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ORIGINAL ARTICLE

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Analysis of the distribution coefficients and mobility characteristics of phenols in different soil types

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Abstract Adsorption studies were carried out on soil samples of high organic and low organic content to analyze the distribution coefficient and mobility of phenols. The results show that the amount of phenols adsorbed by the soil varies linearly with the fraction of organic carbon. Soils that are highly organic compared to those with low organic matter content retain the phenols to a greater extent. Adsorption studies on the different soil types indicated that the extent of adsorption of phenols by different kinds of soils is important, as a smaller amount of adsorption by the soil increases the risk of contamination of the groundwater supply.

Keywords Soil · Adsorption · Organic content · Phenols · India

Introduction

The issue of contaminants in the groundwater supply has peaked as an environmental issue, especially those contributed by hazardous wastes dumped on land. The environmental behavior of organic compounds depends on a number of mechanisms responsible for their migration, or attenuation at the surface and in the subsurface of the soil. Whether the organic compound moves readily or tends to remain fixed in association with the soil depends on the properties of the particular chemical and the soil characteristics. The movement of the contaminant into groundwater is controlled by the distribution coefficient of soils (K_D), which is a measure of the amount of interaction between the organic compound and the make up of separate soil types (Dolan et al. 1998):

$$K_D = \frac{S}{C} \quad (1)$$

where S is the amount of organic compound adsorbed in the soil and C is the amount of the organic compound soluble in water. The amount of organic compound adsorbed by the soil depends on the fraction of organic carbon within the soil (Dolan et al. 1998), assuming that the amount of organic carbon content is

$$K_{OC} = K_D \times f_{OC} \quad (2)$$

where K_{OC} is the organic carbon–water distribution coefficient and f_{OC} is the fraction of organic carbon in a given type of soil. The plot of K_D versus f_{OC} is linear; K_{OC} is the slope of the linear plot. Anything other than a linear plot would imply that the amount of chemical adsorbed into the groundwater is affected by the non-organic make up of soil. This study confirmed that the extent of groundwater contamination by hazardous organics depends on the local soil type (i.e., the organic content of soil). Such soils can be selected as sites for dumping the hazardous waste generated by industries and can be treated by cost-effective methods like bioremediation.

Experimental details

Collection of soil samples

Soil samples were collected from three different sites in Patancheru Industrial Area (Hyderabad, AndhraPradesh, India). Samples were taken from the top 15–20 cm of the soil. A V-shaped hole was dug and sliced from the three sides and this sample was placed in a bucket. This core represented an individual sample and 15 such samples were collected. A composite sample was made by mixing the 15 samples, which was representative of the entire area selected.

After collection of the soil samples, the lumps were broken and stones removed. The soil was completely mixed and stored in polythene bags and taken to the laboratory for analysis. The soils were air dried under shade, sieved through a 2-mm sieve and used for the studies.

Materials

Analar grade phenol, *p*-nitrophenol, 4-chloro-2-nitrophenol, 2,4-dichlorophenol were used for the adsorption studies. Different concentrations of the compound were prepared in the range of 5–25 ppm in 0.01 M $CaCl_2$. The characteristics of the organic compounds are reported in Table 1.

Analysis of percent organic carbon

The soil organic carbon content was determined by the wet digestion method of Walkey and Black (1934) as described by Jackson (1967), which involves oxidation with dichromate and back titration of excess of dichromate with ferrous ammonium sulphate and expressed in percentages 0.5 g of the soil was taken in a 250 ml Erlenmeyer flask. To the flask, 10 ml of 1 N $K_2Cr_2O_7$ and 20 ml of conc. H_2SO_4 was added and allowed to stand for half-hour. After the reaction time was completed 200 ml of distilled water was added along with 10 ml of H_3PO_4, 0.2 g of NaF and 1 ml of diphenylamine indicator. The contents of the flask were titrated against 0.5 N ferrous ammonium sulphate until the solution in the flask turned a persistent bottle green color. A similar procedure was followed for a blank.

