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Sorption of natural organic matter fractions to goethite (α-FeOOH): effect of chemical composition as revealed by liquid-state ^{13}C NMR and wet-chemical analysis

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Abstract

In order to quantify the potential influence of the chemical composition of natural organic matter (NOM) on the extent of its sorption to mineral surfaces, I compared the interaction with synthetic goethite (α-FeOOH) of 18 different NOM (hydrophilic and hydrophobic fractions, fulvic and humic acids) samples from soil and terrestrial surface waters. The chemical composition of NOM was characterised by elemental analysis, titration of acidity, wet chemical analyses of lignin and carbohydrate constituents, and liquid-state ^{13}C NMR spectroscopy. The proportions of resonances due to carboxyl C ranged from 7 to 21% and signals for total aromatic C varied from 0 to 38%. Signals due to O,N-alkyl C comprised 5–65% of the spectral area. The sorption of all tested NOM was adequately described by the Langmuir model. In general, hydrophobic fractions and fulvic and humic acids rich in carboxyl and aromatic C, probably derived from lignin, sorbed much more strongly to goethite than the hydrophilic fractions which were characterised by high abundance of O,N-alkyl C, probably due to carbohydrates, and low abundance of aromatic C. A sample of fulvic acids rich in alkyl C sorbed more weakly than samples rich in aromatic C. Consequently, the strong sorption of the hydrophobic fractions and fulvic acids seemed to be caused by the presence of aromatic structures. Within the groups of samples, however, the major determinant of the extent of the sorption proved to be acidic groups, as revealed by the close relationship between maximum sorption and total acidity and the content of carboxyl C. The maximum sorption of hydrophobic, fulvic and humic acids was inversely related to the ratio of aromatic to carboxyl C, which suggests that the number (and probably the position) of acidic groups attached to aromatics controls the interactions of hydrophobic, fulvic and humic acids with goethite.
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1. Introduction

Natural organic matter (NOM) is a major dissolved component of soils and terrestrial surface waters. Here, it contributes to acidity and is involved in the mobilisation and transport of metals, nutrients, and pollutants.

The mobility of NOM in soils and aquatic systems is limited because of strong sorptive interactions with mineral surfaces, especially those of hydrous Al and Fe oxides (Tipping, 1981; McKnight et al., 1992, 2002; Kaiser et al., 1996). However, sorption of NOM is not uniform. Constituents with higher molecular weight sorb preferentially (Davis and Gloor, 1981; Bose and Reckhow, 1998; Meier et al., 1999) and fractions containing lignin-derived compounds, being rich in aromatic structures (hydrophobic acids, fulvic and humic acids), sorb more strongly than fractions rich in carbohydrates (Jekel, 1986; Gu et al., 1995; Chorover and Amistadi, 2001).

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A key factor in the interaction of strongly-sorbing NOM fraction with oxides is the acidity of the adsorbing compounds. Sorption seems to increase with the number of carboxyl groups per molecule and with increasing acidity of carboxyl groups (Davis, 1982; Edwards et al., 1996; Wang et al., 1997). Aromatic acid structures with multiple functional (carboxyl and phenolic) groups likely control the sorption of fulvic and humic acids (Evanko and Dzombak, 1998). Preferential sorption of aromatic and carboxyl moieties from fulvic acids and hydrophobic fractions of soil and aquatic NOM confirms this consideration (McKnight et al., 1992, 2002; Kaiser et al., 1997; Korshin et al., 1997). Carboxyl groups in NOM strongly adsorbed to oxides form strong complexes with surface metals (Parfitt et al., 1977; Gu et al., 1994, 1995; Wershaw et al., 1995; Kaiser et al., 1997; Kubicki et al., 1999) and so the sorption is barely reversible (Avena and Koopal, 1998; Kaiser and Zech, 1999). Since the interaction of strongly sorbing NOM fractions with oxides seems to depend on aromatic acidic functionalities, simple aromatic acids (e.g., pyromellitic acid) may be used to simulate and model the sorption process (Evanko and Dzombak, 1999). Nevertheless, confirmation for this assumption is not yet available.

In the case of NOM fractions (hydrophilic/non-humic fractions) that interact weakly with oxides, little is known about the factors that control the sorption process. Since these fractions lack aromatic moieties (e.g., Kaiser et al., 2001), the contribution of lignin-derived aromatic acid structures can be excluded. This, however, does not exclude the possibility that the sorption, similar to the situation with strongly sorbing fractions, might depend on acidity. Although lower in carboxyl groups, these fractions contain considerable amounts of acidic functionalities (e.g., Kaiser et al., 2001).

The purpose of the present study was to clarify the role of certain chemical features of the hydrophilic/non-humic fraction and XAD-8-adsorbable fractions (hydrophobic acids, fulvic and humic acids) in the sorption of these compounds to hydrous oxides. I approached this by relating chemical properties such as acidity and structural composition according to ^{13}C NMR and wet chemical analyses to parameters describing their sorption to goethite (α-FeOOH).

