Characteristics of the natural organic matter sorption affects of organic contaminants

LIU Xiao-bing, SONG Chun-yu, XING Bao-shan

(Heilongjiang Institute of Agricultural Modernization, Chinese Academy of Sciences, Harbin 150040, China. E-mail: songli@fmail.hl.cninfo.net)

Abstract: Several soil samples were used to study how the characteristics of natural organic matter (NOM) affect sorption of organic compounds. These soils contains different amounts and types of NOM. Aromaticity of NOM (percentage of aromatic carbons) was determined from solid-state CPMAS ^{13}C NMR spectra and the soil effective polarity was computed from the equation developed by Xing *et al*. Naphthalene was used to examine the sorption characteristics of NOM. Both aromaticity and polarity of NOM strongly affected sorption of naphthalene. Old NOM showed higher affinity than that in the surface, young soils. Sorption increased with increasing aromaticity and decreasing polarity. Thus, the sorption coefficients of organic contaminants cannot be accurately predicted without some consideration of NOM characteristics.

Keywords: characteristics of natural organic matter; sorption of organic compounds; influence

Introduction

Recent research has demonstrated that sorption of hydrophobic organic compounds(HOC) in soils and sediments is controlled by organic matter unless its content is very low(Chiou, 1989). This is particularly true in water-soil systems because water molecules are preferably adsorbed on mineral surfaces as compared to HOC molecules(Chiou, 1989; Xing, 1994a). However, mechanisms for sorption capacity differences of different NOM remain to be addressed. A clear understanding of sorption capacity of NOM will help predict HOC behavior in soils and subsurface environments.

Sorption of HOC in soils and sediments is described by the Freundlich model(Weber, 1996; 1992; Xing, 1996a; 2001; Yuan, 2001):

$$S = K_f C^N, \tag{1}$$

$$\log S = \log K_f + N \log C, \tag{2}$$

where S is the sorbed concentration($\mu g\ g^{-1}$), C is the solution-phase concentration($\mu g\ ml^{-1}$), K_f is the Freundlich sorption coefficient ($ml^N\ \mu g^{1-N}\ g^{-1}$), and N(dimensionless) is the exponent. When N equals one, Equation (1) becomes a linear form:

$$S = K_d C, \tag{3}$$

where S and C are defined earlier and K_d is the linear sorption coefficient with a dimension of ml/g, related to sorption capacity. Equation (3) has been often used in the literature (Chiou, 1989; Schwarzenbach, 1993). This equation is applicable for a narrow range of solute concentration or when partitioning is only sorption mechanism (Weber, 1992; Xing, 1996b).

Because of the high affinity of NOM for HOC, another equation is developed relating sorption capacity to hydrophobicity of HOC (Chiou, 1989; Briggs, 1981):

$$\log K_{oc} = a + b \log K_{ow}, \tag{4}$$

where K_{oc} is the organic carbon-normalized sorption coefficient (i.e., K_d/f_{oc}, where f_{oc} is the fraction of organic carbon in soil or sediment), K_{ow} is the octanol-water partition coefficient, and, a and b are empirical constants. The values of K_{ow} are well-documented. Equation (4) has been widely used in predictive models for movement and risk assessment of organic pollutants in soils and sediments. It should be noted that Eq.(4) is valid only if the NOM is a homogeneous partition phase and if octanol serves as an

appropriate surrogate for it.

Natural organic matter is, however, heterogeneous in nature (Hayes, 1989; Xing, 1999). As a result, it may vary greatly as a function of the location, origin, diagenesis, and mode of transformation (Rullkotter, 1989). Even within a single soil profile, aromatic carbons of humic acids increased with depth (Chen, 1995; Xing, 1999). The variation in characteristics of the NOM strongly affected sorption capacity(K_{oc}; Weber, 1992; Xing, 1994b; Grathwohl, 1990). For example, K_{oc} of trichloroethylene in the shale samples containing condensed organic carbon was more than one order of magnitude greater than that in young, surface soils (Grathwohl, 1990). Sorption of napromide, a nonionic herbicide, by sediment samples was greater than by soil on an organic carbon basis(Gerstl, 1990). Garbarini and Lion(Garbarini, 1986) also documented the dependence of K_{oc} on composition (C, O, S) of NOM. In contrast, Kile *et al* .(Kile, 1995) recently reported minimal variation in K_{oc} for many soil and sediment samples collected from U.S.A. and China. Moreover, Chefetz *et al* .(Chefetz, 2000) observed that aliphatic components were important for pyrene sorption. As one may see, there is presently no agreement about the effect of the characteristics of NOM on sorption of HOC. This information is, however, critical to understanding and predicting the fate and transport of HOC in soil and evaluating exposure risks. Following our previous studies with benzene, toluene, xylene, and naphthol (Xing, 1994b; 1994c), we determined the influence of the characteristics of natural organic matter on sorption coefficient (K_{oc}) of naphthalene (a nonpolar polyaromatic hydrocarbon) in this paper.

