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Sorptive stabilization of organic matter by amorphous Al hydroxide

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Abstract

Amorphous Al hydroxides (am-Al(OH)₃) strongly sorb and by this means likely protect dissolved organic matter (OM) against microbial decay in soils. We carried out batch sorption experiments (pH 4.5; 40 mg organic C L⁻¹) with OM extracted from organic horizons under a Norway spruce and a European beech forest. The stabilization of OM by sorption was analyzed by comparing the CO₂ mineralized during the incubation of sorbed and non-sorbed OM. The mineralization of OM was evaluated based in terms of (i) the availability of the am-Al(OH)₃, thus surface OM loadings, (ii) spectral properties of OM, and (iii) the presence of phosphate as a competitor for OM. This was done by varying the solid-to-solution ratio (SSR = 0.02–1.2 g L⁻¹) during sorption. At low SSRs, hence limited am-Al(OH)₃ availability, only small portions of dissolved OM were sorbed; for OM from Oa horizons, the mineralization of the sorbed fraction exceeded that of the original dissolved OM. The likely reason is competition with phosphate for sorption sites favouring the formation of weak mineral–organic bindings and the surface accumulation of N-rich, less aromatic and less complex OM. This small fraction controlled the mineralization of sorbed OM even at higher SSRs. At higher SSRs, i.e., with am-Al(OH)₃ more available, competition of phosphate decreased and aromatic compounds were sorbed selectively, which resulted in pronounced resistance of sorbed OM against decay. The combined OC mineralization of sorbed and non-sorbed OM was 12–65% less than that of the original DOM. Sorbed OM contributed only little to the overall OC mineralization. Stabilization of OC increased in direct proportion to am-Al(OH)₃ availability, despite constant aromatic C (~30%). The strong stabilization at higher mineral availability is primarily governed by strong Al–OM bonds formed under less competitive conditions. Due to these strong bonds and the resulting strong stabilization, the surface loading, a proxy for the mineral's occupation by OM, was not a factor in the mineralization of sorbed OM over a wide range of C sorption (0.2–1.1 mg C m⁻²). This study demonstrates that sorption to am-Al(OH)₃ results in stabilization of OM. The mineral availability as well as the inorganic solution chemistry control sorptive interactions, thereby the properties of sorbed OM, and the stability of OM against microbial decay.

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1. INTRODUCTION

Dissolved organic matter (OM) produced in the forest floor contributes much to the organic C (OC) input to the mineral soil. About 115–500 kg C ha⁻¹ a⁻¹ enter the mineral subsoil with dissolved OM, of which 40–370 kg C ha⁻¹ a⁻¹ are retained, presumably mostly by sorption to soil minerals (Michalzik et al., 2001; Guggenberger and Kaiser, 2003).

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There are indications that besides Fe (hydr)oxides also Al-containing phases contribute to organic matter stabilization against microbial decay in deeper soil horizons (e.g., Kaiser and Guggenberger, 2000). Reactive Al in acidic soils may exist in the form of poorly crystalline allophane- and imogolite-type mineral phases (e.g., Gustafsson et al., 1999). In this study we used amorphous Al(OH)₃ as a surrogate for such reactive Al-containing phases in terms of OM binding and effects on stabilization.

Sorption of OM to mineral surfaces is considered to be an important process in the stabilization of soil OC (Boudot, 1992; Kaiser and Guggenberger, 2000, 2007; Kalbitz et al., 2005). Strong correlations between indicators of am-Al(OH)₃ and OC (Kaiser and Guggenberger, 2000) suggest a sorptive control on OM stabilization but little is known about the role of am-Al(OH)₃ in organic matter stabilization against microbial decay.

Aluminium hydroxides have points of zero charge between 5.0 and 9.4 (Hsu, 1989). At pH values common in acidic soils (~3.5–4.5), their surfaces are largely protonated, and thus feature positive charge. As a result, surface complexation of negatively charged functional groups of OM (e.g., carboxyl and phenolic OH groups) is the predominant binding mechanism (Mikutta et al., 2007). Besides electrostatic attraction and surface complexation (i.e., ligand exchange), OM can interact with mineral surfaces by a variety of other mechanisms (hydrogen bonding, van der Waals interactions, and cation bridging). Ligand exchange appears to be the most efficient in stabilizing OM against microbial decay (Mikutta et al., 2007).

The stability of mineral-attached OM against microbial decay may depend on (i) the availability of mineral surfaces during sorption, (ii) the structural properties of dissolved OM, and (iii) the presence of inorganic solutes competing with OM for sorption sites.

In batch sorption experiments, mineral surfaces are initially OM-free and easily accessible to OM. This is not, however, the correct representation of soil environments, where the accessibility of mineral surfaces for OM might be restricted either by organic coatings or by aggregation. A better simulation of the situation in soils can be achieved by decreasing the solid–solution ratio (SSR) in sorption experiments, which limits the availability of mineral surfaces for OM and thereby potentially increases the OC loading of the mineral. Kaiser and Guggenberger (2007) found that OM bound tightly to goethite at lower surface OC loading (0.9 mg OC m⁻²) was more resistant against treatment with an oxidizing reagent (NaOCl) than OM bound more loosely at higher surface loading (1.9 mg OC m⁻²). It seems that the fraction of stabilized OM increases as a function of available mineral surfaces, or, in other words, at higher SSR, thus lower OC loadings (Baldock and Skjemstad, 2000; Kaiser and Guggenberger, 2003). We therefore expect increasing biological mineralization of sorbed OM with increasing surface OC loading (at lower SSR). Decreasing the availability of mineral surfaces (at lower SSR) will also increase the competition of OM with inorganic solutes. Phosphate in particular outcompetes OM for sorption sites and even causes desorption of attached OM due to its ability to form strong bonds with oxidic mineral surfaces (Van Hees et al., 2003; Guan et al.,

2006). Phosphate can occupy surface hydroxyl sites, which results in less stable mineral–organic associations (Mikutta et al., 2007). Competition effects are more likely at lower SSR because of the limited number of sorption sites; however, such effects are often not considered in experiments utilizing natural OM solutions, which can contain high concentrations of oxyanions.

