sandy soil, probably because of its lower organic content.

In addition to the above, one should note that, for the organic soil, significant differences of 20–37% did occur between the total percentages of fenchlorphos and, especially, chlorpyrifos, HCB, and bromophos-ethyl determined by liquid–liquid extraction (SDs below 11%, $n = 3$) and calculated for the online procedure, both in the presence and absence of thimerosal. For the rest of the investigated analytes, the calculated recoveries (SDs of less than 7%) were similar to those obtained by the online procedure (differences between both data series of percentages in the range 1–7%).

In an attempt at further explanation, the solid particles of the investigated soils and sediment were separated from the aqueous phase by 30 min centrifugation at 2500g. The two investigated fractions, i.e., the aqueous and the solid particles, were subsequently extracted by 5 min shaking with methyl acetate. The percentages of fenchlorfos, chlorpyrifos, HCB, and bromophos-ethyl found to be sorbed on the precipitate from the organic soil slurry (SDs below 8%, $n = 3$) were higher than those calculated as adsorbed in the insoluble soil particles by the online procedure (differences of 27–33%). Meanwhile, the percentages of these pesticides determined as remaining in solution by both procedures were similar. A good agreement was also found between both series of values for the rest of the investigated compounds in the case of the organic soil as well as for all the test analytes for the sandy soil and the sediment (differences invariably below 11%). As centrifugation gave a clear solution for all the

investigated slurries, it was assumed that the reported differences for the organic soil were due to the colloidal material, which was precipitated and subsequently extracted together with the insoluble soil particles. Previously published results for ground (20) and drinking (21, 22) water have shown that at a pH close to 7 the humic and fulvic acids are not retained on styrene-divinylbenzene-type sorbents. As the pH of the investigated organic soil slurry was 7.2 (Table 1), a similar process could occur in this particular case. Additional work will have to be done to confirm the above explanation. However, this is outside the scope of the present study.

Table 4 shows the single-point linear adsorption coefficients, K_d , calculated on the basis of the data of Table 3 for the two soils and the sediment investigated. The K_d (L kg^{-1}) of a given compound was calculated as the ratio of the concentration found to be adsorbed in the soil (S , $\mu\text{g kg}^{-1}$) and the concentration in the aqueous solution (C , $\mu\text{g L}^{-1}$), $K_d = S/C$. With all three samples types, these K_d values are seen to increase rapidly with increasing hydrophobicity of the analytes. To (partly) eliminate the dependence of the results on the organic matter content of the various samples for this fast sorption process, the K_d data were corrected for the organic matter content, to yield K_{dOC} . These are included in Table 4. This recalculation did not lead to a much more consistent picture, a phenomenon that is not easily explained. On the other hand, the K_d values reported in this study are in the range of data published in the literature for HCB at short contact times (1–3 days), e.g. 100–1000 (23), 1219 ± 95 (24), and 870 (25).

Fast Adsorption of Selected Pesticides under Competitive Conditions. In an attempt at further evaluation of (i) the first steps of the fast adsorption of the pesticides and (ii) the possibility of competitive sorption between pesticides with different polarity, two test sets of four organic soil slurries,

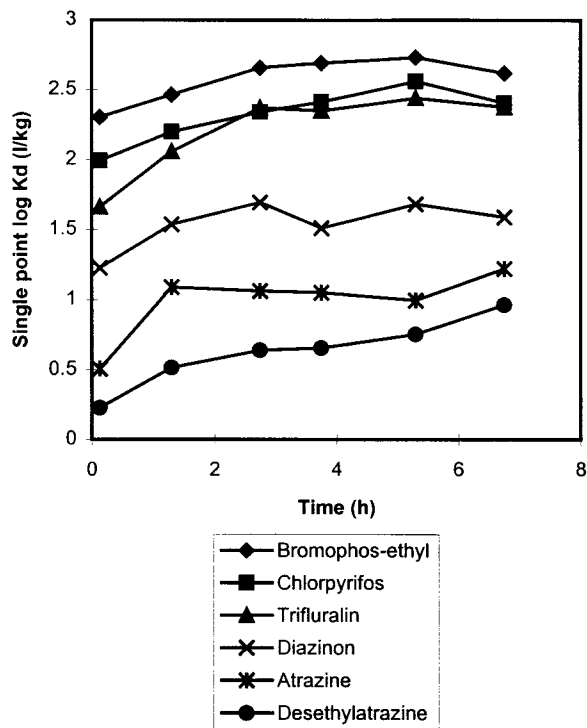


FIGURE 2. Log K_d vs time plots for an organic soil spiked at the $0.36 \mu\text{g mL}^{-1}$ level. See text for conditions.

spiked at the 0.71 , 0.36 , 0.20 , and $0.09 \mu\text{g mL}^{-1}$ level, were prepared and analyzed as described previously. Measurements were continued for 48 h. Data corresponding to the first 7 h were collected every 90 min.