Adsorption studies on 2-mm sieved soils (whole soils)

For the adsorption isotherm studies, batch experiments were conducted by equilibrating the soils with the organics. Soils were shaken at 37°C for 24 h. Identical soil blanks minus the organic were also maintained in every case. The suspensions were centrifuged at 5,000 rpm for 15 min and filtered through Whatman no.1 filter paper. The amount adsorbed was determined by analyzing the equilibrium concen-

Table 1 Characteristics of hazardous organics selected

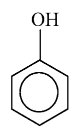
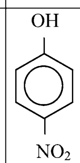
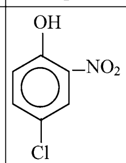
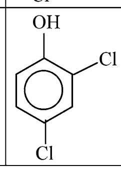
Hazardous organic	Structure	Molecular Formula	Molecular weight	Melting point	λ max(nm)	Toxicity (LD_{50}) (Rat)
Phenol		C_6H_5OH	94.11	40.9	220.5	0.5-5 g/Kg
p-Nitrophenol		$C_6H_5NO_3$	139.11	113	384	50-500 mg/Kg
4-Chloro-2-nitrophenol		$C_6H_4Cl\ NO_3$	173.56	88	236	50-500 mg/Kg
2,4-Dichlorophenol		$C_6H_4\ Cl_2$	163	45	232.5	50-500 mg/Kg

Table 2 Adsorption of hazardous organics on 2-mm sieved soils

Compound	Initial concentration (mg/l)	Soil M		Soil I		Soil B	
		Ce	Qe	Ce	Qe	Ce	Qe
Phenol	5	4.3	11.6	4	16.6	3.5	25
	10	8.3	28.3	6.5	58.3	5	83.3
	15	12	50	11.1	65	8.5	108.3
	20	16	66.6	14.1	98.3	13	116.6
	25	20	83.3	18.5	108.3	17	133.3
	30	24.6	90	23	116.6	21.4	143.3
	35	28.9	101.6	27.8	120	26	150
	40	33.1	115	31.2	130	30.5	158.3
	45	39.9	118.3	36.7	138	35.3	161.6
	50	42.8	120	41.3	145	40	166.6
p-Nitrophenol	5	4.0	16.6	3.5	25	3	33.3
	10	8	33.3	6	66.6	5.5	91.6
	15	11.8	53.3	10	83.3	6	150
	20	15.5	75	12	133.3	9	183.3
	25	19.7	88.3	16	150	12	216.6
	30	24.2	96.6	20.2	163.3	16	233.3
	35	28.4	110	24.8	170	20.5	241.6
	40	32.4	126	29.2	180	25	250
	45	37.2	130	33.5	191.6	29.4	260
	50	41.7	138.3	38.1	198.3	33.8	268.3
4-Chloro-2-nitrophenol	5	3.5	25	3	33.3	2.5	41.6
	10	5.9	68.3	4.5	91.6	3.4	110
	15	7.8	120	6.8	136.6	6.5	166.6
	20	12	133.3	9.7	171.6	7.5	208
	25	15	166.6	12.5	208.3	8	283.3
	30	19.5	175	17	216.6	12.5	291.6
	35	24	183.3	21	233.3	17	300
	40	28.5	191.6	25.7	238.3	21.5	308.3
	45	33	200	30.1	241.6	26.1	315
	50	37.7	205	35	250	30.4	326.6
2,4-Dichlorophenol	5	3.0	33.3	1.5	58.3	1	66.6
	10	5.6	73.3	3.8	103.3	2.5	125
	15	7.8	120	5	166.6	3.5	191.6
	20	11.0	150	9.5	191.6	4.5	258.3
	25	14.5	175	12	216.6	5	333.3
	30	19.1	181.6	16	233.3	9.8	336.6
	35	23.8	186.6	20.2	246.6	14	350
	40	28.3	195	24.9	251.6	18	366.6
	45	32.5	208.3	29.8	253.3	22	383.3
	50	37.1	215	34.4	260	26.5	391.6

Ce equilibrium concentration (mg/l), *Qe* amount adsorbed (μg/g)

tration of the organic compounds by measuring the absorbencies at their respective λ maximum and calculating the difference between them and initial concentration after correcting for soil blanks. The experimental variables considered were: (a) initial concentration of hazardous organics, 5–50 mg/l (b) pH 7 (c) weight of soil, 3 g (d) volume of hazardous organic, 50 ml and (e) soils selected: M, I and B. The amount adsorbed by the soil for the four selected organics is given in Table 2.

