

THE EFFECTS OF COLLOIDAL HUMIC SUBSTANCES ON THE MOVEMENT OF NON-IONIC HYDROPHOBIC ORGANIC CONTAMINANTS IN GROUNDWATER

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ABSTRACT

A controlled experimental study of the sorption of colloidal humic substances (humic acid) and a non-ionic hydrophobic organic compound (naphthalene) onto typical inorganic constituents of aquifer solids was performed using four types of model solid phases (i.e., individual model solids (montmorillonite, kaolinite, amorphous aluminosilicate gel, and amorphous iron oxides) and combined model solids (montmorillonite coated by amorphous aluminosilicate gel or iron oxides)), which are synthesized in the laboratory. The batch experimental results indicated that the sorption of non-ionic hydrophobic organic compounds and colloidal humic substances onto the aquifer solids is significantly influenced by the solid composition. And it was also suggested that the non-ionic hydrophobic organic compounds which have greater hydrophobicity are considered to be sorbed and stabilized by the mobile colloidal humic substances in groundwater, and these colloids may act as a third phase that can increase the amount of compounds that the flow of groundwater can transport. On the other hand, the non-ionic hydrophobic organic contaminants of smaller hydrophobicity may be retarded significantly with the sorption of colloidal humic substances onto the aquifer solids. © 1998 Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Colloidal humic substances; groundwater; model solid phases; non-ionic hydrophobic organic compounds; sorption.

INTRODUCTION

Contaminants have been released through human activities such as waste disposal, spills, and land application. These contaminants enter the subsurface environment (i.e., the vadose (unsaturated) and aquifer (saturated) zones). The establishment of effective disposal procedures for wastes, the protection of public health, and the amelioration of subsurface contamination largely rely on the ability to predict the movement of contaminants in the environment. However, attempts to evaluate and predict the transport of contaminants cannot succeed if major pathways and mechanisms for transport are not defined precisely. Most approaches for evaluating and predicting the movement of contaminants in groundwater hypothesize a two-phase system

in which contaminants distribute (partition) between immobile solid materials and the mobile aqueous phase. Based on the two-phase system, therefore, the non-ionic hydrophobic organic compounds are considered to be retarded in the aquifer (i.e., to move much more slowly than the rate at which groundwater flows).

In the aquifer matrix, a variety of materials exist as colloids, which are particles with diameters less than 10 μm (Stumm and Morgan, 1981). These colloidal particles also may be mobile in groundwater (McCarthy and Zachara, 1989). These colloidal particles could sorb contaminants and stabilize them in the mobile phase. In other words, the colloids act as a third phase that can increase the amount of contaminant that the flow of groundwater can transport. Failure to account for this mode of transport can lead to serious underestimates of the distances that contaminants will migrate. On the transport of the non-ionic hydrophobic organic compounds in groundwater, the most important colloidal particles are macro-molecular humic substances. Among organic and inorganic colloids in the aquifer matrix, humic substances (the largest single component of dissolved organic carbon) have the highest affinity to the non-ionic hydrophobic organic compounds (Schnitzer and Khan, 1972; Stevenson, 1972; Hassett and Anderson, 1979; Means *et al.*, 1980). Colloidal humic substances from surface water or natural solids bind the non-ionic hydrophobic organic compound, enhance its apparent solubility in water (Chiou *et al.*, 1987), and reduce its apparent affinity for binding to natural solids and to reverse-phase chromatographic columns and soil columns (Kile and Chiou, 1989). The observation of solid effect (i.e., measurement of a decreased sorption as the mass of solid used in batch sorption experiments is increased) may also result from increased concentrations of colloidal humic substances and concomitant increase in solute bound to the humic substances (O'Connor and Connolly, 1980; Voice *et al.*, 1983; Gschwend and Wu, 1985; Shimizu and Liljestrand, 1991).

