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SORPTION-DESORPTION OF ATRAZINE ON MINERAL-BOUND HUMIC SUBSTANCES RELATED TO THEIR STRUCTURE

Natalia A. Kulikova[1*] **and Irina V. Perminova**[2]

[1]Department of Soil Science, Lomonosov Moscow State University, Moscow 119992, Russia
[2]Department of Chemistry, Lomonosov Moscow State University, Moscow 119992, Russia

SUMMARY

The content of organic matter is known to control retention of soil-applied pesticides in organic-rich soils. The contribution of chemical nature of organic matter in pesticides sorption both in organic and mineral soils is much less understood. In this study, sorption/desorption isotherms of the herbicide atrazine were obtained on model humic-clay complexes with eleven humic and fulvic acids from soil, peat, coal, and water. The estimated K_{OC} values varied from 121 to 319 $L \cdot kg^{-1}$, which is a factor of two lower than the partition coefficients determined previously for the same HS in soluble form. The mineral-bound K_{OC}s closely correlated with K_{OC} values of the soluble humic materials and with sorption coefficients (K_d) of overall humic-clay complexes. This shows that variations in chemical nature of humic fraction determined sorption affinity of model humic-clay complexes. Structure-property analysis revealed a leading role of hydrophobic domains in atrazine affinity of mineral-bound HS, whereas hysteresis index correlated with the content of carboxylic groups indicating the prevailing role of specific domains in formation of bound residues. Together, the obtained results open a possibility to obtain reasonable predictions of atrazine sorption by organo-clay geosorbents using partition coefficients estimated for soluble organic fractions.

KEYWORDS: atrazine, humic substances, organo-mineral complexes, sorption, desorption.

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) is one of the most widely applied and persistent herbicides [1]. The transport and fate of atrazine in organic-rich soils are known to be controlled by the content of organic matter [2-8]. In mineral soils and vadose zone with organic content not exceeding 0.1 %, the high contents of mineral fractions provide substantial contributions to pesticide sorption [9]. As a result, no correlation with organic carbon content was found between atrazine and other pesticides K_d for these geosorbents [10, 11]. To predict pesticide sorption by mineral-rich sorbents, composite models were proposed [7, 12] with the assumptions that mineral and organic phases contribute independently to pesticide sorption.

Despite the numerous studies on organic contaminants` sorption/desorption by humic substances (HS), HS-clay model sorbents [13-17], the influence of clay and organic matter on the sorptive properties of each other upon their association is still not fully understood [13, 18-20]. Another question under debate concerns structural features, which contribute mostly to affinity and reversibility of atrazine sorption on mineral-bound HS. In our previous studies on atrazine binding with soluble HS [21], the dominating role of aromatic fragments was demonstrated for sorptive affinity of humic materials. However, a number of recent publications [22-25] claim that HS possess an aliphatic component, which plays a major role in controlling the sorption of organic contaminants on humic coatings. At the same time, the systematic comparative studies on sorption affinities of mineral-bound versus soluble HS of different genesis are still missing.

In this publication, we have studied atrazine sorption/desorption on a large set of model humic-clay complexes prepared by modification of kaolin clay with humic and fulvic acids of different genesis. We have used a broad range of molecular descriptors, including more specific ^{13}C-NMR descriptors for deriving structure-sorptive properties relationships [26].

Our objectives were to (1) measure the atrazine K_{OC} for a variety of mineral-bound HS of different genesis, and (2) derive the correlation relationships between the sorptive properties and molecular descriptors of mineral-bound HS.

MATERIALS AND METHODS

Atrazine

Atrazine (99.97%) was purchased from Dr. Ehrenstorfer GmbH (Germany). Stock solution of 10 mg L^{-1} was prepared in distilled water (pH 5.5) and stored in the dark at 4 °C.