2. Materials and methods

2.1. Natural organic matter

2.1.1. Fulvic and humic acids from soil and surface waters

The fulvic and humic acids used (Table 1) were reference materials from the joint research programme ROSIG. The origin, isolation, and preparation of these

materials are given in detail by Abbt-Braun and Frimmel (2002). Briefly, three samples of fulvic acids derive from a bog lake (HO10 FA, HO13 FA, HO14 FA); one sample of fulvic acids (BS1 FA) and the humic acids (BS1 HA) derive from soil seepage water. The sixth sample of fulvic acids (SV1 FA) was from a mining lake filled with concentrated waste water from brown coal processing. The fulvic acids (H^+ form) were provided as a solution in deionized water (1 g organic C l^{-1}) under a N_2 atmosphere. The sample of humic acids was freeze-dried. Aliquots of the samples were freeze-dried for determination of elemental composition, titration of acidity, and NMR analysis.

2.1.2. Hydrophilic and hydrophobic dissolved organic matter fractions from various organic forest floor layers

The forest floor samples comprise bulk organic layers from natural Brazilian savannah (Cerrado, CE) and a 25-year old pine (*Pinus caribaea* Morelet) plantation (PI; Lilienfein et al., 2000), Oa horizons from mor-type forest floors under a 160-year old Scots pine (*Pinus sylvestris* L.; SBR) and under a 80-year old Norway spruce [*Picea abies* (Karst.) L.] stand (WÜR), and the Oi horizon from a mull-type forest floor under a 90-year old European beech (*Fagus sylvatica* L.) stand (IS). The latter three sampling sites are located in the surrounding

Table 1
Elemental composition and acidity of natural organic matter samples studied

Sample[a]	C	O	N	H	S	Total acidity	COOH acidity
	(%)					(mmol mol^{-1} C)	
WÜR HiOM	42.7	49.5	1.9	3.8	0.9	149	134
WÜR HoA	46.9	48.0	1.5	3.6	0.5	181	158
HM HiOM	41.8	52.2	1.9	3.4	0.8	124	115
HM HoA	45.2	50.3	1.6	3.5	0.5	207	182
SBR HiOM	40.6	53.8	1.8	3.7	0.7	174	157
SBR HoA	50.2	48.0	1.2	4.7	0.4	187	170
IS HiOM	41.5	53.0	1.8	3.7	0.6	109	102
IS HoA	45.6	48.7	1.5	4.2	0.4	169	150
CE HiOM	38.7	55.1	1.7	3.8	0.4	82	76
CE HoA	44.5	50.4	0.4	4.3	0.3	191	171
PI HiOM	39.0	52.7	4.0	3.9	0.4	103	94
PI HoA	43.0	51.3	0.6	4.9	0.3	214	179
HO10 FA	53.2	41.7	0.7	3.8	0.7	192	168
HO13 FA	54.5	39.4	0.7	4.1	1.1	231	211
HO14 FA	53.1	41.6	0.6	4.1	0.5	207	188
SV1 FA	54.7	29.2	2.1	4.5	9.5	159	145
BS1 FA	53.5	41.9	0.7	3.6	0.3	201	180
BS1 HA	55.3	39.4	1.0	3.9	0.3	146	133

[a] FA = fulvic acids, HiOM, = hydrophilic organic matter, HA = humic acids, HoA = hydrophobic acids. Elemental contents refer to ash-free organic matter.

area of Bayreuth, NE Bavaria, Germany and are described in Kaiser et al. (1996, 2001). Additionally, the Oa horizon of a mor-type forest floor under a 60-year old Norway spruce stand (HM) was used. Bulk forest floor and Oi horizon samples were mixed by shaking in large plastic bags. Homogenisation of the Oa materials was carried out by sieving to < 2 mm. All samples were stored at −18 °C until extraction of water-soluble organic matter. Extraction was carried out at a water-to-solid organic matter ratio of 10/1 (vol./wt.). After 15 min stirring, the suspensions were allowed to stand for 18 h at 25 °C, then filtered through 0.45-μm poly-ethersulfone membranes (Supor-450, Pall Gelman Science, Ann Arbor, MI) and stored at 3 °C for no longer than 12 h. The bulk water extracts were separated into the operationally-defined, so-called hydrophilic and hydrophobic fraction (Aiken and Leenheer, 1993). To do so, an aliquot of the solutions was acidified to pH 2 with 1 M HCl, analysed for organic C (TOC-5050 analyzer, Shimadzu Corp., Tokyo, Japan), and pumped through columns filled with Amberlite XAD-8 resin (Rohm and Haas Co., Philadelphia, PA). In the effluent of the XAD-8 columns, representing the hydrophilic, non-humic fraction, the organic C concentration was measured. Organic C in the hydrophobic (or humic) fraction was calculated by difference. After passage of the bulk organic matter samples, the columns were rinsed with water adjusted to pH 2 with 1 M HCl. The hydrophobic fraction was eluted from the column with 0.1 M NaOH and the organic C concentration in the effluent was measured. Mass-balance calculations showed that 96–99% of the C in the hydrophobic fraction was recovered from the XAD-8 resin, indicating that the contribution of hydrophobic neutral compounds was small in the samples and therefore that the hydrophobic fraction consisted mainly of acidic substances. The fractions were protonated with a strongly acidic cation exchanger (AG-MP 50), acidified to pH 2 with 1 M HCl, and a portion was freeze-dried and homogenised by grinding.

2.2. Characterisation of natural organic matter

2.2.1. Elemental composition

C, N, H, and S concentrations of organic matter samples were determined using an automatic CHNS analyser (Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany). The concentration of O was calculated as ash-free dry weight minus measured elements.

2.2.2. Titration of acidity

Freeze-dried organic matter samples were titrated to pre-determined pH values with either $Ba(OH)_2$–HCl or Ca acetate–NaOH to estimate the total and carboxyl acidity (Schnitzer, 1982).