This research calls attention to the potentially critical but poorly understood role of colloidal humic substances in influencing the transport of non-ionic hydrophobic organic compounds in groundwater. In this research, with the presence of colloidal humic substances, the sorption of non-ionic hydrophobic organic compounds onto model inorganic solid phases, which were synthesized in the laboratory, was measured by batch sorption experiments. Rather than work with natural aquifer solids which are exceedingly complex, valuable information can be obtained by working with the model solid phases. These model solid phases can be kept intentionally simple, and hence can facilitate the understanding of the basic phenomena governing the sorption of non-ionic hydrophobic organic compounds and the relevance of colloidal humic substances.

EXPERIMENTAL METHODOLOGY

The selection procedure of inorganic model solid phases is described in this section - the details on the preparation procedures of the selected inorganic model solid phases are described in Shimizu *et al.* (1995). The batch experiments for measurement of sorption of non-ionic hydrophobic organic compounds and colloidal humic substances onto the inorganic model solid phases are also described in this section.

Selection of inorganic model solid phases

Individual inorganic model solid phases. Natural aquifer solids are composed of a number of inorganic components, all of which have the possibility of involving the sorption. The major inorganic solid components are clay minerals, aluminosilicates (other than clay minerals), and amorphous metal oxides. In this research, following the approach of other investigators (Guy *et al.*, 1978; Oakley *et al.*, 1981; Davies-Colley *et al.*, 1984; Zieve and Peterson, 1985), a relatively few inorganic model solid phases (i.e., montmorillonite, kaolinite, amorphous aluminosilicate gel, and amorphous iron oxides) were chosen to simulate the functioning of natural aquifer solids with respect to the sorption. Table 1 indicates approximate ranges of natural inorganic solid components and also lists the inorganic model solid phases chosen to represent these inorganic solid components.

Combined inorganic model solid phases. Individual inorganic solid components are associated to some degree in natural aquifer solids. If the individual solid components act independently, it should be possible to predict the sorption onto natural aquifer solids of known composition based on the results of the sorption

for individual solid phases. However, if the interactions of the solid components affect the sorption, possibly by reducing the overall sorption, this approach is not valid. Therefore, it is important to examine the effects of the interactions in natural solids. Some degree of interaction between all pairs of solid phases is possible in principle. However, based on what is known about the interactions of different solid components from selective extraction studies on natural solids and from laboratory studies of pure solid phases, it is possible to identify the stronger and important interactions.

Table 1. Main inorganic constituents of natural aquifer solids and selected inorganic model solid phases

Solid component	Common range in natural aquifer solids (% dry weight)	Inorganic model solid phase (Preparation method)
Clay minerals ($<2 \mu\text{m}$ fraction)	0~70	Montmorillonite & Kaolinite (Purchased and purified)
Aluminosilicates (other than clay minerals)	30~90	Amorphous aluminosilicate gel (Synthesized)
Metal oxides	1~5	Amorphous iron oxides (Synthesized)

There is a great deal of information regarding the interaction between humic substances, and clay minerals (Theng, 1979). The interaction of clay minerals with predominantly negative charged humic substances is slight at neutral pH range (Schnitzer and Kodama, 1967). However, this conclusion somewhat contradicts the fact that the organic content of natural solids often correlates with clay ($<2 \mu\text{m}$) content (Hedges, 1977). Several investigators (Mortland, 1970; Greenland, 1971; Burchill *et al.*, 1981) indicated that cation bridge formation by hydroxy-metal oxides in natural solids neutralizes organic anions and allows the approach of humic substances to the clay surface. This supports the observations that both the amorphous iron and organic content of natural solids correlate well with the clay ($<2 \mu\text{m}$) content (Hedges, 1977; Jenne and Luoma, 1977; Luoma and Bryan, 1981). The formation of an amorphous aluminosilicate or iron hydroxy-cation coatings is followed by complexation of the hydroxy-metal layer by humic substances. This gives a stable ternary complex (Levy and Francis, 1976). Based on these reviews and considerations, the two types of combined inorganic model solid phases (i.e., montmorillonite coated by amorphous aluminosilicate gel and montmorillonite coated by amorphous iron oxides) were selected in this research.