Estimation of distribution coefficient values of the identified organics in the soil water system

The distribution coefficients K_D and K_{OC} have been estimated by using Eqs. 1 and 2, respectively. The organic carbon has been determined by using the experimental method as given above and the corresponding fraction is calculated as f_{OC}. The important assumption is that the organic matter fraction of the soil is solely responsible for sorption and retention of the hazardous organics. Table 3 lists the K_{OC} ranges, corresponding K_D (assuming 1% organic carbon) and R_f values for the selected organic compounds on the three soils. The K_{OC} has been calculated using concentrations μg/g (in soil) and μg/ml (in water) and therefore has the units of ml/g. The R_f(Morril et al. 1982) function is borrowed from chromatography and is a measure of the fractional transport of the organic compound compared to the water solvent. When $K_{OC}=0$, $R_f=1$ and there is no interaction with soil. Consequently, the compound moves freely into water. When $K_{OC}=0$, $R_f=1$ and there is no interaction with soil. Therefore, the compound moves freely into water. When K_{OC} is very large R_f approaches 0,

Table 3 Distribution coefficients and mobility characteristics of the hazardous organics

Soil	Compound	Qe (μg/g)	$K_D = Qe/Ce$	K_{OC}	f_{OC}	R_f	Mobility
M	Phenol	120	2.803	301	107.5	0.4–0.2	Medium
	p-Nitrophenol	138.3	3.316	356.4	107.5	0.4–0.2	Medium
	4-Chloro-2-nitrophenol	205	5.437	584.4	107.5	0.2–0.05	Low
	2,4-Dichlorophenol	215	5.795	622.9	107.5	0.2–0.05	Low
I	Phenol	145	3.510	233.7	66.6	0.4–0.2	Medium
	p-Nitrophenol	198.3	5.204	346.5	66.6	0.4–0.2	Medium
	4-Chloro-2-nitrophenol	250	7.142	475.6	66.6	0.4–0.2	Medium
	2,4-Dichlorophenol	260	7.558	503.3	66.6	0.2–0.05	Low
B	Phenol	166.6	4.165	173.2	41.6	0.4–0.2	Medium
	p-Nitrophenol	268.3	7.937	330.1	41.6	0.4–0.2	Medium
	4-Chloro-2-nitrophenol	326.6	10.743	446.9	41.6	0.4–0.2	Medium
	2,4-Dichlorophenol	391.6	14.77	614.4	41.6	0.2–0.05	Low

Table 4 Distribution coefficients and mobility properties of various classes of organic compounds in soil

K_{OC} (ml/g)	R_f	Mobility	Class (typical)
0–50	1–0.7	Very high	Aliphatic acids
50–150	0.7–0.4	High	Carbamates
150–500	0.4–0.2	Medium	Benzoic acids
500–2,000	0.2–0.05	Low	Triazines
2,000–5,000	0.05–0.02	Slight	Organophosphates
> 5,000	< 0.02	Immobile	Organochlorines

signifying that the compound is completely immobilized.

$$R_f = \frac{\text{Rate of movement of solute}}{\text{Rate of movement of aqueous phase}} \tag{3}$$

According to the above discussion, it is found that the K_{OC} is an integral component of determination of the mobility properties in accordance with K_D and R_f (Vanloon and Duffy2000). Hence, based on the K_{OC} and K_D values the mobility of the four selected compounds are determined by comparing with the standard values (Vanloon and Duffy2000) given in Table 4.