2.2.3. Liquid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR)

Freeze-dried organic matter samples were analysed for chemical structures using liquid-state ^{13}C NMR spectroscopy. The ^{13}C NMR spectra were obtained on an Avance DRX 500 spectrometer (Bruker Analytik GmbH, Karlsruhe, Germany) at 125.77 MHz. About 150 mg of samples were dissolved in 3 ml of 0.5 M NaOD in a 10-mm NMR tube. At a pulse angle of 45°, 2.0 s pulse delay and inverse-gated decoupling, about 15 000 scans were accumulated for each sample. The signal-to-noise ratio was improved by using a line-broadening of 100 Hz. Chemical shifts were given relative to the resonance of tetramethylsilane and signal assignments were made according to the literature (Wilson, 1987; Lambert and Lankes, 2002).

2.2.4. Lignin-derived CuO oxidation products

The contents of lignin-derived phenols and their degree of oxidation were estimated using alkaline CuO oxidation at 170 °C for 2 h (Hedges and Ertel, 1982). Instead of the liquid–liquid extraction, a solid-phase extraction with C_{18} columns (Mallinckrodt Baker Corp., Phillipsburg, NJ) was used. Phenols were eluted and derivatised with a 1:1 mixture of pyridine and N,O-bis(trimethysilyl)trifluoroacetamide. The derivatives were separated by capillary gas chromatography at a split ratio of 30-to-1 using an Ultra 2 fused silica column (25 m, 0.25 mm i.d., 0.33-μm film; Agilent Technologies, Inc., Palo Alto, CA) and N_2 as carrier gas. Separated compounds were detected by flame ionisation. The injector temperature was set to 250 °C and that of the detector to 300 °C. The ramped temperature programme started at 100 °C, was held for 0.5 min, then increased to 250 °C at a rate of 15 °C per min. That temperature was held for 1 min and was then increased to 300 °C at 30 °C per min. After an additional 5 min the temperature was decreased to the initial value. Ethylvanillin was added as internal standard prior to the CuO oxidation and phenylacetic acid before derivatisation. To increase the recovery, 50 mg glucose were added prior to the CuO oxidation (Amelung et al., 1999). Recoveries were between 85 and 108% of the initial spike level.

2.2.5. Neutral and acidic carbohydrates

Individual neutral and acidic carbohydrates were determined according to the method described by Amelung et al. (1996). Freeze-dried organic matter samples were treated with 4 M trifluoroacetic acid at 105 °C for 4 h then filtered through glass fibre filters, dried by rotary evaporation, re-dissolved in deionised water, and purified with Amberlite XAD-7 (Rohm and Haas Co., Philadelphia, PA) and Dowex 50W X8 (Dow Chemical Co., Midland, MI) resins. The carbohydrates were transformed into O-methyloxime trimethylsilyl derivatives,

separated by capillary gas chromatography at a split ratio of 40-to-1 using a HP 5 fused silica column (25 m, 0.25 mm i.d., 0.33-μm film; Agilent Technologies, Inc., Palo Alto, CA), with N_2 as carrier gas. Separated compounds were detected by flame ionisation The ramped temperature programme started at 160 °C, was held for 4 min, then increased to 185 °C at a rate of 8 °C per min. That temperature was held for 1.5 min and was then increased to 250 °C at 4 °C per min. After an additional 0.5 min the temperature was decreased to the initial value. Myo-inositol was added as internal standard prior to hydrolysis and 3-O-methylglucose was added as internal standard prior to derivatisation. The recovery of the carbohydrates in all analyses was between 73 and 112% of the initial spike level.

2.3. Goethite

Well-crystallised goethite (α-FeOOH) was prepared by the method of Atkinson et al. (1967). After intensive dialysis against deionized water, the precipitate was freeze-dried and then passed through a 0.63 mm sieve. X-ray diffraction (D5000, Siemens AG, Karlsruhe, Germany) proved that the sample was pure goethite. It had a specific surface area of 47 m^2 g^{-1} as calculated from N_2 adsorption-desorption data using the Brunauer-Emmett-Teller equation (Quantasorb surface analyzer, QuantaChrome, Inc., Syosset, CA) and the organic C content was <0.1%. Details of the preparation and the sorption-desorption of NOM by this mineral are given in Kaiser and Zech (1997, 1999) and Kaiser et al. (1997).

2.4. Sorption experiments

Batch sorption experiments with goethite were carried out at a solid-to-solution ratio of 1/160 (dry wt./vol.) with 12 initial solutions containing between 2 and 80 mmol DOC l^{-1}. The initial solutions were prepared from stock solutions of fulvic acids, stock bulk water-soluble organic matter solutions, and stock organic matter fraction solutions by dilution with a solution adjusted to pH 4.0 using HCl and an ionic strength of 0.002 M using NaCl. A stock solution of the humic acid was prepared by dissolution of the freeze-dried sample in the same solution as used for dilution of the stock solution of the other samples and then diluted to the final concentration. The chosen initial pH is close to the pH at which maximum sorption of organic matter is observed for pure hydrous oxides and soils (Tipping, 1981; Fischer and Buttchereit, 2002). After 8 h shaking at 5 °C, the suspensions were centrifuged at 2000 *g*, the equilibrium solutions were separated from the goethite by filtration through 0.45 μm membranes (Supor-450), and analysed for DOC (see above). Due to the strong dispersion of goethite at high organic C loadings, solu-