Different components of dissolved OM vary in their affinity for hydrous mineral surfaces. Aromatic acids are preferentially sorbed because of their capability to form strong surface complexes (Kaiser and Guggenberger, 2000; Kalbitz et al., 2005). The abundance of aromatic moieties in the soil solution might be decisive for the proportion of OM being sorbed. Such compounds also exhibit a high intrinsic stability against microbial decay (Qualls and Haines, 1992; Jandl and Sollins, 1997; Jandl and Sletten, 1999). Yet, it remains unclear if the observed sorptive stabilization of OM is mainly due to the selective sorption of recalcitrant compounds and/or due to the formation of strong chemical bonds between OM and mineral surfaces (Kalbitz et al., 2005). Although the sorption of OM to soil minerals can result in reduced mineralization of the sorbed fraction (Jones and Edwards, 1998; Kalbitz et al., 2005; Mikutta et al., 2007), the stability of the non-sorbed DOM has not been addressed so far. The sorptive uptake of dissolved OC can range from 1% to 86% (Kaiser et al., 1996), illustrating that the non-sorbed OC can be an important fraction. Therefore, assessment of the overall effect of sorption on OM stabilization has to consider the non-sorbed fraction as well.

In this study, we determined to what extent sorption to am-Al(OH)₃ can stabilize OM of different origin against aerobic microbial decay. As main factors, we investigated (i) mineral availability and thereby surface loading of the am-Al(OH)₃ with OM, (ii) the chemical composition of OM, and (iii) the presence of phosphate as an inorganic competitor of OM sorption and stabilization. The stabilization effect was addressed by incubation of both sorbed and non-sorbed OM.

2. MATERIALS AND METHODS

2.1. General approach

In our experiments we reacted four different types of OM with am-Al(OH)₃ and determined the overall stabilization of sorption by assessing the mineralization of sorbed and, for the first time, also of non-sorbed OM. Overall stabilization is given when the combined amount of C mineralized is smaller than that of the initial OM. The differential availability of mineral surfaces in soil was investigated at different solid-to-solution ratios (SSR), i.e., surface OC loadings. By decreasing the sorbent's concentration, we expect the surface OC loadings to increase and a smaller OC fraction to be sorptively removed from solution because of less available sorption sites. This novel approach allows for simulating a situation where the access of OM to mineral surfaces is limited. We rationalize that under such conditions, competition between OM and inorganic anions, i.e., phosphate, becomes stronger, thereby affecting the sorption

and subsequent stabilization of OM. The adsorption of phosphate was, therefore, monitored as well. Finally, we analyzed the spectral properties of OM before and after sorption to relate the structural properties and stabilization.

2.2. Preparation of OM solutions

We used samples from Oi and Oa horizons of a Norway spruce (*Picea abies*) and a European beech (*Fagus sylvatica*) forest and deionized water to prepare extracts at a soil-to-water ratio of 1:10. After 24 h of equilibration, solutions were filtered through ceramic filter plates preconditioned with the respective OM solution, and then through 0.2- μm membrane filters (OE 66, Whatman GmbH, Dassel, Germany). Details on the test Oi and Oa horizons and the extraction procedure are given in Scheel et al. (2007). The solutions were diluted with deionized water to about 40 mg C L⁻¹. The solutions differed in their inherent phosphate concentrations, ranging between 2.1 and 5.1 mg L⁻¹. All preparation steps were conducted at 5 °C in an air-conditioned chamber. The diluted solutions are referred to as ‘spruce Oi solution’, ‘spruce Oa solution’, ‘beech Oi solution’ and ‘beech Oa solution’. Properties of the solutions are given in Table 1.

2.3. Preparation of amorphous Al hydroxide

Amorphous Al(OH)₃ was precipitated by slowly neutralizing a solution of 2 M AlCl₃ with NaOH. The precipitate was washed with deionized water, and then freeze-dried. The specific surface area (SSA) of the product was analyzed by adsorption of N₂ at -196 °C, with a Nova 2010 surface area analyser (Quantachrome Corp., Boynton Beach, FL, USA). We estimated the SSA by applying the Brunauer–Emmett–Teller equation to the N₂ sorption data in the P/P_0 range of 0.05 to 0.3 (Brunauer et al., 1938). Prior to measurement, duplicate samples were preconditioned under vacuum (10⁻³ mbar) for 48 h at 40 °C. The synthesized am-Al(OH)₃ had a SSA of 107 m² g⁻¹. The amorphous structure of Al(OH)₃ has been confirmed by X-ray diffraction (D5000, Siemens AG/Bruker AXS, Karlsruhe, Germany).