Kaolin clay

Kaolin clay (Kaolin CF 70) was provided by the Caminauer Kaolinwerk GmbH (Caminau, Germany). The kaolin clay sample was dispersed in 0.1 M $NaClO_4$ using an ultrasonic bath to saturate the clay with sodium ions. The obtained suspension was then centrifuged, the supernatant removed, and the clay-precipitate was three times repeatedly treated with new salt solution. Then, the clay was washed with distilled water, dried, and stored for further use.

Humic materials isolation and characterization

Eleven samples of humic substances (HS) used in this study were isolated from different types of soil, peat, brown coal, and lake water.

Soil humic acids (HA) were isolated from four soils: two Spodosols sampled nearby Moscow under woods (HBW, HBW1) and two Mollisols sampled nearby Voronezh (HST and HSM). HA extraction was performed as described in [27]. It included alkaline extraction (0.1 M NaOH) and follows up extract acidification to pH 1-2. The Mollisol samples were preliminary treated with 0.1 M H_2SO_4. The precipitated HA were purified by dialysis during a month at 4 °C using dialysis membrane with cut-off of 3 kD (Merk, Germany).

Soil fulvic acids (FA) were extracted from two Spodosols nearby Moscow sampled under woods (FBW1), and in the garden (FBG1). FA were isolated after precipitation of HA by passing the acidic supernatant through the Amberlite XAD-2 resin as described elsewhere [28].

Peat HA (T8) were isolated from bog peat Kranichfeldt (western Erzgebirge, Germany). Isolation procedure was as described elsewhere [29] including preliminary treatment of a peat sample with ethanol-benzene mixture (1:1 v/v) to remove bitumen compounds, followed by an extraction with 0.1 M NaOH. HTO sample was a commercial preparation of peat HA purchased from Biolar (Olaine, Latvia).

Coal HA (AGK and Roth HA) were commercial preparations kindly provided by Biotechnology Ltd. (Moscow, Russia) and Roth (Germany), respectively.

Swamp Water HA (HO13HA) was a standard of the Deutsche Forschungsgemeinschaft (DFG) program "ROSIG", kindly provided by Dr. G. Balke (UFZ, Germany). The sample was extracted from the brown waterlake Hohlohsee (Schwarzwald, Germany) using Amberlite XAD-8 as described elsewhere [30].

Chemical characteristics of the target humic materials including contents of elements, molecular weight, distribution of carbon among structural units, and content of acidic groups are summarized in Table 1. *Elemental analyses* (C, H, and N) were conducted on a Carlo Erba Strumentazione analyzer (Italy). Ash content was determined manually by the samples` combustion in quartz tubes at 850 °C for 40 min. Oxygen contents were calculated as a difference. The contents of all the elements were calculated on ash-free basis. *Size exclusion chromatography analyses (SEC)* were performed according to Perminova et al. [31]. Toyopearl HW-50S gel was used for column packing. Polydextrans were used as markers for molecular weight calculations. HS solutions were set at a concentration of 1-2 mg C/L by equilibrating with the SEC mobile phase (0.028 M phosphate buffer, pH 6.8) prior to analysis. *Quantitative ^{13}C solution-state NMR spectra* were recorded on a Varian VXR-400 spectrometer operating at 100 MHz using 0.1 M NaOD as a solvent. All spectra were recorded at quantitative conditions using 4-s delay time and inverse gate decoupling [32]. The assignments were as follows (in ppm): 5-50 – aliphatic H and C-substituted C atoms (C_{Alk}), 50-108 – aliphatic O-substituted C atoms ($C_{Alk\text{-}O}$), 108-145 – aromatic H and C-substituted atoms ($C_{Ar\text{-}H,C}$), 145-165 – aromatic O-substituted C-atoms ($C_{Ar\text{-}O}$), 165-187 – C atoms of carboxylic and esteric groups (C_{COO}), 187-220 – C atoms of quinonic and ketonic groups ($C_{C=O}$). *Potentiometric titrations* were conducted under N_2 atmosphere using an automatic titrator (TitroLine Alpha, Schott, England) according to Frimmel et al. [33]. In brief, a weight of dry HS sample (10 mg) was dissolved in 0.1 M NaOH, then 0.1 M HCl was added to precipitate HA, and titrated with 0.1 M NaOH until pH 11.0. The amount of NaOH consumed for a rise in pH from 2.6 to 7.5, and from 7.5 to 11.0 was normalized to HS weight, and treated as carboxylic and phenolic acidity (mmol g^{-1}), respectively.