tions from these were additionally filtered through polyethersulfone membranes with 0.1 μm pore size (Supor-100, Pall Gelman Science, Ann Arbor, MI) and analysed for DOC. The differences in DOC between the two filtrations proved to be <5%. The 8 h shaking time was sufficient to establish quasi equilibrium conditions and was used to minimise possible microbial degradation of organic matter. The experiments were carried out with four replicates. The variation in the DOC concentrations of the equilibrium solution between replicates was <3%. The results of the sorption experiments were analysed using the Langmuir model:

$$X = \frac{K \cdot Xm \cdot C}{(1 + K \cdot C)}$$

were X is the amount of organic C sorbed (mmol OC kg^{-1}), K represents a constant related to energy of sorption, Xm refers to the sorption maximum of organic C (mmol OC kg^{-1}), and C is the concentration of DOC (mmol l^{-1}) in the equilibrium solution. The sorption isotherms were calculated by fitting the measured data to the Langmuir model using non-linear curve fitting software based on the Marquardt–Levenberg algorithm (SPSS SigmaPlot 7.1, SPSS Inc., Chicago, IL).

3. Results and discussion

3.1. Chemical composition of organic matter

The chemical properties and structural features of the organic materials are summarised in Tables 1–3.

Hydrophilic, non-humic materials contained more O (50–55%) and N (1.7–4.0%) than the hydrophobic, fulvic, and humic acids from soils and bog lake water (O: 39–50%; N: 0.4–1.5%). The fulvic acids derived from brown coal-processing waste water were exceptionally low in O (29%). The hydrophobic, fulvic and humic acids contained more C (43–55%) than hydrophilic organic matter (39–43%). Within the group of XAD-8-adsorbable materials, the fulvic and humic acids tended towards higher C but lower O contents compared to the hydrophobic acids. The contents of S were low for all tested materials except the fulvic acids from brown coal-processing waste water that contained reduced inorganic S. In general, the hydrophilic materials were higher in S than the XAD-8-adsorbable acid fractions.

The total and carboxyl acidity as assessed by titration (Table 1) and the contents of carboxyl C according to ^{13}C NMR spectroscopy (Table 2) were higher in the hydrophobic, fulvic, and humic acids than in hydrophilic materials. This is especially obvious when comparing hydrophilic and hydrophobic materials derived from the same water samples (WÜR, HM, SBR, IS, CE, PI). All three measures of acidity were in agreement

Table 2
Distribution of carbon types of natural organic matter samples as revealed by liquid-state ^{13}C-NMR

Sample[a]	Ketone C 190–220 ppm	Carboxyl C 160–190 ppm	Phenolic C 145–160 ppm	Aromatic C 105–145 ppm	O, N-alkyl C 60–105 ppm	Methoxyl C 55–60 ppm	Alkyl C 0–55 ppm
	(%)						
WÜR HiOM	0	15	0	0	58	3	24
WÜR HoA	4	17	6	25	24	4	20
HM HiOM	1	12	1	5	59	2	20
HM HoA	6	20	5	21	25	3	20
SBR HiOM	0	18	1	6	53	2	20
SBR HoA	5	19	6	24	20	3	23
IS HiOM	0	13	0	7	45	3	32
IS HoA	3	17	6	23	28	3	21
CE HiOM	0	7	1	5	65	3	18
CE HoA	5	19	7	20	26	3	21
PI HiOM	0	11	2	10	63	3	12
PI HoA	5	20	10	23	24	2	15
HO10 FA	4	19	7	26	19	2	23
HO13 FA	6	21	7	26	16	3	21
HO14 FA	5	19	8	25	20	3	20
SV1 FA	4	15	6	31	5	2	37
BS1 FA	4	19	7	27	21	4	18
BS1 HA	4	14	9	29	19	5	20

[a] FA = fulvic acids, HiOM, = hydrophilic organic matter, HA = humic acids, HoA = hydrophobic acids.

with each other. The total and carboxyl acidity according to titration were closely correlated ($r = 0.995$, $P < 0.001$). They were also closely related to the percentage of carboxyl C according to ^{13}C NMR (total acidity: $r = 0.974$, $P < 0.001$; carboxyl acidity: $r = 0.969$, $P < 0.001$). The close relationship between carboxyl C and the total acidity suggests that the difference between total and carboxyl acidity is probably not indicative of phenolic acidity but of carboxyl groups of weaker acidity than those assessed by the titration with Ca acetate. This assumption is in agreement with earlier findings on humic acids extracted from soil under alkaline conditions (Celi et al., 1997).