1 Materials and methods

Five soils were used in the sorption experiments. These soils differed with respect to location, origin, age, diagenesis, and type and amount of organic matter. Also, these soils are pristine (i.e., no known contamination with organic chemicals) and were described elsewhere(Xing, 1994b): a Cretaceous aged soft coal mixed with weathered shale(soil 1), a well humified but relatively young (a few hundred years) sedge peat (soil 2), a White Clay soil formed on Quaternary aged sediments (soil 3) from Heilongjiang Province, China (soil 3), and two soils developed on glacial till in Alberta, Canada, a Black Chernozemic (soil 4) and a Brown Chernozemic (soil 5). Samples were air-dried and gently ground to pass 100 μm sieve before NMR analyses and sorption experiments. Naphthalene was used as the sorbate. Its $\log K_{ow}$ is 3.37 and solubility is 30 mg/L at 25℃ (USEPA, 1992). Naphthalene has been listed as a priority pollutant by the Unite State Environmental Protection Agency(Keith, 1979).

The high-resolution solid-state ^{13}C NMR spectra, with cross-polarization (CP) and magic-angle spinning (MAS), were obtained using a Brucker AM 300 instrument. The details were described elsewhere (Xing, 1999). Percentage of aromatic-C (i.e., aromaticity) of NOM associated with each soil was calculated from the CPMAS ^{13}C NMR spectra using ratio of peak area of 106 – 165 ppm to total area of 0 – 230 ppm (Chen, 1995; Schnitzer, 1991). A wide range of aromaticity is an indicator for difference in characteristics of organic fractions of these soils(Table 1). Total organic carbon contents were measured by an EA 1108 elemental analyzer(Carlo Erba Instruments) and they are also reported in Table 1. Other properties were reported by Xing *et al* .(Xing, 1994b).

Sorption isotherms were obtained using triplicate batch equilibrations in background of 0.01 mole/L CaC_{12} containing 100 μg/ml HgC_{12} to minimize

Table 1 Organic carbon contents of the soils and characteristics of their organic fraction

Sorbents	f_{oc}	Aromatic-C, %	Effective polarity, *PI*	
			Method 1	Method 2
Soil 1	53.4	56	0.51	0.50
Soil 2	32.2	20	0.63	0.63
Soil 3	7.38	28	0.61	0.60
Soil 4	4.53	33	0.57	0.59
Soil 5	2.55	23ᵃ	0.62	nd

Note: f_{oc} = organic carbon fraction in soils; *a* = determined from equation: $PI = 0.702 - 0.00353AR$ at $PI = 0.62$; nd = not determined because of a low quality NMR spectrum as a result of low organic content

microbial activity. Solution-to-solid ratios varied to ensure 25% to 85% sorption: soil 1, 100:1; soil 2, 50:1; soil 3, 30:1; soil 4, 25:1; and soil 5, 20:1. Labeled solutions were prepared by adding ^{14}C-naphthalene to the unlabeled naphthalene solutions (1 to 20 μg/ml) in sufficient amount to produce activity of 100 Bq/ml (~ 6000 cpm/ml). Soils were weighed into glass centrifuge tubes, and then labeled solutions (10 ml were added to minimal headspace). The tubes were immediately sealed with Teflon lined screw-caps and shaken horizontally in a LAB-line Orbit Environ-shaker (300 r/min for 30 hours at 25 ± 1 ℃). After centrifuging (1000 × g for 30 min), an aliquot (1.0 ml) of supernatant was removed to measure naphthalene by liquid scintillation counting. The difference between the initial and final concentrations was attributed to uptake or sorption by the soils. Preliminary tests confirmed that the glass centrifuge tubes did not adsorb naphthalene, and that centrifuging at 2000 × g rather than at 1000 × g did not significantly change sorption results. Also, the apparent equilibrium was reached at 30 hours because sorption for 48 hours did not significantly differ from that at 30 hours and we did not detect any biodegradation of naphthalene from gas chromatograms after 30 hours.