Organo-mineral complexes

Organo-mineral complexes (OMC) were prepared as described previously [34]. Each sample was prepared in a 24-mL glass vial with PTFE lid. 1 g of kaolin clay was dispersed in 20 mL of 250 mg L^{-1} HS in 0.1 M NaCl as a background electrolyte at pH 5.6. This kaolin to HS mass ratio was chosen as maximum adsorption capacity for HS, and was demonstrated to be reached under those conditions [ibid.].

The samples were equilibrated for 12 h in the rotary shaker and centrifuged (10 min, 4000 rpm). Reversibly adsorbed humic materials were washed out using eight step-desorption by 0.1 M NaCl. Each time, the suspension was shaken for 12 h, centrifuged, and concentration of desorbed HS was determined by UV-absorption at 254 nm. Desorption was repeated until HS content in supernatant reached a plateau at about 1 mg L^{-1}. The prepared OMC samples were freeze-dried and used for OC analysis. The OC content was measured using catalytic combustion (900 °C; 5 min; 20–40 mg sample weight; 3 replicates) with subsequent NIR CO_2 determination (C-Mat 1100, Stroehlein Inst., Germany).

Sorption-desorption experiments

Sorption isotherms were obtained using equilibrium batch experiments. Kaolin or OMC (500 mg) was dispersed in 10 mL of atrazine solution (2-20 μM, pH 5.6) in 0.1 M NaCl. Suspensions were shaken for 12 h, centrifuged (10 min, 4000 rpm), and supernatant was analyzed for atrazine content using HPLC. HPLC system used was Gold™ Model 126 equipped with UV detector. The Ultrasphere Beckman column (USA), 4.6 mm×15 cm, was used for separation. The mixture of acetonitrile and water (50:50, v/v) containing 3.18×10^{-3} M HCl (pH 2.5) was used as a mobile phase. The absorbance of the eluate was detected at 220 nm. Desorption isotherms were obtained on the samples prepared at the highest atrazine concentration used for sorption isotherm. After centrifugation, supernatant was replaced with 10 mL of 0.1 M NaCl. After shaking for 12 h, the suspension was centrifuged and the supernatant was analyzed for atrazine content. Desorption was conducted in three steps. All sorption-desorption experiments were conducted in triplicate.

Data treatment

To quantify the obtained sorption isotherms, distribution coefficients K_d (L kg^{-1}) were determined as a slope of the following relationship:

$$C_s = K_d C_e \tag{1}$$

where C_s is atrazine quantity adsorbed on a weight of OMC at the equilibrium concentration C_e.

To calculate sorption coefficients on organic phase K_{OC}, the following equation of Karickhoff [7] was used:

$$K_d = f_m \cdot K_m + f_{OC} K_{OC} \tag{2}$$

where K_m is the sorption coefficient on clay phase, and f is the mineral or organic fraction in the organic–clay particles. K_m was put equal to K_d value obtained for the unmodified mineral, and f_m was calculated as $1\text{-}f_{OC}$.

To estimate reversibility of atrazine sorption, sorption and desorption isotherms were fitted to the following Freundlich equations:

$$C_s = K_f C_e^{nf} \tag{3}$$

$$C_s = K_{fd} C_e^{nfd} \tag{4}$$

where K_f and K_{fd} are Freundlich sorption and desorption constants, respectively; n_f and n_{fd} are indexes of nonlinearity of the sorption and desorption isotherms, respectively. A hysteresis index (H) was calculated following Celis et al. [35], as a ratio of n_f/n_{fd}.