Similar to the elemental composition, the structural features of hydrophilic, non-humic materials differed greatly from those of the hydrophobic, fulvic, and humic acids. The hydrophilic materials were usually rich in O,N-alkyl C and comprised little to no phenolic and aromatic carbon, which is in agreement with high contents of hydrolysable carbohydrates and low contents of lignin-derived phenolic CuO oxidation products (Table 3). These compositional features fit with previous results obtained for hydrophilic, non-humic organic fractions (Bose and Reckhow, 1998; Kaiser et al., 2001; Jahnel et al., 2002) and may indicate that these fractions were dominated by microbial products and metabolites (Guggenberger et al., 1994; Kaiser et al., 2001). In contrast, the hydrophobic, fulvic, and humic fractions from

Table 3
Contents of total lignin-derived CuO oxidation products (Σ VSC = sum of vanillyl, syringyl, and cinnamyl units) and of total hydrolysable carbohydrates (Σ sugars = sum of neutral and acidic carbohydrates) for organic matter samples

Sample[a]	Σ VSC	Σ sugars
	(mg g^{−1})	
WÜR HiOM	< 0.2	45
WÜR HoA	32.7	11
HM HiOM	< 0.2	42
HM HoA	36.1	13
SBR HiOM	< 0.2	42
SBR HoA	35.4	10
IS HiOM	< 0.2	35
IS HoA	27.0	13
CE HiOM	< 0.2	49
CE HoA	23.3	12
PI HiOM	< 0.2	33
PI HoA	32.1	11
HO10 FA	33.2	13
HO13 FA	35.2	12
HO14 FA	34.6	12
SV1 FA	1.6	< 1
BS1 FA	31.9	12
BS1 HA	34.2	10

[a] FA = fulvic acids, HiOM, = hydrophilic organic matter, HA = humic acids, HoA = hydrophobic acids. Contents refer to ash-free organic matter.

soils and bog water were rich in phenolic and aromatic C and comparably low in O,N-alkyl C, which is in line with low contents of hydrolysable sugars and high contents of phenolic CuO oxidation products (Table 3). This suggests that the XAD-8-adsorbable materials tested largely represent decomposition products of lignin (e.g., Guggenberger et al., 1994; Kaiser et al., 2001). The fulvic acids from brown coal-processing waste water showed a composition distinctly different from the other XAD-8-adsorbable materials and was characterised by a high abundance of alkyl C (Table 2).

3.2. Sorption of organic matter to goethite

Sorption of all tested organic materials to goethite was initially steep, suggesting high affinity interactions between sorbate and sorbent followed by gradual approach to a maximum (Fig. 1). Consequently, the sorption data could be adequately modelled by the Langmuir approach (Table 4).

The hydrophilic organic matter always showed a far weaker sorption to goethite than the hydrophobic, fulvic, and humic acids (Fig. 1, Table 4). This finding is in good agreement with previous observations indicating that the hydrophilic, non-humic materials seem to sorb more weakly to hydrous oxides than XAD-8-adsorbable compounds (e.g., Kaiser and Zech, 1997; Bose and Reckhow, 1998). The latter may outcompete hydrophilic organic matter in the sorption to hydrous oxides when present in the same solution and even replace hydrophilic organic matter already sorbed to mineral surfaces (Kaiser and Zech, 1997). The strong sorption of the
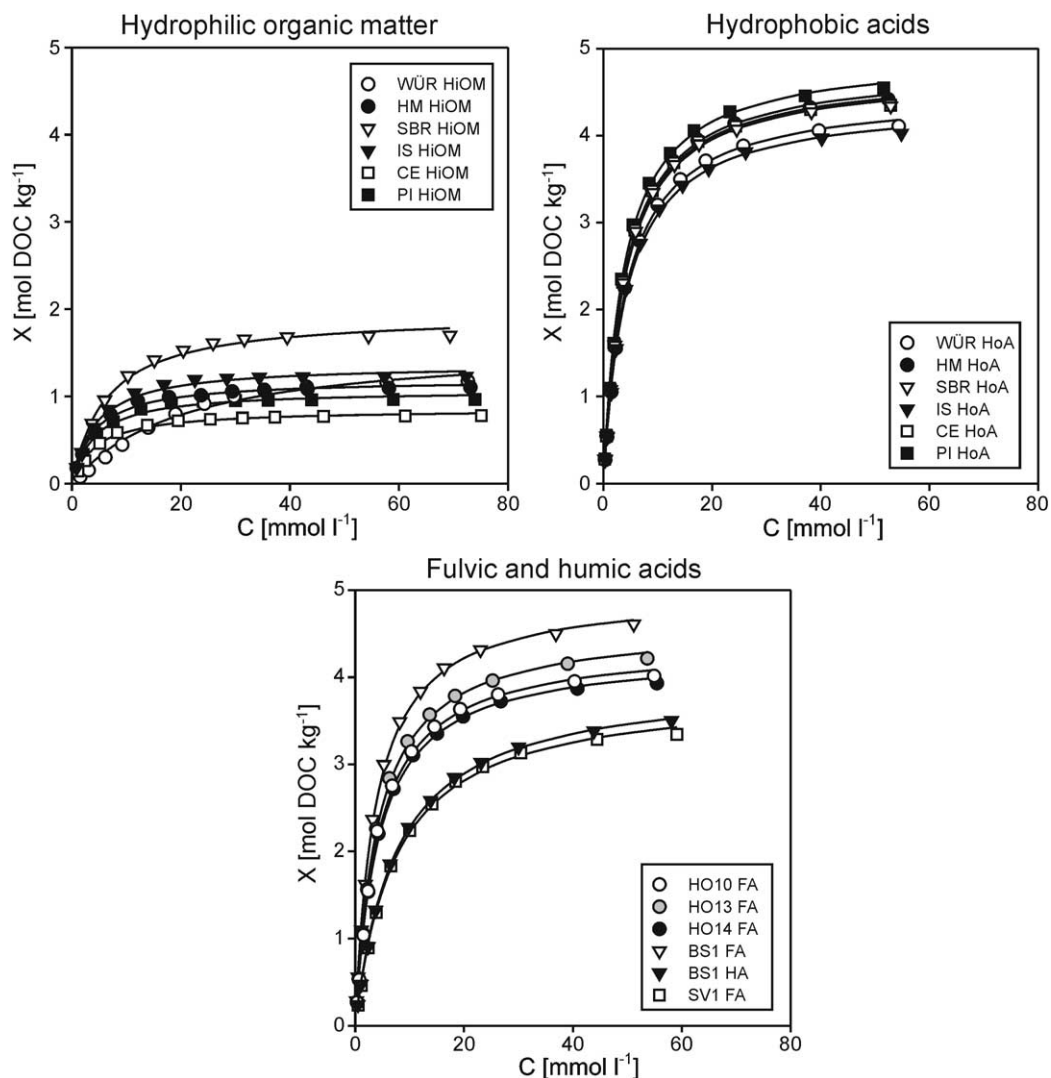

