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TRANSPORT OF NON-POLAR ORGANIC POLLUTANTS IN A RIVER WATER - GROUNDWATER INFILTRATION SYSTEM: A SYSTEMATIC APPROACH

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ABSTRACT

Laboratory batch and column experiments have been conducted to elucidate the sorption behaviour of volatile non-polar organic pollutants (e.g., halogenated alkenes and benzenes) in a river water - groundwater infiltration system. It has been found that sorption is reversible and that the degree of sorption (expressed by an equilibrium partition coefficient) can be estimated for any non-polar organic compound. Calculations of the velocities (relative to water) of migration in groundwater for a series of compounds show that during infiltration volatile organic compounds are rapidly transported from the river to the groundwater.

INTRODUCTION

The behaviour of water contaminants during infiltration of river waters to groundwaters is of great interest because infiltration is an important process for groundwater recharge and because many waterworks place wells close to a river in order to use bank filtration as a first step in the treatment of river water for public water supplies. In a natural river water - groundwater infiltration system the behaviour of organic pollutants is determined by many physical, biological, and chemical processes. In a field study it is often difficult to assess the importance of each of these processes in determining the net mobility of a particular compound in the ground. In the laboratory, however, experimental conditions can be controlled so that the effect of individual transport phenomena can be observed. In this paper we report the results of a laboratory study on the sorption behaviour of volatile non-polar organic pollutants. Some results of a related field study are given elsewhere in this volume (ref. 1).

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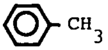
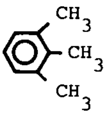
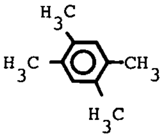
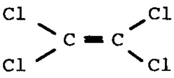
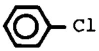
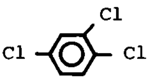
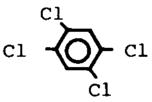
EXPERIMENTAL

The sorption of various volatile non-polar organic pollutants (see Table 1) by river sediments, aquifer materials, lake sediments and pure oxides has been investigated in batch and column experiments.

For the majority of the experiments with the natural materials the size fraction passing a 125 µm sieve was used. In batch experiments the sorbent/water ratios were typically between 1 : 5 and 1 : 10 (g dry weight of sorbent/g water). The initial concentrations of the compounds were in the range between 20 to 100 µg/L.

TABLE 1

Examples of non-polar organic pollutants investigated in this study

Compound name	Structure	log octanol/water partition coefficient $\log K_{ow}^{z}$ 1)
toluene		2.69
1,4-dimethylbenzene		3.15
1,2,3-trimethylbenzene		3.60
1,2,4,5-tetramethylbenzene		4.05
perchloroethylene		2.60
chlorobenzene		2.71
1,4-dichlorobenzene		3.38
1,2,4-trichlorobenzene		4.05
1,2,4,5-tetrachlorobenzene		4.72

1) see ref. 5.

The quantitative determination of the compounds was carried out with the closed loop gaseous stripping/adsorption/elution procedure described by Grob and Zürcher (ref. 2) in combination with high resolution glass capillary gas chromatography (ref. 3). The organic carbon contents of the sorbents were determined by the method of Baccini (ref. 4).

RESULTS

The results of this laboratory sorption study are summarized below. For a more detailed discussion of the various experiments conducted as well as for a review of the literature on this topic, the reader is referred to another paper by the same authors (ref. 5).

For non-polar organic compounds of low to intermediate lipophilicity it has been found that:

(1) Sorption by sediments and aquifer materials is reversible.

(2) For concentrations typically encountered in natural waters, a linear sorption isotherm is appropriate to describe sorption equilibrium:

$$S(z) = K_p^z(s) \cdot C(z)$$

where $S(z)$ = concentration of compound z on solid phase $[\frac{\mu mol}{g_s}]$

$C(z)$ = concentration of compound z in liquid phase (water) $[\frac{\mu mol}{cm^3_\ell}]$

$K_p^z(s)$ = sorbent/water partition coefficient of the compound z $[\frac{cm^3_\ell}{g_s}]$

(3) The partition coefficient $K_p^z(s)$ of a given compound z between a natural sorbent s and water increases with increasing organic carbon content of the sorbent. As exemplified in Figure 1 for a series of chlorinated benzenes, a highly significant correlation was found between the $K_p^z(s)$ values of a given compound z and the organic carbon contents $f_{oc}(s)$ of the sorbents containing more than 0.1 % organic carbon ($f_{oc}(s) \geqq 0.001$ g org. C/g_s).