2.4. Sorption experiments

Sorption experiments were carried out in triplicates at seven different solid-to-solution ratios (SSR), ranging from 0.02 to 1.2 g L⁻¹ (Table 2). These ratios were chosen to obtain a gradient in mineral surface availability and to ensure reliable analysis of the mineralization of sorbed OM. The pH of the solutions was adjusted to 4.5 before sorption by adding NaOH or HCl. After 18 h shaking at 5 °C in the dark, the suspensions were filtered through 0.4- μm polycarbonate membranes (HTTP 04700, Millipore Inc., Bedford, MA, USA). The am-Al(OH)₃ with sorbed OM, collected on the filters, and the filtrates (containing the non-sorbed OM) were then used for the incubation experiment.

The amount of OC sorbed was calculated as the difference between the solution OC concentrations before and after sorption. At low SSR (0.02–0.08 g L⁻¹), this was not feasible because of the very small change in solution OC. In these cases, we calculated the amount of sorbed OC by summing up the three OC fractions at the end of the mineralization experiment (see below): mineralized OC as calculated from CO₂ measurements, OC concentration in solution after incubation, and sorbed OC remaining on am-Al(OH)₃ after incubation (CNS analyser, Vario EL, Elementar GmbH, Hanau, Germany). This approach was verified by comparing, where possible, the variability of sorbed OC calculated by the two methods. Statistical analysis (univariate ANOVA) suggested that the results of the two approaches did not differ significantly.

2.5. Incubation experiments

The polycarbonate filters with the am-Al(OH)₃–OM associations produced in the sorption experiments were placed into incubation flasks (120 mL). Fifty nine mL of an incubation solution, prepared from ultrapure water and analytical grade NH₄NO₃ and K₂HPO₄ (Merck AG, Darmstadt, Germany), containing in total 0.4 mg N, 0.3 mg P and 0.8 mg K, were added. We did not vary the added amounts of N, P and K between the different samples but added enough nutrients to avoid limitations to degradation of samples

Table 1
Properties of the used forest floor solutions.

Solution	Spruce Oa	Beech Oa	Spruce Oi	Beech Oi
Organic C (mg OC L ⁻¹)	39.4	35.3	39.2	38.8
Aromatic C (% of OC)	31.1	22.1	7.3	10.4
Carboxyl C (% of OC) ^a	24.6	22.7	14.6	17.7
Total N (mg L ⁻¹)	2.4	5.3	4.0	3.7
NO ₃ -N (mg L ⁻¹)	0.1	1.1	0.1	nd
NH ₄ -N (mg L ⁻¹)	0.8	2.4	0.5	0.6
Total Al (mg L ⁻¹)	0.4	0.2	nd	nd
Ca ²⁺ (mg L ⁻¹)	0.3	1.7	0.8	1.4
SO ₄ ²⁻ (mg L ⁻¹) ^b	1.3	1.3	0.8	0.6
H ₂ PO ₄ ⁻ (mg L ⁻¹)	2.1	5.1	5.1	4.4

nd, not detectable.

^a Determined by solution ¹³C NMR, data from Scheel et al. (2007).

^b Data from Scheel et al. (2007).

Table 2

Sorption of organic matter and phosphate to amorphous Al(OH)₃ (am-Al(OH)₃) at different solid-to-solution ratios (SSR). Dissolved organic matter (DOM) solutions extracted from the four forest floor samples and adjusted to 40 mg organic carbon (OC) L⁻¹. Numbers given represent means and standard errors of three replicates.

