INTERACTIONS OF ORGANIC POLLUTANTS WITH SOIL CONSTITUENTS IN AQUEOUS AND OIL-CONTAMINATED SYSTEMS

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1. ABSTRACT

Different soil samples and synthetic goethite were reacted with γ-HCH, anthracene, 2,4-D and atrazine in a solid/water and a solid/oil system. The non-polar compounds γ-HCH and anthracene were only sorbed from aqueous solution, in particular by soil samples with a high content of organic carbon. When dissolved in oil these non-polar compounds were not sorbed by any of the soil samples investigated. For atrazine, little sorption was observed whereas for 2,4-D, sorption from the oil phase was much higher than from aqueous solution. This effect is probably connected to modifications of the electric double layer on the particle surfaces.

2. MATERIALS AND METHODS

2.1 Soils. The experiments were conducted with soil samples of the Ah- and the Bt-horizon of an orthic luvisol (Parabraunerde, Typic Hapludalf) and a synthetic goethite (G). Some selected properties of the soil samples (particle size fraction <2mm) are given in Tab. 1.

TABLE. 1. Selected properties of the soil samples (<2mm).

	<2μm %	pH[1]	C_{org} %	Fe_d[2] % .	CEC[3] m.e./100g
Ah	2.4	4.5	1.1	0.8	3.0
Bt	12.6	4.5	0.1	1.7	5.4

[1] in 0.01M $CaCl_2$
[2] dithionite extractable iron
[3] cation exchange capacity

Of these two samples, the clay fractions (<2μm) were isolated and termed LA and LB, respectively. The synthetic goethite had a specific surface area of 62 m^2/g and a zero point of charge at pH 6.8.

2.2. Organic pollutants. Anthracene and γ-hexachlorocyclohexane (γ-HCH) were chosen as non-polar compounds. Atrazine (2-chloro-4-ethylamino-6-methylethylamin-s-triazine) is a weak base

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(pK_a=1.7) and 2,4-D (2,4-dichlorophenoxy acetic acid) is an acid (pK_a=2.7).

2.2. Sorption studies in aqueous solution. 4g of air-dried soil sample (Ah and Bt) was mixed with 20ml of an 0.01M $CaCl_2$ solution which contained small concentrations of the particular organic pollutant. The solid-to-solution ratio was 200g/l according to the OECD guideline No. 106 "adsorption/desorption". After an 18-hour shaking period the samples were centrifuged and solution concentrations determined using ^{14}C-labelled compounds. The amount of sorbed contaminants was calculated from the difference between the initial and the final solution concentration. To study the pH dependency of the binding of 2,4-D and atrazine between pH 3.5 and 8, the soil suspensions were titrated with small amounts of HCl and $Ca(OH)_2$, respectively.

A similar method was used for the experiments with the soil clay fractions and goethite. By using this material the experiments can be conducted with much smaller amounts of solid and smaller solution volumes. In this case, 20mg of solid was suspended in a solution volume of 6 ml (solid-to-solution ratio: 3.33g/l). The advantage of this method also lies in the small amounts of ^{14}C-contaminated waste produced.

2.3. Sorption studies in oil. This experimental section was conducted with the soil clay fractions and goethite only. 10mg of freeze-dried solid was mixed with 3ml of a synthetic oil which was made up with the particular organic contaminant. The oil consisted of: hexadecane (45% w/w), pristane (20%), cis-decaline (10%), n-nonylbenzene (16.8%), 2-methylnaphthaline (6.45%), dibenzothiophene (1.5%), anthracene (0.2%) and perylene (0.05%). For sorption experiments with anthracene the concentration of this component was changed. The difference between the initial and the final solution concentration (after an 18-hour shaking period) was again used to calculate the amount of sorbed contaminants.

3. RESULTS AND DISCUSSION

3.1. Sorption in the solid/water system. Figure 1 shows sorption isotherms of γ-HCH for both the soil samples Ah and Bt and the clay fractions LA and LB which were isolated from these samples. The sorption data can be described by the Freundlich equation

$y/m = K_f \ c^{1/n}$,

where y/m is the sorbed amount of contaminant in mg per Kg sorbent and c is the solution concentration in mg/l; n und K_f are constants. K_f denotes the amount sorbed at c=1; 1/n is the slope of the isotherm in a double logarithmic scale. With values for 1/n between 0.902 und 0.931 the isotherms in Fig. 1 are almost parallel. The difference in the K_f-values of Ah (14.3) and Bt (0.9) shows the much stronger sorption of γ-HCH by sample Ah. This effect can be explained by the higher content of organic carbon in this material. The clay fractions LA and LB exhibit much higher K_f values (64.8 and 4.4,

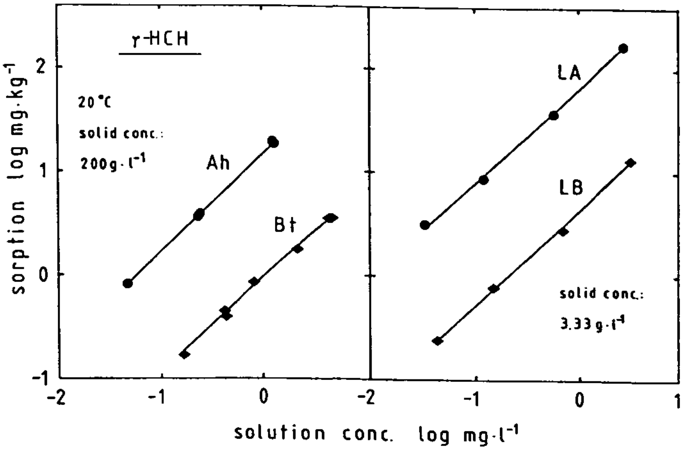

FIGURE 1. Sorption isotherms of γ-HCH for the soil samples Ah and Bt and their clay fractions LA and LB.