Effective polarity was developed by Xing et al. (Xing, 1994b) to predict the sorptive behavior of soils and geologic materials according to the characteristics of their organic phase. They reported two methods to derive soil effective polarity: (1) $PI = (1.83 + 0.625 \log K_{ow} - \log K_{oc})/2.34$ using K_{oc} values for sorption of o-xylene by each soil; and (2) $PI = 0.702 - 0.00353 AR$, where AR is the percent of C as aromatic C measured using CPMAS ^{13}C NMR (Table 1). The polarity of the five soils is shown in Table 1.

2   Results and discussion

2.1   Sorption isotherms

Sorption isotherms of the five soils are shown in Fig.1. Both linear and Freundlich models were used to fit sorption data. The parameters K_f and N were determined by linear regression of log-transformed data (Equation 2). The fitting parameters of linear and Freundlich equations are reported in Table 2. The regression coefficients (r^2) of the Freundlich model were higher than or equal to that of linear fitting, indicating the better fit of the data to Freundlich equation. The deviation of N values from one was consistent with the heterogeneous nature of NOM as revealed by the NMR results (Table 1). Compared to N values in other sorption studies (Weber, 1992; Xing, 1996b; 1997), the N values were much closer to one, which may be caused by the relatively narrow concentration range used in this work.

The Freundlich equation is empirical with two adjustable parameters (K_f and N) and the K_f value changes with N values. Furthermore, the unit ($ml^N \mu g^{1-N} g^{-1}$) of K_f (Table 2) is related to N. As a result, the carbon normalized coefficients (K_{oc-f}) have different units among the soils and they are not comparable. Consequently, the linear equation was selected to derive K_d and K_{oc} for the purpose of comparison between soils and with literature values even though the K_{oc-f} values of the five soils showed the same decreasing trend with declining aromaticity as the K_{oc} (Tables 1 and 2). The linear fitting accounted for more than 98% of the sorption effect (see r^2 value in Table 2) in this study and the K_{oc} values in the literature are usually obtained from a linear model. The detail discussion on the use of linear and Freundlich models can be found elsewhere (Chen, 1996).
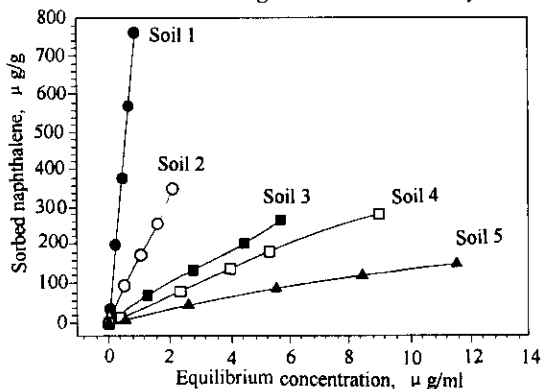

Fig.1   Naphthalene sorption isotherms

Table 2 Fitting parameters of linear and Freundlich models

Sorbents	Linear			Freundlich				
	K_d, ml/g	r^2	K_{oc}, ml/g	K_f, $ml^N \mu g^{1-N} g^{-1}$	N	r^2	K_{oc-f}
Soil 1	781	0.998	1460	775	1.00	0.999	1450
Soil 2	158	0.998	492	164	0.988	0.998	508
Soil 3	45.4	0.998	615	56.5	0.877	0.999	756
Soil 4	31.9	0.996	704	35.7	0.964	0.999	788
Soil 5	13.4	0.986	526	16.5	0.949	0.993	648

Note: K_{oc-f} = organic carbon normalized Freundlich coefficient

The K_d values of the soils decreased in order of soil 1 > soil 2 > soil 3 > soil 4 > soil 5 (Table 2), reflecting the predominance of NOM for sorption of naphthalene. This observation is consistent with the work by other investigators (Chiou, 1989; Means, 1980).
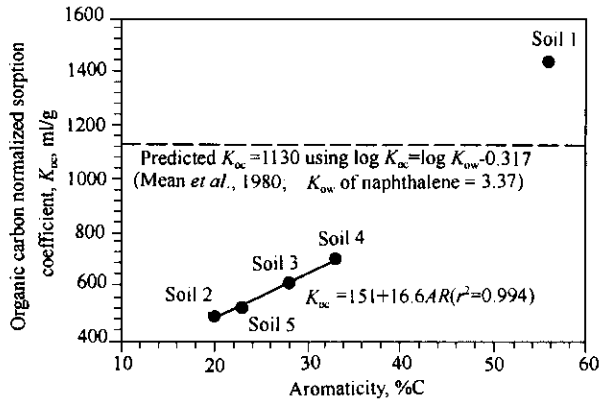
However, the K_{oc} values were not constant among the soils and had a different decreasing order from K_d (Table 2). The order of K_{oc} was soil 1 (1460 ml/g) > soil 4 (704 ml/g) > soil 3 (615 ml/g) > soil 5 (526 ml/g) > soil 2 (492 ml/g)(Table 2). This variation in K_{oc} implies that the characteristics of NOM affect its sorption capacity of HOC like naphthalene. This result was consistent with the earlier work with benzene, toluene, and *o*-xylene(Xing, 1994b).