Fig. 1. Sorption of hydrophilic organic matter (HiOM), hydrophobic acids (HoA), and fulvic and humic acids (FA, HA) on goethite. Symbols represent the means of four replicates and lines non-linear fits according to Langmuir model.

Table 4
Langmuir isotherm parameters of sorption of natural organic matter (as organic carbon, OC) to goethite. Corrected correlation coefficient refers to agreement between measured and fitted data

Sample	K	Xm		r^2
		(mol OC kg^{-1})	(mg OC m^{-2})	
WÜR HiOM	0.05	1.61	0.41	0.984
WÜR HoA	0.24	4.50	1.15	0.998
HM HiOM	0.24	1.19	0.30	0.987
HM HoA	0.26	4.80	1.23	0.999
SBR HiOM	0.16	1.94	0.50	0.991
SBR HoA	0.25	4.74	1.21	0.999
IS HiOM	0.23	1.36	0.35	0.985
IS HoA	0.24	4.41	1.13	0.998
CE HiOM	0.23	0.85	0.22	0.988
CE HoA	0.26	4.76	1.22	0.998
PI HiOM	0.24	1.07	0.27	0.980
PI HoA	0.27	4.99	1.28	0.999
HO10 FA	0.23	4.40	1.12	0.998
HO13 FA	0.24	4.62	1.18	0.999
HO14 FA	0.23	4.30	1.10	0.998
SV1 FA	0.14	3.85	0.98	0.998
BS1 FA	0.27	4.99	1.28	0.999
BS1 HA	0.14	3.98	1.02	1.000

hydrophobic fraction is likely to result from the presence of aromatic acid structures derived from lignin decomposition products that accumulate within the XAD-8 adsorbable fractions (e.g., Jekel, 1986; Kaiser et al., 1997).

Within the group of hydrophilic organic matter samples and among the hydrophobic acids, the variation in sorption was relatively small (Fig. 1, Table 4) although the materials derived from different sources had differing chemical compositions (Tables 1–3). This contrasts with

the observations made by Moore and Matos (1999) who found large variations in the sorption of dissolved organic matter and dissolved organic matter fractions that originated from the litter of different tree species. A plausible reason for the contrasting results cannot be given here.

Within the fulvic and humic acids, those fulvic acids deriving from bog lake and soil seepage water showed similar sorption to goethite (Fig. 1, Table 4). Also the sorption of these samples was largely similar to the sorption of the hydrophobic acids. The humic acids from soil seepage water and the fulvic acids from the brown coal processing waste water sorbed more weakly than the rest of the fulvic acids and the hydrophobic acids. The samples were the richest in aromatic and alkyl C (Table 2). Thus, aromatic and aliphatic structures alone probably have little influence on the sorption of organic matter to mineral surfaces. Preferential exclusion of alkyl C has been observed for sorptive interaction of natural organic matter with hydrous oxides (McKnight et al. 1992, 2002; Kaiser et al., 1997). Aromatic moieties have so far been recognised as structural units strongly involved in the sorption of organic matter to hydrous oxides, most likely because of carboxyl and other functional groups attached to them (Jekel, 1986; Gu et al., 1994, 1995; Kaiser et al., 1997).

Of the two parameters of the Langmuir isotherm, the sorption maximum Xm represented the difference in the sorption of hydrophilic organic matter and the XAD-8-adsorbable acids much better than the distribution coefficient K which was often similar (Table 4).

3.3. Correlation between sorption and composition of organic matter

The sorption maxima of XAD-8-adsorbable acids and of hydrophilic organic matter showed a positive and
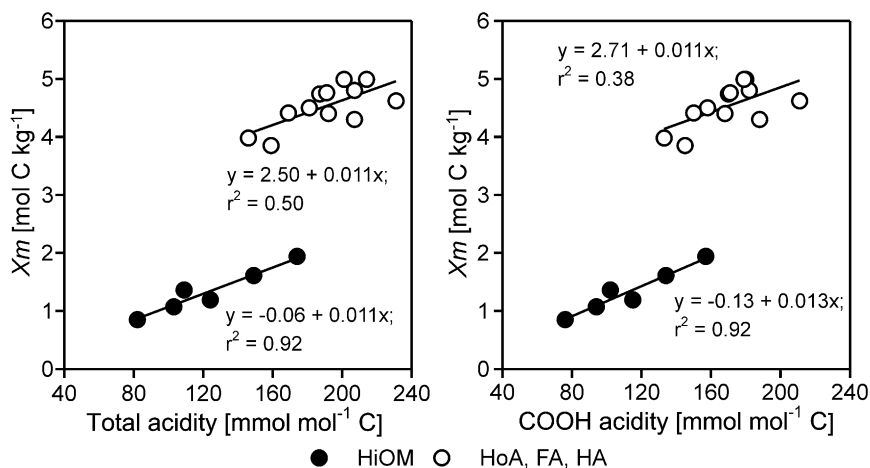
Fig. 2. Relationship between sorption maximum according to Langmiur model and total and carboxyl (COOH) acidity of hydrophilic organic matter (HiOM), hydrophobic acids (HoA), and fulvic and humic acids (FA, HA).