Figure 2 shows the typical (apparent single-point) adsorption data obtained during the first 7 h. Results correspond to the mean linear K_d calculated from two separate analyses of the organic soil slurry spiked at the $0.36 \mu\text{g mL}^{-1}$ (52 mg g^{-1}) level. The calculated K_d values are seen to increase with the hydrophobicity of the pesticides. Under the experimental conditions of this study, a large part of the adsorption of the least, and also the medium, polar compounds in the insoluble soil particles was found to occur almost instantaneously, i.e., within the first 1.40–2.75 h. A deviating pattern was observed only for the much more polar desethylatrazine: its concentration in the soil continued to increase even after 7 h of equilibration. The present results nicely confirm earlier work (14) and demonstrate that 24 h is indeed sufficient for all the test compounds to reach an apparent equilibrium.

Comparison of the single-point linear K_d values calculated during the first hours of equilibration at different spiking levels showed that competition between pesticides with different polarity for the adsorption in the soil particles only occurred at the highest concentration investigated ($0.71 \mu\text{g mL}^{-1}$). Nevertheless, no evidence of total saturation of the adsorption sites by the least polar analytes existed even at such a spiking level. As an example, Figure 3 shows that at the $0.09 \mu\text{g mL}^{-1}$ (13 mg g^{-1}) level an apparently instantaneous adsorption was found for the three test compounds selected. However, the K_d values calculated for the more polar pesticides, terbutryn, and, even more so, atrazine, during the first contact hours at the $0.71 \mu\text{g mL}^{-1}$ (104 mg g^{-1}) level were distinctly lower than those determined at the $0.09 \mu\text{g mL}^{-1}$ level. This indicates that the concentration of these pesticides adsorbed in the insoluble soil particles was proportionally lower in the $0.71 \mu\text{g mL}^{-1}$ situation: the least polar pesticides effectively filled the most available adsorption sites. As a further illustration, the adsorption rates of the selected pesticides with intermediate and, specifically, with

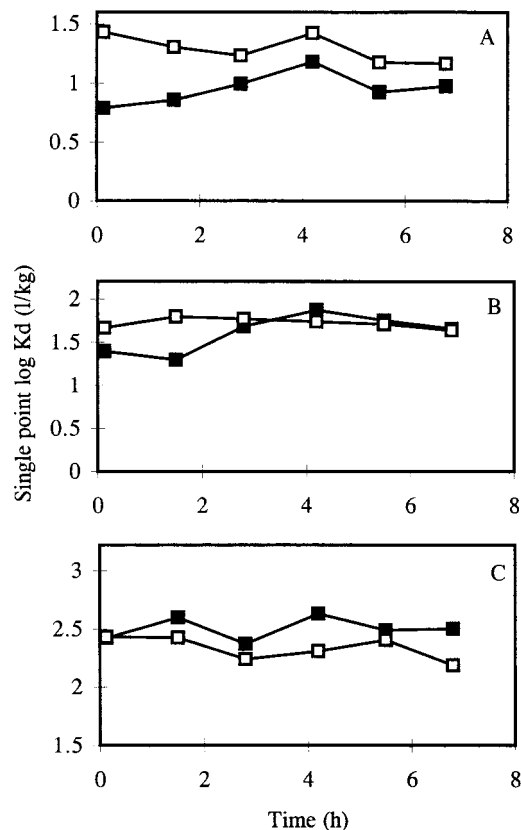


FIGURE 3. Log K_d vs time plots for (A) atrazine, (B) terbutryn, and (C) bromophos-ethyl, for an organic soil spiked at the 0.71 (■) and 0.09 (□) $\mu\text{g mL}^{-1}$ level in solution. See text for conditions.

high polarity were found to be lower at the highest concentration level. Additional examples showing the dependence of the adsorption behavior on the initial concentration (5, 10) and the occurrence of competitive sorption between hydrophobic (9) as well as hydrophilic (26) analytes in soils can be found in the literature.