RESULTS AND DISCUSSION

Chemical properties of humic materials used for preparing model complexes

The bulk chemical properties of humic materials were analyzed using elemental analysis, potentiometric titration, ^{13}C-NMR spectroscopy and SEC, to gain a better understanding of the sorption interactions of atrazine with mineral-bound HS. The obtained results are given in Table 1.

As it can be seen, the aquatic humic acid HO13HA and both soil fulvic acids are characterized with the largest values of total acidity (4.3-4.6 mmol/g). This indicates hydrophilic character of these materials. At the same time, humic acids from Mollisol (HSM and HST) and coal (Roth HA and AGK) are characterized with the highest content of aromatic fragments ranging from 55 to 66 %. Lipophilic-lipophobic balance of humic materials was estimated as a ratio of hydrophobic aromatic ($C_{Ar\text{-}C,H}$) to hydrophilic carbohydratic (C_{AlkO}) moieties, and allowed arrangement of the target humic materials in the following descending order

TABLE 1 - Chemical properties of humic substances used in this study.

HS sample	Atomic ratios[a]		Acidic groups[b], (mmol·g^{-1})		Carbon distribution among structural fragments[c], (%) of total C[c]						M_W[d] (kD)
	H/C	*O/C*	*COOH*	*Ar-OH*	$C_{C=O}$	C_{COO}	$C_{Ar\text{-}O}$	$C_{Ar\text{-}H,C}$	$C_{Alk\text{-}O}$	$C_{Alk\text{-}H,C}$	
Swamp Water HA											
HO13HA	0.80	0.52	2.9	1.4	4	13	12	27	29	17	12.8
Soil FA											
FBW1	0.99	0.60	3.4	1.2	4	20	12	23	19	27	10.2
FBG1	1.15	0.75	3.3	1.1	3	18	12	29	19	19	11.7
Soil HA											
HBW	0.99	0.58	3.4	0.2	1	17	13	32	19	19	15.9
HBW1	1.02	0.51	2.9	0.3	4	20	9	24	14	26	14.5
HSM	0.86	0.51	3.3	0.2	2	14	12	43	14	14	13.0
HST	0.77	0.52	3.8	0.4	3	15	14	42	13	13	12.7
Peat HA											
HTO	1.05	0.57	1.6	1.0	3	13	13	31	24	16	20.0
H8	1.19	0.72	2.4	0.3	2	16	18	37	13	13	11.7
Coal HA											
AGK	0.94	0.46	3.4	0.2	1	17	10	48	4	21	15.6
Roth HA	0.97	0.76	2.9	1.2	3	18	18	48	3	11	16.4

[a] *H/C* and *O/C* ratios were calculated on ash- and water-free basis. [b]Content of acidic groups was determined using potentiometric titration. [c]Content of carbon in the structural fragments was determined by ^{13}C-NMR spectroscopy as the integral intensity (%) of the following regions, ppm: 187-220 – C atoms of quinonic/ketonic groups ($C_{C=O}$); 165-187 – C atoms of carboxylic/esteric groups (C_{COO}); 145-165 – aromatic O-substituted C-atoms ($C_{Ar\text{-}O}$); 108-145 - aromatic H and C-substituted atoms ($C_{Ar\text{-}H,C}$); 50-108 – aliphatic O-substituted C atoms ($C_{Alk\text{-}O}$); 5-50 – aliphatic H and C-substituted C atoms (C_{Alk}). [d]M_W values were determined by SEC (calibration by polydextrans) and listed in kilodaltons (kD).

according to their hydrophobicity: coal HA > Mollisol HA >> peat HA ≅ Spodosol HA ≅ swamp water HA >> soil FA.