linear correlation with the total and the carboxyl acidity, indicating that the content of acidic functional groups is likely to be the major determinant for the sorptive interactions of all organic matter fractions with hydrous oxide surfaces (Fig. 2). Although the relationships between the sorption maxima and the measures

for acidity had comparable slopes for the XAD-8-adsorbable acids and the hydrophilic organic matter, the intercepts were different.

Similar to the results for total and carboxyl acidity, the sorption maxima of XAD-8-adsorbable acids and of hydrophilic organic matter increased linearly with

Fig. 3. Relationship between sorption maximum according to Langmiur model and different C types according to liquid-state ^{13}C NMR of hydrophilic organic matter (HiOM), hydrophobic acids (HoA), and fulvic and humic acids (FA, HA).
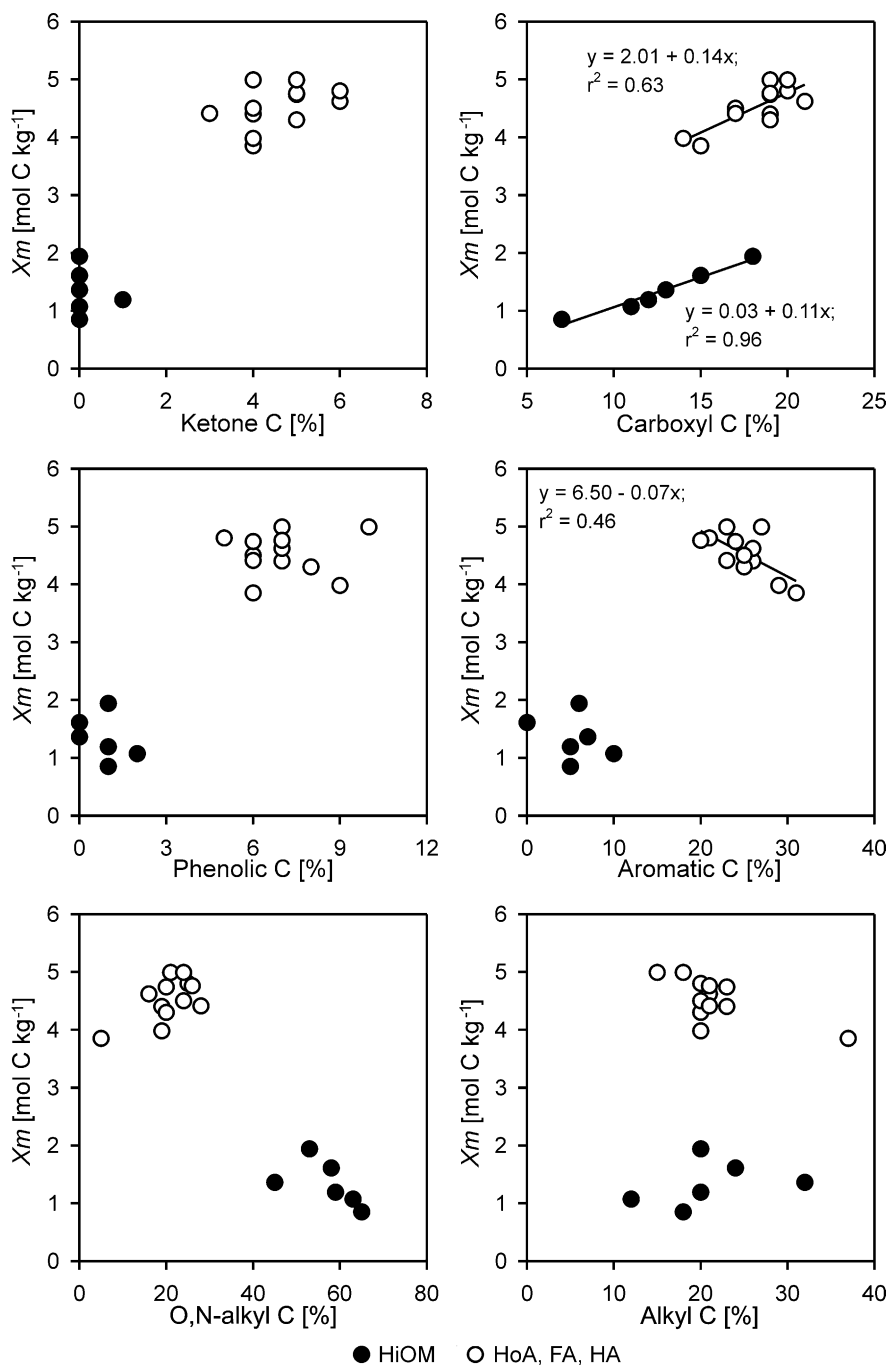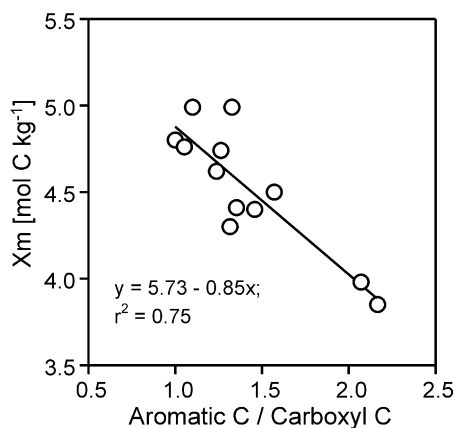
Fig. 4. Relationship between sorption maximum according to Langmiur model and ratio of carboxyl C to aromatic C as revealed by liquid-state ^{13}C NMR of hydrophobic acids (HoA), and fulvic and humic acids (FA, HA).