2.2 Relationship of K_{oc} with aromaticity and effective polarity

The K_{oc} values increased with increasing aromaticity of the organic fraction of five soils (Fig.2). The K_{oc} values of soil 2 – 4 were lower than that predicted from the $K_{oc} - K_{ow}$ equation derived by Means *et al*. (Means, 1980), but the K_{oc} of soil 1 was higher than the predicted value (Fig.2). The shale (soil 1) is at a more advanced stage of diagenesis than the surface young soils (soils 2 – 5) and may have condensed aromatic structure as indicted by its aromaticity (Table 2). As a result, soil 1 sorbed much more naphthalene than other soils. Higher sorption by the shale

Fig.2 K_{oc} of naphthalene increases with aromaticity (AR), the dash line represents the predicted K_{oc} value

was also reported elsewhere(Weber, 1992; Young, 1995). Because of the very high sorption in soil 1, it was excluded from the regression analysis. A linear relationship is obtained between the K_{oc} and aromaticity with a slope of 16.6 and an intercept of 151 (Fig.2). In studying the impact of mineral-bound humic substances on the sorption of anthracene, carbazole, and dibenzothiophene, Murphy *et al*. (Murphy, 1990) reported that the most aromatic coating (peat humic acid) consistently displayed the greatest K_{oc}. Other investigators have also reported the similar dependence of K_{oc} of aromatic compounds on the aromaticity of NOM(Xing, 1994b; Chen, 1996; Gauthier, 1987).

The K_{oc} of naphthalene decreased with increasing effective polarity. A log-linear relationship was obtained by regression with a slope of – 3.97(Fig.3). Fig.3 also displays
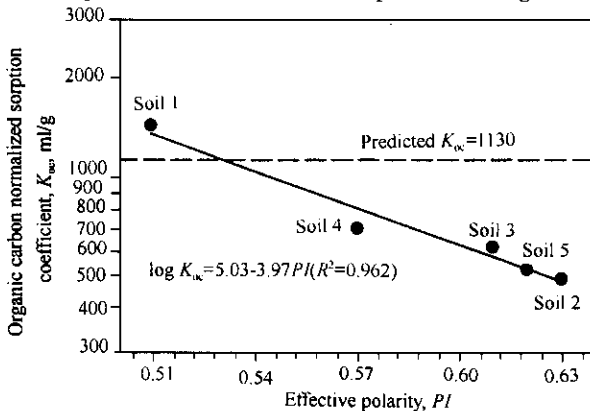
Fig.3 K_{oc} of naphthalene decreases with effective polarity (*PI*), the dash line represents the predicted K_{oc} value

that K_{oc} values were either higher or lower than the K_{oc} value (1130 ml/g) predicted from K_{ow}. This illustrates that polarity of NOM markedly influences sorption capacity of organic chemicals. Similar evidence was presented for uptake of phenol into other organic sorbents (Xing, 1994a). The effect of polarity of NOM on sorption of organic compounds is consistent with the well-known effect of solvent polarity on solute solubility. In studying the influence of NOM composition on the partition of benzene and carbon tetrachloride, Rutherford *et al*. (Rutherford, 1992) also reported that K_{oc} values for both chemicals increased with decreasing polar content of organic sorbents. Several other authors (Grathwohl, 1990; Garbarini, 1986) have noted a relationship between elemental composition of NOM and sorption of organic chemicals. The small difference of K_{oc} reported by Kile *et al*. (Kile, 1995) may be because: (1) variation of samples in diagenesis was low, and (2) the sediment samples might be contaminated with the surface soils.

3   Conclusions

Characteristics (e.g., elemental composition and aromaticity) of natural organic matter significantly affected uptake of naphthalene by soils and sediments. Organic carbon normalized sorption coefficient (K_{oc}) changed inversely with effective polarity and directly with aromaticity. Young, surface organic matter had lower sorption capacity than the old organic matter in shale. These relationships between HOC sorption and NOM characteristics have to be further examined and tested with a large set of soil and/or sediment samples. Nevertheless, the results of this study indicate that it would not be accurate to predict K_{oc} from K_{ow} without consideration of the characteristics of organic matter.

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