Added am-Al(OH) ₃ (g)	0.015	0.015	0.015	0.030	0.060	0.120	0.240
DOM solution (L)	0.8	0.4	0.2	0.2	0.2	0.2	0.2
SSR ^a (g L ⁻¹)	0.02	0.04	0.08	0.15	0.30	0.60	1.20
Spruce Oa							
Total C added (mg)	31.5	15.8	7.9	7.9	7.9	7.9	7.9
C removed (%)	4.2 ± 0.1	6.4 ± 0.4	15.4 ± 0.7	28.1 ± 1.2	72.8 ± 0.8	87.4 ± 0.3	89.4 ± 0.2
C sorbed (mg)	1.33 ± 0.02	1.01 ± 0.06	1.21 ± 0.05	2.21 ± 0.09	5.73 ± 0.06	6.88 ± 0.02	7.04 ± 0.02
C loading (mg C m ⁻²)	0.83 ± 0.01	0.63 ± 0.04	0.75 ± 0.03	0.69 ± 0.03	0.89 ± 0.01	0.53 ± 0.00	0.27 ± 0.00
P loading (mg P m ⁻²)	0.10 ± 0.00	0.09 ± 0.00	0.07 ± 0.00	0.04 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Molar (P/C) _{sorbed}	0.05	0.06	0.04	0.02	0.01	0.01	0.01
Beech Oa							
Total C added (mg)	28.2	14.1	7.1	7.1	7.1	7.1	7.1
C removed (%)	6.7 ± 0.2	9.2 ± 0.3	12.2 ± 0.6	16.0 ± 1.4	41.6 ± 1.3	69.7 ± 0.3	75.7 ± 0.3
C sorbed (mg)	1.88 ± 0.06	1.30 ± 0.05	0.86 ± 0.04	1.13 ± 0.10	2.93 ± 0.09	4.91 ± 0.02	5.34 ± 0.02
C loading (mg C m ⁻²)	1.17 ± 0.04	0.81 ± 0.03	0.54 ± 0.03	0.35 ± 0.03	0.46 ± 0.01	0.38 ± 0.00	0.21 ± 0.00
P loading (mg P m ⁻²)	0.19 ± 0.00	0.16 ± 0.00	0.13 ± 0.00	0.09 ± 0.00	0.05 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
Molar (P/C) _{sorbed}	0.06	0.08	0.09	0.10	0.04	0.02	0.02
Spruce Oi							
Total C added (mg)	31.4	15.7	7.8	7.8	7.8	7.8	7.8
C removed (%)	1.8 ± 0.1	3.4 ± 0.0	7.7 ± 0.3	12.0 ± 0.6	26.4 ± 0.7	36.2 ± 0.4	42.2 ± 0.1
C sorbed (mg)	0.57 ± 0.03	0.54 ± 0.00	0.60 ± 0.02	0.94 ± 0.05	2.07 ± 0.05	2.84 ± 0.03	3.31 ± 0.01
C loading (mg C m ⁻²)	0.36 ± 0.02	0.34 ± 0.00	0.38 ± 0.01	0.29 ± 0.01	0.32 ± 0.01	0.22 ± 0.00	0.13 ± 0.00
P loading (mg P m ⁻²)	0.15 ± 0.00	0.13 ± 0.01	0.13 ± 0.00	0.10 ± 0.00	0.05 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
Molar (P/C) _{sorbed}	0.16	0.15	0.13	0.13	0.06	0.04	0.03
Beech Oi							
Total C added (mg)	31.0	15.5	7.8	7.8	7.8	7.8	7.8
C removed (%)	3.5 ± 0.0	5.3 ± 0.2	10.2 ± 1.1	23.2 ± 0.4	40.4 ± 1.2	49.9 ± 0.3	55.2 ± 0.3
C sorbed (mg)	1.08 ± 0.01	0.82 ± 0.03	0.79 ± 0.09	1.80 ± 0.03	3.13 ± 0.10	3.87 ± 0.03	4.29 ± 0.02
C loading (mg C m ⁻²)	0.67 ± 0.01	0.51 ± 0.02	0.49 ± 0.05	0.56 ± 0.01	0.49 ± 0.01	0.30 ± 0.00	0.17 ± 0.00
P loading (mg P m ⁻²)	0.14 ± 0.01	0.14 ± 0.00	0.12 ± 0.00	0.09 ± 0.00	0.04 ± 0.00	0.02 ± 0.00	0.01 ± 0.00
Molar (P/C) _{sorbed}	0.08	0.11	0.09	0.06	0.03	0.03	0.02

^a Solid-to-solution ratio.

with the highest C contents. All incubation solutions were adjusted to pH 4.5 by adding HCl or NaOH. Then, 1 mL of an inoculum was added to each flask. The inoculum was obtained by extracting spruce and beech Oa material (each pre-equilibrated at 20 °C for 14 days at 60% water capacity) with 4 mM CaCl₂ solution (SSR = 0.5 g mL⁻¹). After 30 min of shaking, the suspensions were filtered through 5-µm filters (Millipore SMWP 4700) and combined.

After adding the inoculum the incubation flasks were sealed air tight with a septum and gas samples were taken with a syringe in order to measure the CO₂ concentration in the headspace. To avoid small scale O₂ limitations, flasks were shaken manually each day of measurement and incubated in the dark at 20 °C for 60 days. The CO₂ concentration in the headspace of each flask was determined at increasing intervals ranging from 2 days at the beginning to 21 days towards the end of the experiment (Scheel et al., 2007), using a gas chromatograph (HP 6890, with thermal conductivity detector; Agilent GmbH, Böblingen, Germany). Within the 60 day period, CO₂ evolution decreased until no further mineralization occurred. Maximum CO₂ concentrations in the headspace during the incubation did not exceed 1.7%. At the end of incubation, we measured

the OC concentration of a 40 mL solution aliquot with a TOC analyser (Elementar HighTOC) as well as the C and N content of the freeze-dried solids (Elementar Vario EL CNS analyzer). The pH recorded immediately after the end of the 60 days incubation was used to calculate the fraction of CO₂ dissolved in the incubation solution.

The total amount of OC incubated ranged from about 0.25 to 7 mg per flask. The OM remaining in solution after each sorption experiment was incubated as well with the same amounts of nutrients (0.4 mg N, 0.3 mg P and 0.8 mg K), added with a highly concentrated solution, and the same volume of inoculum. As controls, we incubated the original spruce Oa, beech Oa, spruce Oi and beech Oi solutions ('original OM'; 2.4 mg C per flask), the OM-free am-Al(OH)₃, deposited onto a polycarbonate filter, and an OM-free nutrient solution. The controls were all spiked with the inoculum. The OC added with the inoculum represented 0.05–2% of the total C in the incubation flasks. This small extra C should not affect the fate of the sorbed OM and the small amounts of CO₂ derived from the inoculum were subtracted from the samples.

Applying the same incubation method to all types of samples (original solution OM, OM sorbed to am-Al(OH)₃,

non-sorbed OM) enabled us to calculate the overall stabilizing effect of sorption, i.e., changes in C mineralized from sorbed and non-sorbed OM in comparison to the original OM. An alternative would be the incubation of sorbed OM in solid rather than in immersed forms, at certain water content, which is closer to field conditions. However, results might then be affected by differences in the incubation methods. On the other hand, the immersed incubation of mineral-bound OM differs from conditions in soil because it promotes desorption and subsequent mineralization (Mikutta et al., 2007). Therefore, overall stabilization as determined here represents a conservative estimate.