Sorption-desorption of atrazine on model humic-clay complexes

Sorption and desorption isotherms of atrazine on model organo-mineral complexes are shown in Figs. 1 and 2. In the range of atrazine concentrations studied, sorption isotherms are mostly linear, with the exception of HO13HA, HBW, HTO and Roth HA. In all cases, humic modifications enhanced atrazine sorption to OMCs relative to sorption by the unmodified kaolin clay, despite of the low content of organic carbon in all OMCs (Table 2). This is consistent with the larger K_{OC} for atrazine binding by soluble HS used in this study versus partition coefficient to kaolin clay (Table 2).

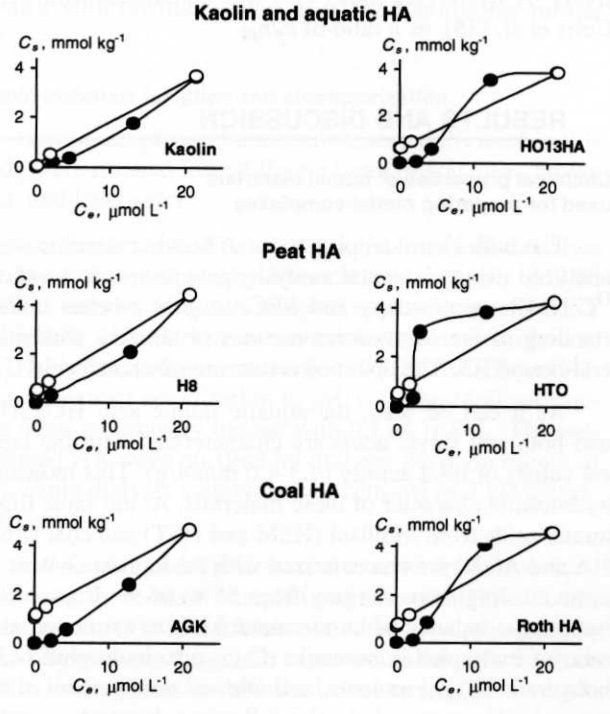

FIGURE 1 - Sorption-desorption isotherms of atrazine on kaolin clay and its organo-mineral complexes with aquatic, peat, and coal HS. Sorption isotherms (black points) were obtained using the following conditions: initial atrazine concentration 2-20 μM in 0.1 M NaCl, pH 5.6, equilibration time 12 h. Desorption isotherms (white points) were obtained on the samples prepared at the highest atrazine initial concentration used for the adsorption isotherm.

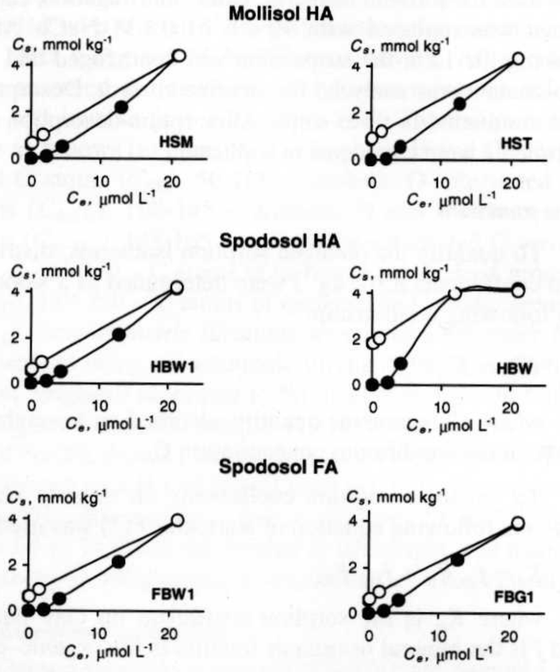

FIGURE 2 - Sorption-desorption isotherms of atrazine on organo-mineral complexes of kaolin clay with soil HS. Sorption isotherms (black points) were obtained using the following conditions: initial atrazine concentration 2-20 μM in 0.1 M NaCl, pH 5.6, equilibration time 12 h. Desorption isotherms (white points) were obtained on the samples prepared at the highest atrazine initial concentration used for the adsorption isotherm.