Isotherms. The suitability of three isotherms, linear, Freundlich, and Langmuir, for fitting the experimental data corresponding to the fast adsorption of the selected pesticides in an organic soil at different equilibration times was studied. Isotherms were fitted after 0.13, 1.40, 2.75, 4.20, 5.50, and 7.00 h of equilibration and compared with those fitted when the system reached an apparent equilibrium, i.e., after 24–30 h of equilibration. The Freundlich isotherm ($S = K_f C^n$; where S ($\mu\text{g kg}^{-1}$) and C ($\mu\text{g L}^{-1}$) are the adsorbed and aqueous concentrations, respectively, K_f is the Freundlich unit-capacity coefficient and n is a dimensionless coefficient) was fitted by linear regression using a log-transformed expression (3, 5, 7, 10). Models were fitted by using eight data points except for atrazine because for this pesticide values corresponding to the highest concentration level used were found to be outliers in some experiments. Because the amount of desethylatrazine adsorbed in the insoluble soil particles was below the detection limit for the lowest concentration level studied, only three concentration levels (six points) were used to fit the curves for this pesticide. Values corresponding to the apparent equilibrium were fitted by using 18–20 points, except for desethylatrazine (10 points).

Not unexpectedly (3, 7), the ideal Langmuir isotherm ($S = S_f KC / (1 + KC)$, where S and C are the adsorbed and aqueous concentrations, respectively, S_f is the adsorbed concentration at complete monolayer coverage, and K is a constant related to the affinity of the soil surface for the solute) rarely fitted adsorption data corresponding to as heterogeneous a matrix

TABLE 5. Comparison of the Fit of the Linear and Freundlich Isotherms at Selected Equilibration Times

| pesticide | time (h) | linear r^2 | Freundlich | | |
|-------------------|------------------|--------------|------------|--------------|--------------|
| | | | r^2 | $\log K_f^a$ | n^a |
| desethyl-atrazine | 0.13 | 0.92 | 0.96 | 0.8 (0.3) | 1.0 (0.2) |
| | 1.40 | 0 | 0.3 | -1.7 (1.2) | -0.7 (0.9) |
| | 2.75 | 0.8 | 0.8 | -1.5 (0.3) | -0.6 (0.2) |
| | 4.20 | 0.2 | 0.2 | -1.1 (0.8) | -0.3 (0.5) |
| | Eq. ^b | 0 | 0.2 | -0.87 (0.07) | -0.07 (0.04) |
| atrazine | 0.13 | 0.8 | 0.6 | 0.2 (0.5) | 0.5 (0.3) |
| | 1.40 | 0.92 | 0.7 | 0.8 (0.6) | 0.9 (0.4) |
| | 2.75 | 0.8 | 0.90 | 0.7 (0.2) | 0.7 (0.2) |
| | 4.20 | 0.95 | 0.91 | 0.6 (0.2) | 0.6 (0.1) |
| | Eq. | 0.6 | 0.7 | 0.6 (0.2) | 0.7 (0.1) |
| diazinon | 0.13 | 0.90 | 0.92 | 0.4 (0.1) | 0.39 (0.07) |
| | 1.40 | 0.94 | 0.992 | 0.98 (0.05) | 0.62 (0.03) |
| | 2.75 | 0.93 | 0.90 | 1.1 (0.3) | 0.7 (0.2) |
| | 4.20 | 0.997 | 0.995 | 1.71 (0.06) | 1.00 (0.04) |
| | Eq. | 0.8 | 0.8 | 1.0 (0.1) | 0.59 (0.07) |
| terbutryn | 0.13 | 0.6 | 0.2 | 0.1 (0.2) | 0.2 (0.1) |
| | 1.40 | 0.96 | 0.994 | 1.28 (0.06) | 0.79 (0.04) |
| | 2.75 | 0.95 | 0.997 | 1.33 (0.06) | 0.79 (0.03) |
| | 4.20 | 0.94 | 0.994 | 1.25 (0.06) | 0.61 (0.03) |
| | Eq. | 0.94 | 0.95 | 2.2 (0.1) | 1.08 (0.06) |
| trifluralin | 0.13 | 0.96 | 0.91 | 1.9 (0.5) | 1.0 (0.2) |
| | 1.40 | 0.98 | 0.92 | 2.1 (0.3) | 1.0 (0.1) |
| | 2.75 | 0.98 | 0.97 | 2.1 (0.2) | 1.0 (0.1) |
| | 4.20 | 0.95 | 0.8 | 2.0 (0.5) | 0.8 (0.3) |
| | Eq. | 0.96 | 0.95 | 2.6 (0.2) | 1.12 (0.07) |
| fenchlorfos | 0.13 | 0.991 | 0.93 | 2.0 (0.4) | 1.0 (0.2) |
| | 1.40 | 0.99 | 0.99 | 2.4 (0.2) | 1.06 (0.08) |
| | 2.75 | 0.99 | 0.92 | 2.1 (0.4) | 1.0 (0.2) |
| | 4.20 | 0.996 | 0.99 | 2.2 (0.5) | 1.0 (0.2) |
| | Eq. | 0.90 | 0.8 | 2.6 (0.3) | 1.1 (0.1) |
| chlorpyrifos | 0.13 | 0.94 | 0.96 | 0.9 (0.3) | 0.50 (0.07) |
| | 1.40 | 0.995 | 0.98 | 2.1 (0.2) | 0.95 (0.08) |
| | 2.75 | 0.93 | 0.97 | 2.6 (0.4) | 1.2 (0.1) |
| | 4.20 | 0.99 | 0.99 | 3.4 (0.2) | 1.52 (0.09) |
| | Eq. | 0.90 | 0.90 | 2.5 (0.4) | 1.10 (0.09) |
| HCB | 0.13 | 0.98 | 0.99 | 3.0 (0.2) | 1.24 (0.09) |
| | 1.40 | 0.98 | 0.96 | 2.8 (0.4) | 1.1 (0.1) |
| | 2.75 | 0.95 | 0.97 | 3.2 (0.3) | 1.2 (0.1) |
| | 4.20 | 0.93 | 0.96 | 4.6 (0.7) | 1.9 (0.3) |
| | Eq. | 0.90 | 0.90 | 2.6 (0.4) | 1.0 (0.1) |
| bromophos-ethyl | 0.13 | 0.93 | 0.90 | 1.3 (0.3) | 0.6 (0.1) |
| | 1.40 | 0.96 | 0.99 | 2.8 (0.2) | 1.13 (0.08) |
| | 2.75 | 0.94 | 0.998 | 3.5 (0.1) | 1.52 (0.05) |
| | 4.20 | 0.97 | 0.91 | 4.6 (0.6) | 1.9 (0.3) |
| | Eq. | 0.97 | 0.95 | 3.2 (0.2) | 1.31 (0.07) |