Characterization of inorganic model solid phases. The synthesized aluminosilicate gel and iron oxides were amorphous: amorphous precipitates with X-ray diffraction analysis and totally (100%) extractable in acid ammonium oxalate reagent (Klute, 1982). The metal contents of these amorphous model solids were measured by Inductively Coupled Plasma (ICP) spectroscopy using a Perkin-Elmer Plasma 40 emission spectrophotometer, after digesting with $\text{HNO}_3\text{-H}_2\text{O}_2$. The measured values were, respectively, 19.9% aluminum and 20.1% silicon (Al/Si molar ratio = 1.03), and 51.8% iron on a moisture free weight basis. Therefore, the empirical formulae of these inorganic model solids were approximately $\text{AlSi}(\text{OOH})_{2.5}$ and $\text{Fe}(\text{OH})_3$. The metal content of the two combined inorganic model solid phases were also determined with the standard acid ammonium oxalate treatment (Klute, 1982). The metals to montmorillonite ratios were 3.68 and 3.92 meq-metal(s)/g-montmorillonite for the combined inorganic model solids of aluminosilicate and iron, respectively. And the empirical formulae of metals in the combined inorganic model solids were $\text{AlSi}(\text{OOH})_{2.7}$ and $\text{Fe}(\text{OH})_3$, which were similar to those of the corresponding individual inorganic model solid phases. These analytical values on the synthesized amorphous aluminosilicate gel and iron oxides are typical of literature values (Klute, 1982).

The cation exchange capacity (CEC) and specific surface area of the prepared inorganic model solids, which were two of the most important solid properties for the sorption, were also measured (Table 2). The CBC was analyzed using the sodium acetate method (Klute, 1982), while the specific surface area was determined by the Ethylene Glycol Monoethyl Ether Method (Klute, 1982). The CBC and specific surface area of the

combined inorganic model solids are not a simple weighted mean of the individual solids, which indicates the presence of the solid phase interactions.

Table 2. Physicochemical properties of inorganic model solid phases

Inorganic model solid phase	Cation exchange capacity (meq/100g)	Specific surface area (m ² /g)
Montmorillonite	57.6	565
Kaolinite	16.4	10
Amorphous aluminosilicate gel	12.0	400
Amorphous iron oxides	15.4	273
Montmorillonite coated by amorphous aluminosilicate gel	79.0	331
Montmorillonite coated by amorphous iron oxide	45.2	253

Batch sorption experiments

In order to evaluate the relevance of the colloidal humic substances on the sorption of non-ionic hydrophobic organic compounds, two types of batch sorption experiments were performed, which were: (1) sorption of colloidal humic substances onto inorganic model solid phases; and (2) sorption of non-ionic hydrophobic organic compounds onto colloidal humic substances and inorganic model solid phases. For both batch sorption experiments, the experimental aqueous phase was prepared for a constant pH (7.0 by 0.01 M NaHCO₃/0.01 M Na₂CO₃ buffer and 12 N HCl or 10 N NaOH) and ionic strength (0.2 M by NaCl). The equilibration was carried out in the dark at 20°C with a rotating tumbler (30 rpm). Preliminary investigation on the sorption kinetics for both batch experiments indicated that the equilibrium was reached within 24 hours.

Sorption of colloidal humic substances onto inorganic model solid phases. For the purpose of the present research, a commercially available humic acid (Aldrich Chemical Co.) was chosen to represent the colloidal humic substances. The Aldrich humic acid (sodium salt) was used without further purification. In this research, inorganic matter in the humic acid, such as salts and metals, were therefore considered as an integral part of the humic acid structure rather than as labile complexes. The fraction of organic carbon in this humic acid was analyzed by direct injection to a Beckman total organic carbon analyzer Model 915-B and was determined to be 38.5 wt% on moisture free basis.