TABLE 2 - Atrazine sorption-desorption parameters to OMCs, content of organic carbon in OMCs, and K_{OC} values to soluble HS.

Sorbent	OC, kg OC/kg OMC	$K_d$$^{a)}$, L/kg OMC	K_d-calc$^{b)}$, L/kg OMC	$K_{OC}$$^{c)}$, L/kg OC	K_{OC}(solution)$^{d)}$, L/kg OC	$H^{e)}$
kaolin clay	–	1.72±0.09$^{f)}$				1.21
H013HA	0.229±0.003	2.08±0.09	n.d.	157	n.d.	9.24
FBW1	0.165±0.008	1.93±0.09	2.03	128	192±12	5.90
FBG1	0.166±0.009	1.94±0.09	2.17	137	275±17	8.30
HBW	0.249±0.008	2.20±0.09	2.66	194	380±12	7.17
HBW1	0.264±0.008	2.09±0.07	2.46	143	281±17	5.73
HSM	0.245±0.009	2.17±0.08	2.94	184	501±31	5.93
HST	0.248±0.006	2.17±0.09	2.72	184	404±23	7.76
HTO	0.274±0.009	2.20±0.07	2.54	178	300±10	2.31
H8	0.286±0.009	2.06±0.06	n.d.	121	n.d.	3.19
AGK	0.237±0.005	2.28±0.09	3.08	238	575±35	7.18
Roth-HA	0.240±0.004	2.48±0.09	n.d.	319	n.d.	5.40

^{a}Experimentally measured K_d values; ^{b}predicted estimates of K_d values using composite model (eq 2); ^{c} K_{OC} values estimated for mineral-bound HS; ^{d}K_{OC} values to soluble HS measured in our previous study [21]; ^{e}Hysteresis coefficient calculated as a n_f/n_{fd} ratio; ^{f}± denotes one standard deviation for triplicate measurements.

Despite higher atrazine affinity for OMCs, there was no significant correlation ($r = 0.48$) observed between calculated K_d values and OC content. This is typical for mineral-organic associates with low organic carbon [10], which is explained by a substantial contribution of mineral fraction into sorption of pesticide. Estimates of the contributions of clay fraction and humic phase to the atrazine sorption were attempted using a simple composite model described previously by eq. 1. The atrazine partition coefficients K_{OC} to 8 out of 11 HS samples in dissolved state used for preparing OMCs were determined in our previous study [21]. The humic fraction (f_{oc}) was estimated by the measured organic C content, the remaining mass was assumed to be the clay mineral fraction (f_m). The clay sorption coefficient K_m was estimated from the sorption isotherm for unmodified clay (Fig. 1) and accounted for 1.72 $L \cdot kg^{-1}$. The summation of predicted sorption by humic and clay fractions is shown in form of the K_d-calc coefficients in Table 2.

The predicted values are within a factor of 1.1-1.4 of the measured values for all OMCs. Moreover, a close correlation was observed between the predicted and measured K_d values ($r = 0.91$). The obtained results indicate that, in general, sorption by HS-clay complexes can be reasonably well estimated by summing up their individual contributions to atrazine sorption.

The composite model used for K_d predictions was further applied to estimation of K_{OC} values to mineral-bound HS. For this purpose, the measured K_d values were represented as sums of mineral and organic terms. Substituting the known f_{oc}, f_m and K_m values in eq. 2, the corresponding K_{OC} values were calculated. As it can be seen from Table 2, the calculated K_{OC} values to mineral-bound soil HS ranged from 128 to 194 $L \cdot kg\ OC^{-1}$, which corroborates well the reported data for soils [8]. Based on the measured K_{OC} values, the mineral-bound HS can be roughly arranged in the following order: coal HA > Mollisol HA > Spodosol HA, peat HA, swamp water HA > Spodosol FA. This sequence follows closely the magnitude of lipophilic-lipophobic balance of soluble humic materials used for modification of kaolin clay indicating the dominating role of hydrophobic aromatic domains in sorption affinities of both soluble and mineral-bound humic materials.