^a Standard error predicted by the fitted model for this specific parameter. ^b Eq.: values calculated when an apparent equilibrium has been reached (between 24 and 30 h).

as an organic soil. The coefficients of correlation (r^2) obtained by fitting the experimental data to the Langmuir isotherm were in the range 0–0.8 for desethylatrazine, 0.3–0.8 for atrazine, 0.8–0.994 for diazinon, 0.3–0.90 for terbutryn, 0.7–0.96 for trifluralin, 0.5–0.96 for fenchlorfos, 0.6–0.8 for chlorpyrifos, 0.5–0.8 for HCB, and 0.5–0.93 for bromophos-ethyl. The linear and, specifically, the nonideal Freundlich isotherms, in which the n coefficient reflects the relative magnitude as well as the diversity of energies associated with a particular sorption process (7), provided a better fit of our experimental data. As an example, the results of fitting these isotherms to the data for the test pesticides at some selected times are summarized in Table 5. As both models predicted a similar variation of the adsorption coefficients over time (for a typical example, see Figure 4), only those corresponding to the Freundlich isotherms (K_f) are included in Table 5.

During the first 7 h of equilibration, the coefficients of correlation calculated by fitting the data for the pesticides with high to intermediate polarity, i.e., from atrazine to fenchlorfos, to the linear model indeed improve as the Freundlich coefficient, n , approaches unity (Table 5). The very low coefficients of correlation obtained for desethyl-

atrazine and the above-mentioned low mass balance found for the less polar analytes, especially chlorpyrifos, HCB, and bromophos-ethyl, does not allow any discussion for these four pesticides. For the rest of the studied compounds, the Freundlich model predicted n coefficients lower than 1 for the most polar ones, including atrazine, diazinon, and terbutryn. The calculated n coefficients for these three pesticides tended to increase within the first 1.40 h of equilibration, but similar values were obtained for the rest of the measurements carried out during the first day (mean n of values 0.7, 0.6, and 0.7, respectively). Similar low n coefficients were found at the apparent equilibrium, i.e., after 24 h of equilibration, for atrazine and diazinon (0.7 and 0.59, respectively). An n value of 1.08 was predicted for terbutryn at this time. Some dependence of the n values on the equilibration time has been previously published, but it is interesting to note that the n coefficients reported in the present study were below the range 0.8–1.0 usually published for both nonlinear adsorption isotherms and competitive sorption (5). On the other hand, linear isotherms (i.e., $n = 1.0$) were found for trifluralin and fenchlorfos at the various equilibration times investigated in this study.