2.6. Possible toxic effects of dissolved Al^{3+} on OC mineralization

Concentrations of total Al (Al_{tot}) in solution after sorption were low ($<3.3 \text{ mg L}^{-1}$), indicating that maximally 2 wt.% of am- $\text{Al}(\text{OH})_3$ dissolved under the experimental conditions. After 60 days of incubation, Al_{tot} concentrations increased in all samples containing am- $\text{Al}(\text{OH})_3$. Aluminium might be toxic to some soil microorganisms at concentrations as low as $50 \mu\text{M}$ (Pina and Cervantes, 1996); other species can survive concentrations of 100–200 mM Al (Kawai et al., 2000; Zhang et al., 2002). The toxicity of Al to microorganisms is mainly caused by monomeric Al species (e.g., Al^{3+}), whereas organically complexed Al is generally assumed to be non-toxic (Illmer and Mutschlechner, 2004). We calculated the contribution of Al^{3+} to Al_{tot} to test if the observed reduction in mineralization could partly be explained by the effects of toxic Al^{3+} . We calculated concentrations of free Al^{3+} based on Al_{tot} , P concentrations, and solution pH at the end of the incubation, using the chemical equilibrium model Visual MINTEQ vers. 2.53 (<http://www.lwr.kth.se/English/OurSoftware/vminteq/>).

For samples with $0.6 \text{ g Al}(\text{OH})_3 \text{ L}^{-1}$, the Al^{3+} concentrations after 60 days of incubation increased to $3.7\text{--}2.4 \text{ mg L}^{-1}$; for the samples with a SSR of $1.2 \text{ g Al}(\text{OH})_3 \text{ L}^{-1}$, values were $41.2\text{--}59.6 \text{ mg L}^{-1}$. In similar incubation experiments, Scheel et al. (2008a) did not find toxic effects of Al^{3+} up to 12 mg L^{-1} at pH values of 3.8 and 4.5. Thus, we cannot exclude Al^{3+} toxicity being partly responsible for observed reduction in OC mineralization in samples with SSR of 1.2 g L^{-1} . However, for all other samples, with SSR between 0.02 and $0.3 \text{ g Al}(\text{OH})_3 \text{ L}^{-1}$, the calculated Al^{3+} concentrations at the end of incubation were $<2 \text{ mg L}^{-1}$. Here, OC mineralization of sorbed OM was low or even lower than in the samples comprising higher dissolved Al (see Section 3), thus toxic effects of Al^{3+} are unlikely.

2.7. Other analytical methods

The OM solutions and filtrates were analyzed for total OC and total N (Elementar HighTOC), NO_3^- and PO_4^{3-} (ion chromatography, DX 100, Dionex, Idstein, Germany), NH_4^+ (photometric, flow injection analyser (FIA), Medizin- und Labortechnik Engineering GmbH, Dresden, Germany), total Ca and Al (ICP-OES, Vista-Pro radial,

Varian, Darmstadt, Germany), and pH (potentiometric, pH 323, WTW, Weilheim, Germany).

Solutions for spectral measurements were immediately frozen after sampling. The OC content of these solutions was adjusted to 10 mg L^{-1} before analyses to ensure comparability of all OM samples. The specific UV absorbance at 280 nm of the OM solutions before and after sorption was determined (UVIKON 930, BIO-TEK Instruments, Bad Friedrichshall, Germany) as an estimate for the aromaticity of OM (Traina et al., 1990; Kalbitz et al., 2003a). Scheel et al. (2007) found a linear relationship between UV absorbance at 280 nm and the aromatic C content as revealed by ^{13}C nuclear magnetic resonance spectroscopy. We used changes in UV absorbance after contact to the mineral phase to calculate the aromatic C content of the sorbed OM.

Emission fluorescence spectra were recorded at an excitation wavelength of 254 nm (SFM 25, BIO-TEK Instruments, Bad Friedrichshall, Germany). We calculated the humification index (HIX) as $\text{HIX} = (I_{435-480 \text{ nm}})/(I_{300-345 \text{ nm}})$ where I corresponds to the integrated emission of the fluorescence spectra in the given wavelength range (Zsolnay et al., 1999). The UV absorbance and HIX increase with the content of aromatic structures, with the degree of condensation and/or conjugation, and with the C/H ratios of organic molecules (Zsolnay, 2003). Further details on fluorescence measurements are given by Kalbitz and Geyer (2001). Low-molecular-weight organic acids in the original OM solutions, representing potentially labile organic components, were determined by a capillary electrophoresis system equipped with a diode array detector (3D-CE; Agilent Technologies, Santa Clara, USA) and a 75 mm (i.d.) fused silica capillary (Dahlen et al., 2000).

2.8. Statistics

Statistical analysis was performed with the statistical package SPSS v10. Differences in OC mineralization between treatments were tested by the non-parametric Kruskal–Wallis rank test. In addition, the Mann–Whitney U -test was performed to reveal differences between means. For all statistical analyses we used a p level of 0.05 unless stated otherwise.