At the same time, the determined atrazine K_{OC}s were a factor of two less than the corresponding K_{OC} values to soluble HS. This could be indicative of a decreased availability of binding sites in mineral-bound HS, partially used for binding with kaolin clay. Of particular importance is that a close correlation was observed between K_{OC} values ($r = 0.90$), as well as between K_d and K_{OC} values both to mineral-bound and soluble HS ($r = 0.94$ and 0.79, respectively). This can be explained by the dominant contribution of variations in sorptive properties of humic-bound HS to atrazine affinity when both content of clay, and organic fractions do not vary substantially among organo-mineral associates (the case for the obtained OMCs).

Along with sorption affinity, sorption reversibility is a parameter of crucial importance for prediction of pesticide migration in the soil or aquatic environments. Desorption isotherms are shown in Figs. 1 and 2, together with sorption isotherms. In almost every case, the desorption isotherm is located above sorption isotherm. This is indicative of hysteretic sorption of atrazine on OMCs. To characterize sorption hysteresis quantitatively, sorption and desorption isotherms were fitted to the Freundlich equations (eqs. 3-4). Given the composite character of atrazine sorption onto obtained OMCs with low organic content, the calculated Freundlich parameters were not given other consideration than for using n_f parameters for calculation of hysteresis index H.

The obtained H values are shown in Table 2. The lowest H value of 1.21 was observed for the unmodified kaolin clay. Values close to one represent almost complete desorption. H values for all OMCs were much higher and ranged from 2.31 to 9.24 with peat and swamp water HA, respectively, defining the low and upper ranges. The hysteretic behavior of atrazine was evidently different from that of hydrophobic organic contaminants (e.g. PAHs) which were reported to display lowest hysteresis for geosorbents having the least diagenetically-altered organic matter (peat), and highest hysteresis for geosorbents having the most diagenetically altered organic matter (kerogen) [see 36 for overview]. In our case, no clear tendency was observed for dependence of hysteretic behavior of atrazine on genesis of HS used for OMCs preparation. For example, H values for OMCs with HS originated from peat, ranged from 2.31 (HTO) to 3.19 (H8). This might be a consequence of different mechanisms underlying irreversible sorption of relatively polar, low hydrophobic atrazine ($K_{ow} = 2.5$) and of non-polar, highly hydrophobic PAHs.

Relationship between sorption-desorption parameters and structural features of mineral-bound HS

For compiling a set of structural parameters for a simple linear regression analysis, an approach was undertaken as described in detail in our previous publication [26]. In brief, it implied a numerical description of HS structure using a combination of molecular descriptors of elemental, fragmental and molecular weight compositions given in Table 1. In deriving molecular descriptors, the ^{13}C-NMR data were given primary importance as most meaningful descriptors of HS structure. Correlations with sorption parameters were evaluated for both individual descriptors reflecting carbon content in each of the main structural fragment, as well as combined descriptors reflecting sums and ratios of the individual descriptors. These more complex expressions may reveal interaction features within the HS structure, such as relative enrichment or depletion of HS structure with aliphatic versus aromatic units. The full correlation matrix included six individual and eight combined ^{13}C-NMR descriptors.