(4) The more lipophilic a compound is, the stronger it is sorbed. The octanol/water partition coefficient K_{ow}^z of a compound can be used as a measure of its lipophilicity. For all non-porous sorbents investigated, a highly significant linear correlation was found between the logarithms of the partition coefficients $K_p^z(s)$ of the different compounds and the logarithms of the corresponding octanol/water partition coefficients K_{ow}^z (cf. examples in

Figure 2):

$$\log K_p^z(s) = a(s) \log K_{ow}^z + b(s)$$

The slope a(s) of the regression line yields information on the chemical nature of the material responsible for sorption (ref. 5).

(5) Sorption equilibrium can be assumed at flow velocities less than 0.1 cm min^{-1}. At higher velocities it is possible that a compound may be transported faster in the ground than one would assume from equilibrium considerations.

From the results of this study an empirical expression can be derived for estimation of the partition coefficient $K_p^z(s)$ of any non-polar organic compound z between a given natural sorbent s (size fraction < 125 µm) and water:

$$\log K_p^z(s) = 0.72 \log K_{ow}^z + \log f_{oc}(s) + 0.49$$

(for sorbents with $f_{oc}(s) \geq 0.001$).

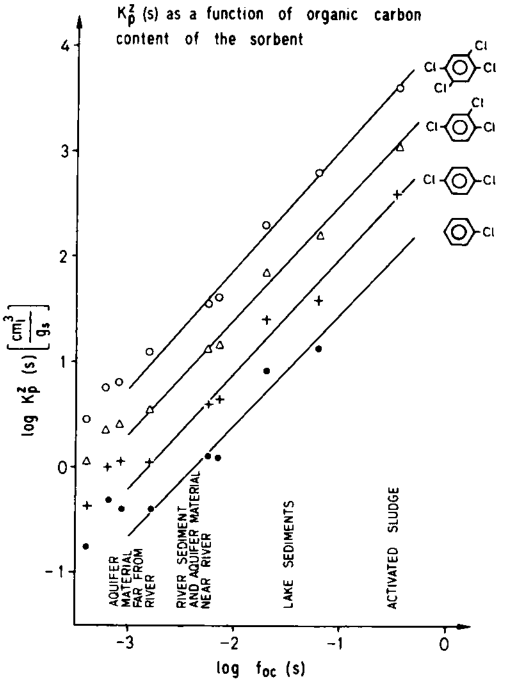


Fig. 1. Partition coefficients $K_p^z(s)$ for some selected non-polar organic compounds as a function of the organic carbon content of the sorbents.

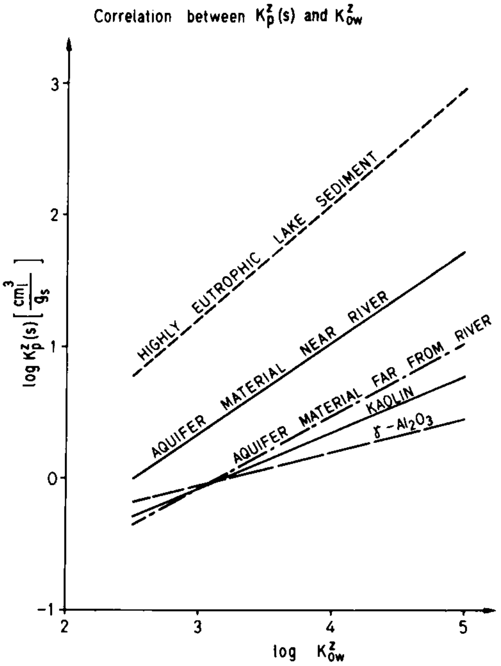


Fig. 2. Log $K_p^z(s)$ as a linear function of log K_{ow}^z: Regression lines for some sorbents (K_{ow}^z = octanol/water partition coefficient).