3. RESULTS

3.1. Sorption of organic matter

Dissolved OC from Oa horizons had a higher affinity to am- $\text{Al}(\text{OH})_3$ than that from Oi horizons. At a SSR of 1.2 g L^{-1} , am- $\text{Al}(\text{OH})_3$ sorbed up to 76–89% of added OC derived from Oa horizons but only 42–55% of OC derived from Oi horizons (Table 2). Increasing the SSR, thus the availability of mineral surfaces, resulted in increasing removal of OC from solution. Generally, the OC loadings ($\text{mg OC m}^{-2} \text{ Al}(\text{OH})_3$) were higher for OM derived from Oa than from Oi horizons, again indicating differences in the affinity of the OM from different sources to the mineral (Table 2). When decreasing the availability of am- $\text{Al}(\text{OH})_3$ by changing the SSR from 1.2 to 0.3 g L^{-1} , the OC loadings

increased strongly (Table 2). Except for the treatment with beech Oa solution, further decrease in mineral concentrations ($SSR < 0.3 \text{ g L}^{-1}$) had only a negligible effect on the OC loadings, suggesting that the hydroxide's sorption capacity had been reached (Table 2). The different affinity of the types of OM used for the mineral phase and the variations in available amounts of am-Al(OH)_3 resulted in a large range of OC loadings ($0.1\text{--}1.2 \text{ mg OC m}^{-2}$; Table 2).

3.2. Properties of original, sorbed and non-sorbed organic matter

The specific UV absorbance and humification indices (HIX) suggested a higher aromatic C content of OM from Oa horizons than from Oi horizons (Table 1, Fig. 1; UV data not shown). Low-molecular-weight organic acids (formate, malate, oxalate, and citrate) were present in the original OM solutions but represented $< 0.1\%$ of total DOC (data not shown). The OM remaining in solution after sorption was characterized by lower specific UV absorbance and lower HIX values (Fig. 1; UV data not shown). This indicates preferential sorption of aromatic, more complex compounds, probably derived from lignin. Based on the close relationship between UV absorbance and aromatic C measured by ^{13}C NMR (Scheel et al., 2007), we estimated that the aromatic C content of the sorbed OM increased from $< 10\%$ to $\sim 30\%$ after removal of the first 20% of OC from the solutions, irrespective of the OM source (Fig. 2). The

HIX values of the beech Oa solutions, in contrast to all other test solutions, increased at low SSR after removal of $\sim 10\%$ of OC from solution (Fig. 1), which indicates preferential sorption of less aromatic compounds when little am-Al(OH)_3 is available.

In three samples (spruce Oa, beech Oi, partly beech Oa), we observed a decrease in the OC/ON ratio of non-sorbed OM (Table 3), implying that N-containing compounds were discriminated against during sorption. The beech Oa sample again showed a contrasting behaviour in that the OC/ON ratio increased at the lowest SSR where only a small portion of OM was sorbed (Table 3). This suggests preferential sorption of N-rich compounds and is consistent with the higher HIX values of the non-sorbed OM. Compounds with high HIX values, typically derived from lignin, should be low in N (Kalbitz et al., 2003b).

3.3. Competitive sorption of phosphate

In agreement with the high sorption affinity of phosphate, P loadings and molar P/C ratios of the am-Al(OH)_3 were always highest at the lowest solid concentration, hence lowest SSR (Table 2). At the lowest am-Al(OH)_3 concentration, P loadings ranged from $0.1\text{--}0.2 \text{ mg P m}^{-2}$, reflecting the differences in the phosphate content of the original OM solutions (Table 1). These loadings translate into surface P concentrations of $3.2\text{--}6.1 \mu\text{mol m}^{-2}$, suggesting that the hydroxide's surfaces are largely occupied by phosphate

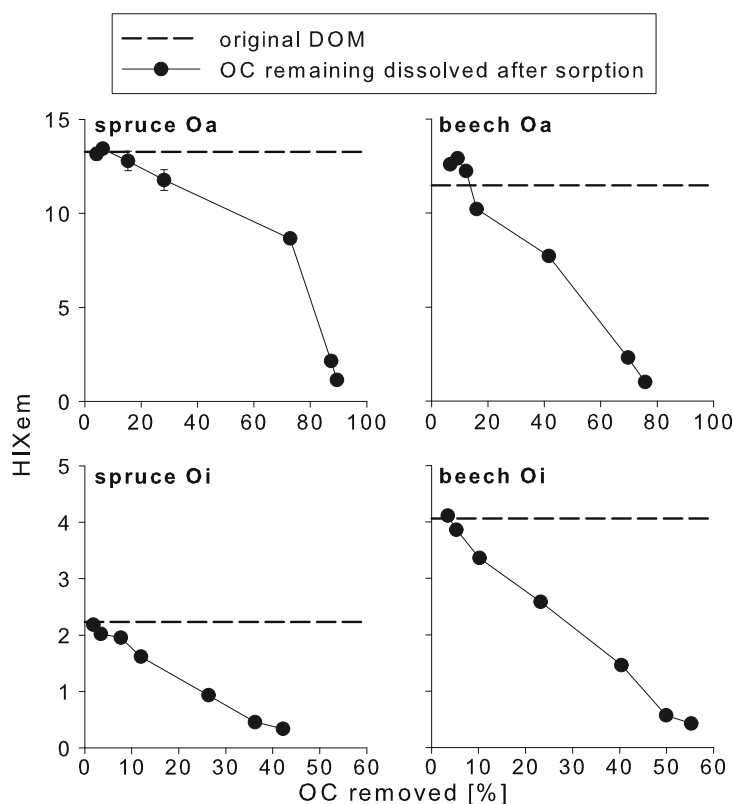


Fig. 1. Changes in humification indices deduced from fluorescence emission spectra of the four original dissolved organic matter (DOM) solutions (horizontal lines) and of the OM remaining in solution after interaction with amorphous Al(OH)_3 . Error bars indicate the standard error of the mean of three replicates.