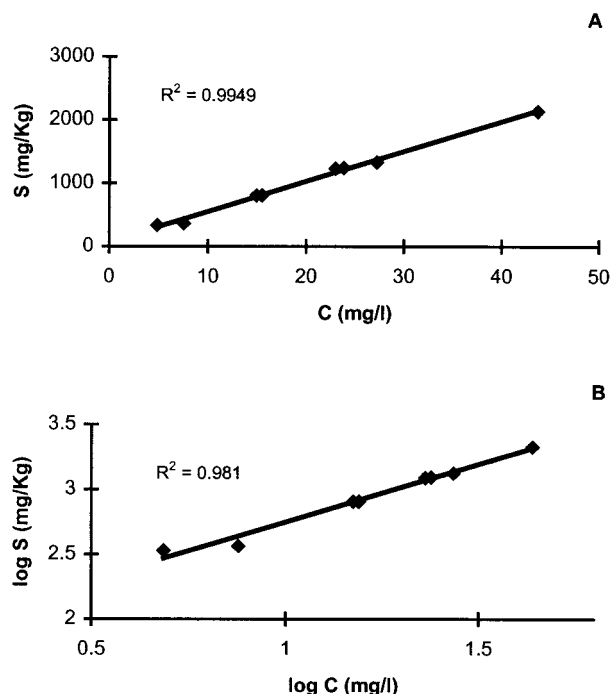


FIGURE 4. Fitting of the (A) linear and (B) Freundlich isotherms to the diazinon adsorption data after 5.5 h of equilibration. See text for conditions.

The above results show that the linearity of the fast adsorption isotherms depends on the polarity of the considered compound. Generally speaking, the more polar the analyte is, the more nonlinear is the isotherm. Furthermore, the time-independent linear isotherms obtained for pesticides with intermediate polarity such as trifluralin show that nonlinearity observed for the polar compounds is not an artifact due to insufficient contact time. One of the more important consequences of this difference among the n values calculated for different compounds is that, whereas with trifluralin fast adsorption in soil particles is independent of the initial concentration, for polar compounds (i.e., those with $n < 1$) sorption decreased when concentration increased (5). This kind of result has been previously reported not only for the competitive adsorption of atrazine on soils after 48 h of equilibration (10) but also for the fast (24 h) adsorption of compounds with intermediate polarity (5). In both cases it was concluded that for these analytes sorption was less ideal than simple partition (5, 8). This paper reports a similar trend at very early contact times, thereby showing some exceptions to the generally assumed linear fast adsorption of pesticides in soil (5).

Finally, the K_f values calculated for the investigated compounds (Table 5) indicate that, without exception, the adsorption of the test analytes increased within the first 1.40 h of equilibration. However, closely analogous values of the K_f coefficients were calculated from the rest of the isotherm constructed during the first day. Comparison of the mean log K_f values calculated for atrazine, diazinon, terbutryn, trifluralin, and fenclorfos from the set of measurements carried out between 1.40 and 7.00 h (0.7, 0.8, 1.3, 2.0, and 2.2, respectively) with values calculated at the apparent equilibrium conditions (0.6, 1.0, 2.2, 2.6, and 2.6, respectively) showed that the K_f values decrease with the polarity of the selected analytes, but it also showed K_f as another time-dependent parameter which increased over time (5). As no evidence of saturation of the adsorption sites was observed, this finding is also compatible with the possibility of interactions between the analytes and specific sites in the soil.

In summary, the organic matter can be considered as the most important compartment for fast sorption of pesticides in soils. However, contrary to what is generally assumed, in some cases this process is less ideal than simple partition. The reported examples of nonlinear adsorption isotherms at short contact times and the observed dependence of the n and K_f Freundlich coefficients on the contact time demonstrate that the Xing and Pignatello model (5) regarding the sorption in the soil organic matter as a dual process involving partition as well as interaction with specific sites is compatible with the results found in the present study for fast adsorption.

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