increasing content of carboxyl C as revealed by ^{13}C NMR (Fig. 3). Again, the relationships between the sorption maxima and carboxyl C for XAD-8-adsorbable acids and hydrophilic organic matter had comparable slopes but different intercepts. Thus, properties other than the content of acidic functional groups seem to be responsible for the different sorption of the XAD-8-adsorbable acids and of hydrophilic organic matter.

The major difference in the chemical composition between XAD-8-adsorbable acids and hydrophilic organic matter is the absence or low level of aromatic structures in the latter. This and the preferential sorption of aromatic and carboxyl C from XAD-8-adsorbable fractions of soil and aquatic NOM (McKnight et al., 1992, 2002; Kaiser et al., 1997) suggest that acidic groups attached to aromatic structures have a stronger affinity for the surface of goethite than the acidic groups of hydrophilic organic matter. A possible reason for the stronger binding capability of aromatic acids as compared with other organic acids is their strong acidity (e.g., Edwards et al., 1996), which agrees with the larger apparent acidity constants of hydrophilic acids as compared with hydrophobic ones (Dai et al., 1996).

The sorption maxima of XAD-8-adsorbable acid fractions were negatively correlated with aromatic C (Fig. 3), which would contradict the assumption of aromatic acid structures controlling the sorption of organic matter to hydrous oxides (Jekel, 1986; Gu et al., 1994; 1995; Kaiser et al., 1997). The correlation, however, was likely the result of the strong negative correlation between carboxyl and aromatic C within this group of samples ($r = 0.827$, $P < 0.01$). Moreover, the relationship strongly depended on two samples rich in aromatic C and low in carboxyl C, BS1 HA and SV1 FA. Exclusion of these two samples from the regression analysis resulted in the negative correlation disappearing. An

explanation for the lack of a clear relationship between aromatic C and the sorption of XAD-8-adsorbable acids is probably that the 105–145 ppm region of ^{13}C NMR includes various aromatic functionalities of different reactivity, depending on their origin. Phenols and aromatic acids derived from lignin may contribute more strongly to the sorption to the goethite surface that is positively charged at the experimental pH than do condensed aromatics formed by thermal processes. However, the sorption maxima were not, or only weakly, correlated with phenolic C (Fig. 3) and the sum of CuO oxidation products ($r = 0.126$, $P > 0.05$, excluding SV1 FA).

The sorption maxima of XAD-8-adsorbable acid fractions related, however, negatively to the ratios of aromatic C to carboxyl C (Fig. 4). The sorption of XAD-8-adsorbable acids to goethite, therefore, likely increased with the number of acidic groups attached per aromatic structure. This assumption agrees with the finding that the sorption of benzene carboxylic acids to goethite increases with the number of carboxyl functional groups (Evanko and Dzombak, 1998). The dependence of the sorption of XAD-8-adsorbable acids on the ratios of aromatic C to carboxyl C may also be seen in the light of an increasing probability of functional groups in *ortho* positions. Among aromatic compounds, those with functional groups attached to the aromatic ring in *ortho* positions have the strongest affinity for the surfaces of Al and Fe oxides (Evanko and Dzombak, 1998; Gu et al., 1994, 1995).

Other C moieties were neither negatively nor positively correlated with the sorption maxima and, thus, seem not to control the sorption of organic matter to hydrous oxides. However, this does not rule out the possibility that certain C moieties might be discriminated against in the sorption process, as has been shown for alkyl C (McKnight et al., 1992, 2002; Kaiser et al., 1997).

4. Conclusions

The study shows that the sorption of organic matter to oxide surfaces such as those of goethite are controlled by the chemical composition of the organic matter. Hydrophilic materials mainly composed of carbohydrates and low in acidic groups and aromatic structures sorb much more weakly than hydrophobic organic matter rich in acidic groups and aromatic C, probably due to the presence of aromatic acids derived from lignin. Within the two types of organic matter, hydrophilic and hydrophobic fractions, the amount of acidic functional groups controls the extent of the sorption. Sorption of the hydrophobic fraction related inversely to the ratio of aromatic to carboxyl C, indicating that the number (and possibly position) of acidic groups

attached to aromatics might be crucial for the interaction of these compounds with goethite and other hydrous oxides.

The sorption of the two major fractions of organic matter, hydrophilic materials rich in carbohydrates and hydrophobic materials, including fulvic and humic acids, depends on their acidity. This supports recent approaches to estimating and modelling sorption of bulk dissolved organic matter based on acidity. Nevertheless, the two fractions sorb differently. Treating them separately in models may therefore improve prognosis of the sorption and transport of dissolved organic matter in soils and sediments, at least where the hydrophilic fraction is prominent.

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