The batch sorption experiments were carried out in 50 mL (nominal volume) borosilicate glass centrifuge tubes with Teflon-lined screw caps. After 24 hours of mixing of the experimental aqueous phase containing humic acid (<4 mg organic carbon/L) and the inorganic model solids, the aqueous phase was separated from the solids by centrifugation (20,000 g for 20 minutes) (Tipping, 1981). A portion of the supernatant was removal from the centrifuge tube, diluted to a concentration within the range of the humic acid calibration curve, and analyzed for the free (unadsorbed) humic acid by measurement of the absorbance at 254 nm. A Shimadzu UV-200S spectrophotometer was used for the absorbance measurements, and it was calibrated by measuring the absorbance of five standard solutions diluted from a stock solution. The amount of humic acid sorbed onto the solid was calculated by a mass balance. The difference between the initial and the final supernatant humic acid concentrations was used to determine the mass removed from solution and thus the amount sorbed.

Sorption of non-ionic hydrophobic organic compounds onto colloidal humic substances and inorganic model solid phases. In order to measure the sorption of non-ionic hydrophobic organic compounds, in this research the headspace technique developed by Garbarini and Lion (1985) was employed. This technique

cannot be influenced by the disadvantage of the various physical separation techniques (e.g., centrifugation, settling, or filtration) due to the incomplete separation of colloidal materials from the aqueous phase. In this research, naphthalene was selected as a non-ionic hydrophobic organic compound. The naphthalene was purchased from Nacalai Tesque and used without further purification. With preliminary investigation, for naphthalene it was verified that there is a linear relationship between the aqueous and gas phase concentrations (i.e., Henry's law) when the aqueous phase concentration is less than 10 mg/L.

The batch sorption experiments were carried out in 50 mL (nominal volume) borosilicate glass bottles. The humic acid solution or model inorganic solids were first introduced into the bottles, then spiked naphthalene solutions were added to make 30 mL of the aqueous phase containing 10 mg/L of naphthalene. The bottles were immediately sealed with Teflon-lined rubber septa and aluminum crimp caps. After 24 hours of equilibration, 0.5 mL of the gaseous headspace was withdrawn with a gas-tight syringe and the naphthalene concentration was analyzed by a gas chromatograph with flame ionization detector (Shimadzu, GC-9A).

RESULTS AND DISCUSSION

The non-ionic hydrophobic organic compounds in the aquifer distribute among three phases (i.e., the immobile aquifer solid phase, the mobile aqueous phase, and the colloidal humic substances). In this section, first the results of two types of batch sorption experiments are described. Then, a mathematical model with the three phase system, which is formulated in this research to predict the distribution of non-ionic hydrophobic organic compounds, is described in detail. Based on the experimental results and the mathematical model, the importance of colloidal humic substances on the transport of non-ionic hydrophobic organic compounds in the aquifer is finally evaluated.

Results of batch sorption experiments

Sorption of humic acid onto inorganic model solid phases. Within the range of humic acid concentrations used in this research (<4 mg organic carbon/L), linear sorption isotherms were observed. Table 3 summarizes the sorption coefficients of humic acid onto the inorganic model solids.

Table 3. Sorption coefficients of humic acid onto the inorganic model solid phases

Model solid phase	Sorption coefficient (mL/g solid)
Montmorillonite	800
Kaolinite	334
Amorphous aluminosilicate gel	3,642
Amorphous iron oxides	1,179
Montmorillonite coated by amorphous aluminosilicate gel	2,904
Montmorillonite coated by amorphous iron oxide	7,356

Among the individual inorganic model solids, kaolinite has the least sorption coefficient, which is considered due to its least specific surface area. The sorption coefficients onto amorphous aluminosilicate gel and iron oxides are greater than that onto montmorillonite, which has the largest specific surface area. As the pH_{ZPC} of these two amorphous metal oxides is around 7 (Stumm and Morgan, 1981), these amorphous metal oxides are neutral or positively charged at $pH = 7.0$, which may contribute the sorption of negatively charged humic acid onto these solids. The sorption of humic acid onto the combined inorganic model solids is greater than that onto the purified montmorillonite, although the specific surface areas of these combined solids are less than that of montmorillonite. This indicates that the presence of amorphous metal oxides in montmorillonite enhances the affinity of humic acid. Although the amorphous metal oxides

may block the available sorption sites of montmorillonite, they act favorably for the sorption of humic acid. The amorphous metal oxides can provide additional sorption sites and may change the surface characteristics of montmorillonite by the cation bridge formation.