Thus, if the octanol/water partition coefficient K_{ow}^{z} of a compound z and the organic carbon content of the sediment or aquifer material (size fraction < 125 µm) are known, the velocity of the compound (relative to water) in the ground can be estimated. Table 2 contains such calculated relative velocities for various pollutants. These values predict volatile non-polar organic pollutants (compounds 1 to 6) to be very mobile in the ground.

TABLE 2

Calculated average relative velocities of some non-polar organic pollutants in the ground: (a) river sediment, (b) aquifer material. See description of field system (refs. 1 and 5).

a) River sediment

Compound z No	Name	K_p^z (< 125 µm)$^{1)}$ $[cm_\ell^3/g_s]$	K_p^z (soil)$^{2)}$ $[cm_\ell^3/g_s]$	Average relative velocity $[\bar{v}_z/\bar{v}_{water}]^{3)4)}$
1	chloroform	0.6	0.25	0.3
2	perchloroethylene	2.0	0.85	0.1
3	chlorobenzene	2.0	0.85	0.1
4	p-xylene	4.2	1.75	0.05
5	p-dichlorobenzene	6.1	2.55	0.04
6	trichlorobenzene	18.6	7.80	0.01
7	hexachlorobenzene (HCB)	520	218	0.0004

1) f_{oc} = 0.0073. 2) Size fraction Ø < 125 µm (evenly distributed!) = 42 %, ρ = 2.5 g/cm^3, ε = 0.20. 3) $\bar{v}_z/\bar{v}_{water} = (1 + \frac{\rho(1-\varepsilon)}{\varepsilon} K_p^z)^{-1}$, ref. 6. 4) Sorption equilibrium.

b) Aquifer

Compound z No	Name	K_p^z (< 125 µm)$^{5)}$ $[cm_\ell^3/g_s]$	K_p^z (soil)$^{6)}$ $[cm_\ell^3/g_s]$	Average relative velocity $[\bar{v}_z/\bar{v}_{water}]^{7)8)}$
1	chloroform	0.1	0.02	0.8
2	perchloroethylene	0.3	0.06	0.6
3	chlorobenzene	0.3	0.06	0.6
4	p-xylene	0.6	0.12	0.45
5	p-dichlorobenzene	0.8	0.16	0.4
6	trichlorobenzene	2.6	0.52	0.15
7	hexachlorobenzene (HCB)	71	14	0.007

6) f_{oc} = 0.001. 6) Size fraction Ø < 125 µm (evenly distributed!) = 20 %, ρ = 2.5 g/cm^3, ε = 0.20. 7) $\bar{v}_z/\bar{v}_{water} = (1+ \frac{\rho(1-\varepsilon)}{\varepsilon} K_p^z)^{-1}$, ref. 6. 8) Sorption equilibrium.

CONCLUSIONS

(1) In a natural river water - groundwater infiltration system volatile organic compounds are rapidly transported from the river to the groundwater. Thus, if a river is permanently loaded with such pollutants and if these compounds are not eliminated by biological or chemical processes during infiltration, large groundwater areas may be contaminated. The results of a recent field study (ref. 1) confirm this conclusion. These findings are, in principle, also valid for less volatile non-polar organic pollutants, although such compounds are less mobile in the ground (cf. e.g., relative velocity of hexachlorobenzene (HCB), compound 7 in Table 2).

(2) The degree of sorption of a given non-polar organic pollutant by any natural river sediment or aquifer material can be estimated. Thus, by using a relatively simple infiltration model (including advection, dispersion and sorption/desorption), it is, for example, possible to predict the impact of a sudden increase in concentration of a given persistent non-polar organic pollutant in the river on the quality of the groundwater close to the river. Such predictions of the temporal variations in concentration to be expected for a given compound in the groundwater (as a response to an incident in the river) can be of great importance in cases where bank filtered water is used for public water supplies.

(3) The conclusions of this study are applicable to a wide range of sorption and transport problems including artificial groundwater recharge, and leaching of pollutants from landfills.

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