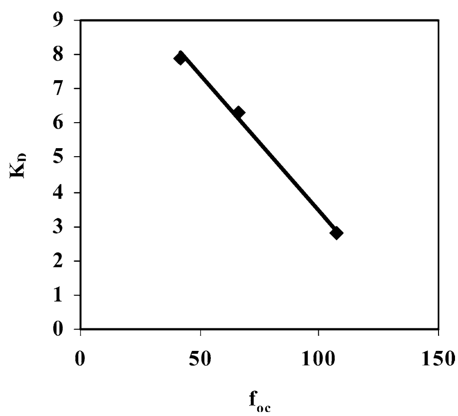


Fig. 1 Distribution coefficient (K_D) as a function of organic carbon (phenol) (f_{OC})

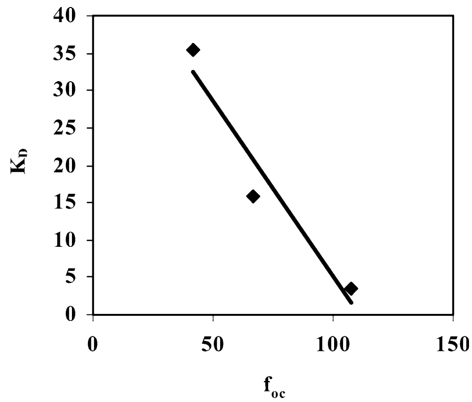


Fig. 2 Distribution coefficient (K_D) as a function of the fraction of organic carbon (*p*-nitrophenol) (f_{OC})

Summary and conclusions

The soils used in this experiment contain organic carbon in the following order: soil B (2.4%) < soil I (1.5%) < soil M (0.93%). The data gathered in these experiments support the theory that soil with more or-

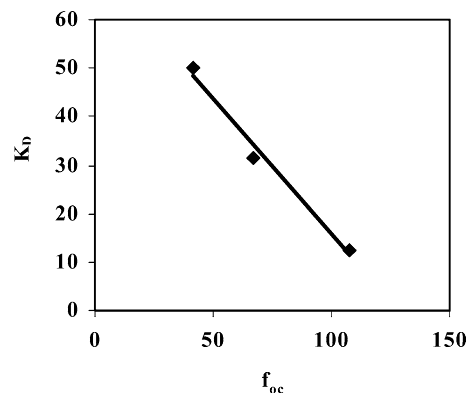


Fig. 3 Distribution coefficient (K_D) as a function of organic carbon (4-chloro-2-nitrophenol) (f_{OC})

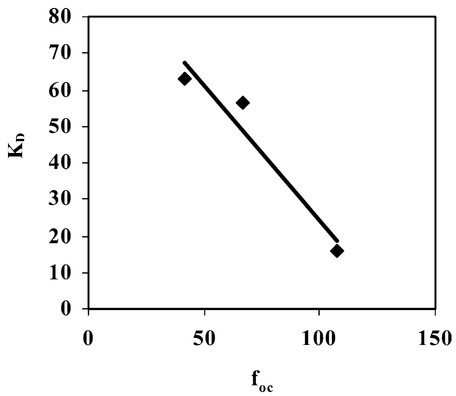


Fig. 4 Distribution coefficient (K_D) as a function of the fraction organic carbon (2,4-dichlorophenol) (f_{OC})

ganic carbon adsorbs organic compounds better than soil with little or no organic carbon (Table 2). The plot of the distribution coefficient versus the fraction of organic carbon appears to be linear (Figs. 1, 2, 3, 4) supporting the idea that the organic content of soil increases the amount of organic compound adsorbed into the soil (Borggard and Streibig1988). Among the four compounds studied it was found that adsorption was maximum for 2,4-dichlorophenol due to the high hydrophobicity (Gao et al. 1998) and least for phenol (Table 2).

The study shows that groundwater supply could be saved from hazardous organic contamination if the soil type adsorbs most of the organic compounds. The soils containing high organic carbon content adsorbs most and therefore are the most likely to prevent contamination of the groundwater supplies. Such soils can be used as sites for dumping the hazardous waste generated by industries allowing their further treatment by methods like bioremediation and phytoremediation.

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