Sorption of naphthalene onto humic acid and inorganic model solid phases. According to the experimental results of humic acid sorption, it was found that among the inorganic model solids, montmorillonite, amorphous aluminosilicate gel, and amorphous iron oxides have greater affinity to humic acid, being important for the movement of non-ionic hydrophobic organic compounds in the aquifer. Also it has been known that the majority of amorphous metal oxides are binded to clay minerals in natural aquifer solids (Hedges, 1977). Therefore, for the measurement of the sorption of naphthalene, three inorganic model solid phases (i.e., montmorillonite and two combined inorganic model solids) were used. The naphthalene sorption isotherms were linear for humic acid and these three inorganic model solids, and the measured sorption coefficients are presented in Table 4. The sorption coefficient of naphthalene onto humic acid is well within the range reported in the literature (Schwarzenbach and Westall, 1981). The order of sorption coefficients found for naphthalene onto three inorganic model solids is as follows: montmorillonite coated by amorphous iron oxides > montmorillonite coated by amorphous aluminosilicate gel > montmorillonite.

Table 4. Sorption coefficients of naphthalene binding to humic acid and inorganic model solid phases

Model solid phase	Sorption coefficient
Humic acid (mL/g organic carbon)	1,563
Montmorillonite (mL/g solid)	116
Montmorillonite coated by amorphous aluminosilicate gel (mL/g solid)	157
Montmorillonite coated by amorphous iron oxide (mL/g solid)	319

Mathematical model formulation

Sorption isotherms are linear if the equilibrium aqueous phase non-ionic organic compound concentration is below one half of the aqueous phase solubility (Karickhoff, 1984). Therefore, the sorption coefficient of non-ionic organic compound onto colloidal humic acid (K_d^{HS}) is expressed by

$$K_d^{HS} = \frac{C_b}{C_{fr}[HS]} \quad (1)$$

In Equation (1), [HS] is the aqueous phase humic acid concentration (mg organic carbon/L), C is the non-ionic organic compound concentration in the aqueous phase (mg/L), and fr and b, respectively, represent the free (unbound) and humic acid binded non-ionic organic compounds.

Similarly, the sorptions of free and humic acid binded non-ionic organic compounds onto inorganic solids are given by the following linear sorption isotherms.

$$q_{fr} = K_{dfr} C_{fr} \quad (2)$$

$$q_b = K_{db} C_b \quad (3)$$

In Equations (2) and (3), q is the sorbed non-ionic organic compound concentration in the inorganic solids (mg/g solid). Combining Equations (1) through (3) yields the overall sorption coefficient of the non-ionic organic compound onto inorganic solids in the presence of the colloidal humic acid in the aqueous phase (K_d^*).

$$K_d^* = \frac{q_{fr} + q_b}{C_{fr} + C_b} = \frac{K_{dfr} + K_{db} K_d^{HS} [HS]}{1 + K_d^{HS} [HS]} \quad (4)$$

The molecular weight of humic acid is generally much greater than that of non-ionic organic compound. Therefore, it can be assumed that the sorption coefficient of humic acid binded non-ionic organic compound onto inorganic solids (K_{db}) may be almost identical to that of humic acid itself (K_{dHS}) (Rav-Acha and Rebhun, 1992). Then, the value of K_d^* can be predicted by the following equation.

$$K_d^* = \frac{K_{dfr} + K_{dHS} K_d^{HS} [HS]}{1 + K_d^{HS} [HS]} \quad (5)$$

Importance of colloidal humic substances in the aquifer

The sorptions of non-ionic hydrophobic organic compounds onto colloidal humic acid and inorganic solids from the aqueous phase result primarily from van der Waals-London forces reinforced by the hydrophobic interaction. The combined effect of these two mechanisms is often referred to as hydrophobic sorption. Therefore, the sorption coefficients of non-ionic hydrophobic organic compounds onto colloidal humic acid (K_d^{HS}) and inorganic solids (K_{dfr}) can be estimated from the hydrophobicity of the non-ionic hydrophobic organic compound, such as octanol/water partition coefficient (K_{ow}).