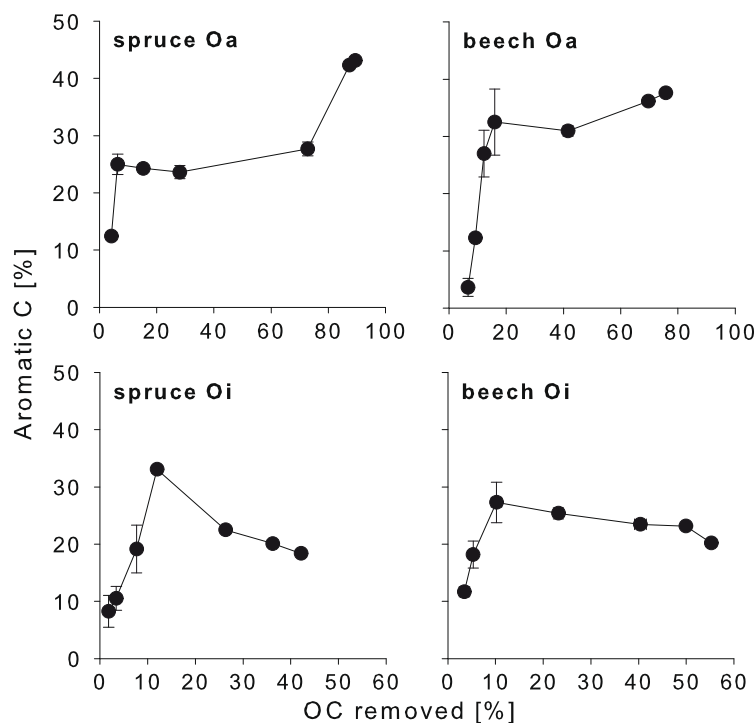


Fig. 2. Aromatic carbon content of OM sorbed by amorphous Al hydroxide, as related to the portion of organic carbon sorbed from solution. Error bars indicate the standard error of the mean of three replicates.

Table 3

Aromatic carbon content (%) and organic carbon to organic nitrogen (OC/ON) ratios of the original dissolved organic matter (DOM) solutions and the remaining solutions after sorption at different solid-to-solution-ratios (SSR). Numbers given represent means and standard errors of three replicates. Aromatic carbon content was calculated using the close relationship between UV absorbance and aromatic carbon measured by ^{13}C NMR spectroscopy (Scheel et al., 2007).

SSR (g L^{-1})	DOM	0.02	0.04	0.08	0.15	0.3	0.6	1.2
Spruce Oa								
Aromatic C	31.0 ± 0.2	29.4 ± 0.1	28.6 ± 0.1	28.2 ± 0.1	25.8 ± 0.4	15.2 ± 0.6	1.9 ± 0.2	0.7 ± 0.3
(OC/ON)	28.2 ± 0.3	25.8 ± 0.3	25.9 ± 0.3	24.7 ± 0.3	22.0 ± 0.2	12.9 ± 0.3	8.2 ± 0.1	7.0 ± 0.5
Beech Oa								
Aromatic C	22.1 ± 0.2	21.3 ± 0.3	20.4 ± 0.1	19.6 ± 0.3	18.5 ± 0.3	13.0 ± 0.5	4.3 ± 0.2	2.0 ± 0.1
(OC/ON)	19.3 ± 0.4	21.1 ± 0.3	19.6 ± 0.3	17.5 ± 0.1	14.1 ± 0.2	10.9 ± 0.3	7.6 ± 0.1	6.8 ± 0.0
Spruce Oi								
Aromatic C	7.3 ± 0.1	6.9 ± 0.1	6.8 ± 0.1	6.2 ± 0.3	4.2 ± 0.1	2.7 ± 0.1	1.6 ± 0.1	1.2 ± 0.1
(OC/ON)	11.6 ± 0.1	11.3 ± 0.3	11.1 ± 0.8	11.6 ± 0.8	14.1 ± 1.5	10.1 ± 0.9	11.7 ± 0.2	10.9 ± 0.0
Beech Oi								
Aromatic C	10.4 ± 0.3	9.5 ± 0.2	9.2 ± 0.1	8.3 ± 0.1	5.9 ± 0.1	3.1 ± 0.1	1.5 ± 0.1	1.8 ± 0.1
(OC/ON)	12.3 ± 0.1	12.8 ± 0.1	12.8 ± 0.1	12.6 ± 0.2	11.5 ± 0.1	10.2 ± 0.1	9.6 ± 0.1	8.9 ± 0.0

at low SSR. Phosphate effectively competes with OM for sorption sites when the reactive am-Al(OH)₃ surfaces become less available. Phosphate loadings significantly declined to $0.3 \mu\text{mol P m}^{-2}$ at higher mineral concentrations.