Among the individual descriptors, the closest correlation coefficients r with K_d and K_{OC} values were observed for the content of unsubstituted aromatic fragments $C_{Ar\text{-}H,C}$ (0.77 and 0.76, respectively). Of interest is similar strong correlation observed between this molecular descriptor and K_{OC} values measured for the same humic materials in soluble form ($r = 0.95$). As to aliphatic fragments, there was no statistically significant correlation observed with both O-substituted and unsubstituted aliphatics. Among the combined descriptors, the closest correlations with both K_d and K_{OC} values were observed for two hydrophobicity indices of humic molecules represented by a ratio of total aromatics to carbohydrates contents $\Sigma C_{Ar}/C_{Alk\text{-}O}$ (0.82 and 0.90, respectively) and by a ratio of the sum of unsubstituted aromatic and aliphatic fragments to the content of carbohydratic fragments $(C_{Ar\text{-}H,C}+C_{Alk})/C_{Alk\text{-}O}$ (0.80 and 0.88, respectively). This might be indicative of aromatic fragments determining a large fraction of atrazine affinity. A hydrophobic mechanism can be hypothesized as the driving force of atrazine affinity for mineral-bound HS, as in the case of soluble HS.

With regard to the structural features mostly contributing into irreversibility of atrazine sorption, a positive correlation ($r = 0.76$) was observed between hysteresis index and the content of carboxylic groups (*COOH*). This could be indicative of the role of specific sorption domains – functional groups – in irreversible atrazine sorption, which is consistent with the mechanisms of H-bonding and charge-transfer discussed in the literature for atrazine binding to HS [37, 38].

The obtained results do not support aliphatics` thesis that HS possess an aliphatic component, which plays a major role in controlling the sorption of organic contaminants on humic coatings [22-25], and suggest that in the case of atrazine multiple sorption mechanisms may be operative including atrazine binding both to non-specific (hydrophobic) and specific (functional groups) sorption domains of humic molecules. This concept has been discussed by several investigators [39-41]. It is predicated on both thermodynamic assessments and results of structural studies of HS-atrazine complexes. Our results suggest that hydrophobic binding to aromatic fragments of HS controls a fast and reversible stage of atrazine sorption, which is followed by a slower one of binding to specific sorption domains via formation of charge-transfer complexes or H-bonding.

CONCLUSION

In this study, we have successfully demonstrated that atrazine sorption by humic-clay model complexes with content of organic carbon not exceeding 0.3 % was governed by chemical properties of humic coatings. This shows the important role of organic matter for atrazine migration not only in organic-rich soils, but for mineral soils and aquifers as well. Of particular practical value is a finding on comparable sorption affinity of atrazine both to mineral-bound and soluble HS. This opens a possibility to obtain reasonable predictions of atrazine sorption by mineral geosorbents using partition coefficients estimated for soluble organic fractions. The observed structure-activity relationships indicate that, as in case of soluble HS, the mineral-bound humic materials rich in aromatics mainly contribute to sorption affinity of atrazine. The obtained results support the concept developed by Gamble et al. [42] that the molecular level mechanisms based on stoichiometry can be applied both to humic materials and whole soils, and used for predictive calculations and engineering purposes.

ACKNOWLEDGEMENTS

We extend our deepest appreciations to Dr. Gerd Balcke (UFZ, Germany) for friendly assistance and analytical facilities provided to Dr. Kulikova during her research stay at the UFZ supported by Saxonian educational program “Leonardo”, and to Dr. Kirk Hatfield (UF, USA) for editorial work on the manuscript. Dr. Kulikova thanks the Lomonosov Moscow State University for 2004 and 2006 scholarship award. This research was supported by the grants of the Russian Foundation for Basic Research (#04-04-49679), International Science and Technology Center (#KR-964) and Interdisciplinary Science Project 04 from Lomonosov MSU in 2007.

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Received: November 30, 2006
Revised: February 02, 2007
Accepted: April 10, 2007

CORRESPONDING AUTHOR

Natalia A. Kulikova
Department of Soil Science
Lomonosov Moscow State University
Moscow 119992
RUSSIA

E-mail: knat@darvodgeo.ru

FEB/ Vol 16/ No 9a/ 2007 – pages 1061 - 1068