$$\log K_d^{HS} = A_1 \log K_{ow} + B_1 \quad (6)$$

$$\log K_{dfr} = A_2 \log K_{ow} + B_2 \quad (7)$$

In Equations (6) and (7); A_1 , A_2 , B_1 , and B_2 are constants resulting from regression analysis of real measurements. In this research, referred to the regression analysis obtained by Shimizu (1990), the values of B_1 and B_2 were set at 0.26. The values of A_1 and A_2 were calculated using the sorption coefficients of naphthalene obtained in this research (Table 4) and anthracene by Shimizu (1990) and the values of K_{ow} for naphthalene ($\log K_{ow} = 3.35$ and 4.45, respectively). Using Equations (6) and (7), K_d^{HS} and K_{dfr} were estimated for other non-ionic hydrophobic organic compounds. Furthermore, based on these estimated values for K_d^{HS} and K_{dfr} , and the values of K_{dHS} obtained in this research (Table 3), the overall distribution coefficients of non-ionic hydrophobic organic compounds between the aqueous and immobile solids under the presence of the colloidal humic acid in the aqueous phase (K_d^*) were predicted by Equation (5).

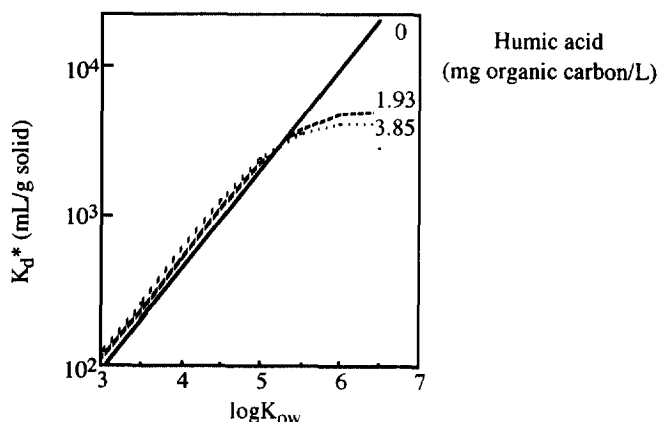


Figure 1. Effect of colloidal humic acid on the distribution of different non-ionic hydrophobic organic compounds (immobile solid: montmorillonite coated by amorphous aluminosilicate gel).

The predicted result for the combined inorganic model solid of montmorillonite coated by amorphous aluminosilicate gel is shown in Figure 1. From Figure 1, it is indicated that for the non-ionic hydrophobic organic compounds of relatively small and large hydrophobicity, the values of K_d^* , therefore the amounts of the non-ionic hydrophobic organic compound immobilized by the solid are, respectively, greater and smaller with the presence of the colloidal humic acid in the aqueous phase than those without the humic acid. Furthermore, these effects become greater with increasing humic acid concentration. At similar tendency was observed for the other two types of model inorganic solids (i.e., montmorillonite and montmorillonite coated by amorphous iron oxides).

CONCLUSIONS

The results of this research indicate that the non-ionic hydrophobic organic contaminants which have greater hydrophobicity are considered to be sorbed and stabilized by the mobile colloidal humic substances in groundwater, and these colloids may act as a third phase that can increase the amount of contaminants that the flow of groundwater can transport. On the other hand, the non-ionic hydrophobic organic contaminants of smaller hydrophobicity may be retarded significantly with the sorption of colloidal humic substances onto the aquifer solids. By properly using these effects of colloidal humic substances on the transport of non-ionic hydrophobic organic contaminants in the aquifer, it may be possible to find appropriate techniques (i.e., by the addition of colloidal humic substances into the aquifer of known solid compositions) for the remediation of the contaminated aquifer and for the suppression of the further dispersion of the contaminants in the polluted region.

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