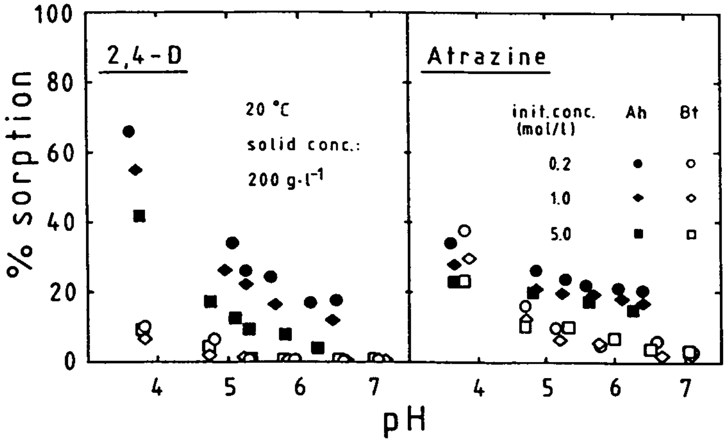

FIGURE 2. pH dependent sorption of 2,4-D and atrazine by the soil samples Ah and Bt.

respectively), because these samples represent a concentrate of the highly reactive soil particles. However, for both the soil samples and the clay fractions the ratio of the K_f values (Ah/Bt = 15.8, LA/LB = 14.6) is similar. This indicates that the sorption properties of soils can also be characterized by investigating the clay fractions.

The binding of 2,4-D and atrazine increases with decreasing pH at different initial concentrations (Fig. 2). This effect has also been demonstrated by Kukowski and Brümmer (1987) and is strongest for 2,4-D and sample Ah. At pH<4 and different initial concentrations sorption amounts to between 40 and 70%. The binding of this compound by sample Bt is relatively low. For atrazine, however, the sorption by this sample is higher at pH<4.5 than by sample Ah and reaches even 39% at pH 3.8.

3.2. Sorption in the solid/oil system. Within the concentration range investigated (γ-HCH: 1-1000mg/l; anthracene: 0.03-1000mg/l) the non-polar compounds are not sorbed by the soil components from the oil phase. This agrees with the results of Boyd and Sun (1990) who showed that oil is a much more effective partition medium for non-polar contaminants than soil organic matter which in this case is concentrated in sample LA.

Atrazine is sorbed to a small extent only by samples LA and G while sample LB shows considerable sorption of this compound at a low initial concentration of 0.38 mg/l (Tab. 2). This result demonstrates that the surfaces are not chemically inactivated when contaminated with oil. Even though the exact composition of the soil clay fractions has not been analyzed yet it has already been established that LB mainly consists of silicate clay minerals. Atrazine is therefore possibly bound by cation exchange related processes.

TABLE 2. Percent sorption in the solid/oil system.

	init. conc.		sorbent	
	mg/l	LA	LB	G
atrazine	0.38	1.0	37.0	0.1
atrazine	1.4	1.2	3.1	2.2
atrazine	5.8	1.1	0.3	1.6
2,4-D	0.02	90.9	93.9	97.8
2,4-D	1.0	80.8	80.2	97.5

2,4-D is bound up to 98% by goethite and up to 80 and 94% by the clay fractions LA and LB depending on the initial concentration. This means that the sorption of this compound is much higher than in the aqueous system. Explanations for this effect have to be rather speculative because little is known about the solid/oil interface. When mixed with the oil the solids were freeze-dried and probably had a few layers of water molecules on the surface only. As compared to an aqueous suspension the electric double layer on the surface can be assumed to be very thin with a relatively high concentration of ions. When bound at this interface the 2,4-D anions are probably unable to built up a complete hydration sheath because the availability of water is very limited. The COO$^-$-group of the molecule can thus approach the surface more closely and bind more strongly to a positive charge. The amount of charge on the surface is also likely to be higher because of the increased electrolyte concentration in the reduced double layer. This interpretation has to be substantiated, however, by further experimental work.

4. CONCLUSIONS

The oil phase in oil-contaminated soils is an effective partition medium for non-polar organic contaminants. A sorption of these compounds by soil organic matter does not occur in the presence of oil. Weakly basic and especially anionic organic compounds can be sorbed by soil particles from the oil phase. The sorption of anions is even higher than in the aqueous system. The mechanism of this effect is unknown and can probably be related to modifications of the electric double layer on the particle surfaces.

5. REFERENCES

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