3.4. Stability of organic matter against microbial decay

3.4.1. Mineralization of sorbed organic matter

The mineralization of sorbed OC, irrespective of the source, was highest at the lowest SSR and decreased significantly with increasing concentration of am-Al(OH)₃

(Fig. 3). High mineral availability caused almost complete inhibition of microbial decay of sorbed OM. Sorbed spruce OM was less strongly mineralized than beech OM. Sorbed OC from Oi solutions was significantly less mineralizable than that of the corresponding original OM solutions over the whole range of mineral availability (Fig. 3). The mineralization of sorbed OC ranged from 2% to 33% while ~50% of the original solution OC was mineralized within 60 days of incubation. Sorbed OM from Oa horizons did not necessarily exhibit a higher stability than the original solution OM. At low SSR, when only small portions (spruce

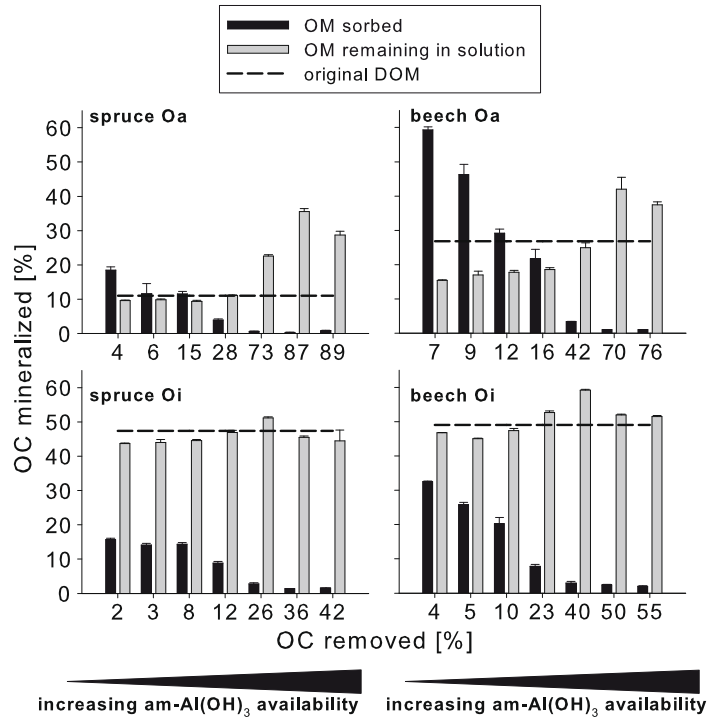


Fig. 3. Carbon mineralization (in % of the initial carbon of each fraction) from sorbed and non-sorbed organic matter (OM) during 60 days of incubation at 20 °C, as related to the portion of organic carbon sorbed from solution by amorphous $\text{Al}(\text{OH})_3$. Dashed lines represent carbon mineralization of the original dissolved organic matter (DOM) solution. Error bars indicate the standard error of the mean of three replicates.

Oa: 4%; beech Oa: 7%) of the solution OC were sorbed, the mineralization of sorbed OC (spruce Oa: 19%; beech Oa: 59%) exceeded that of the original solution OC (spruce Oa: 10%; beech Oa: 28%). At higher SSR, with >40% of the added OC being sorbed, the mineralization of sorbed OC dropped to 0.3–1% for spruce Oa and to 0.2–4% for beech Oa OM.

3.4.2. Mineralization of non-sorbed organic matter

The mineralization of non-sorbed Oa OM related to the mineral surface availability (i.e., SSR). The mineralization exceeded that of the original solution OM at high SSR (>0.15 for spruce Oa; >0.30 beech Oa), where large portions of the added solution OC (>50%) were sorbed (Fig. 3). Likely, more stable compounds sorbed preferentially, leaving the more easily mineralizable in solution. At lower SSR, with only a small fraction of added OC being sorbed, non-sorbed OC was equally (spruce Oa) or less mineralizable (beech Oa) than the original solution OC. The high mineralizability of sorbed OC from the beech Oa solution at low availability of $\text{am-Al}(\text{OH})_3$ was accompanied by a rather low mineralization of the respective non-sorbed OC. In most cases, the mineralization of non-sorbed OC from Oi horizons was similar and statistically not different from that of the original solution OC.

3.4.3. Overall stabilization of organic matter by sorptive interactions

The overall stabilization of solution OM by sorption to $\text{am-Al}(\text{OH})_3$ was calculated by summing up the mineraliza-

tion of the sorbed and non-sorbed OC. In all treatments, the sum of mineralized C ($\text{mg C g}^{-1} \text{C}^{-1}$) was less than mineralized C of the original solution OM. This demonstrates that the sorption of OM to $\text{am-Al}(\text{OH})_3$ induced stabilization against microbial decay (Fig. 4). The overall stabilization was almost negligible at low additions of $\text{am-Al}(\text{OH})_3$ and increased considerably with increased amounts of the mineral phase. Due to sorption, the overall mineralization of Oi solutions decreased from 474 (spruce) and 491 $\text{mg C g}^{-1} \text{C}$ (beech) to 264 and 242 $\text{mg C g}^{-1} \text{C}$ at the highest $\text{am-Al}(\text{OH})_3$ additions (highest SSR). Consequently, mineralization of C for spruce and beech Oi solutions decreased by 44% and 51%. The overall stabilization was even higher for spruce and beech Oa OM where the mineralization decreased by 65% and 63% as compared with the original solution OM. In all cases, sorbed OM, although comprising a large portion of the total OC (up to >50%), contributed only little to total mineralizable C. The maximal contribution of sorbed OM to total C mineralization (~21%) was observed for the beech Oa solution.

4. DISCUSSION

4.1. Organic matter properties affecting carbon stabilization of sorbed organic matter

Dissolved OM from the Oa horizons featured more carboxylic groups and aromatic structures than OM derived from Oi horizons (Table 1). Such OM is relatively stable against microbial decay (Marschner and Kalbitz, 2003)

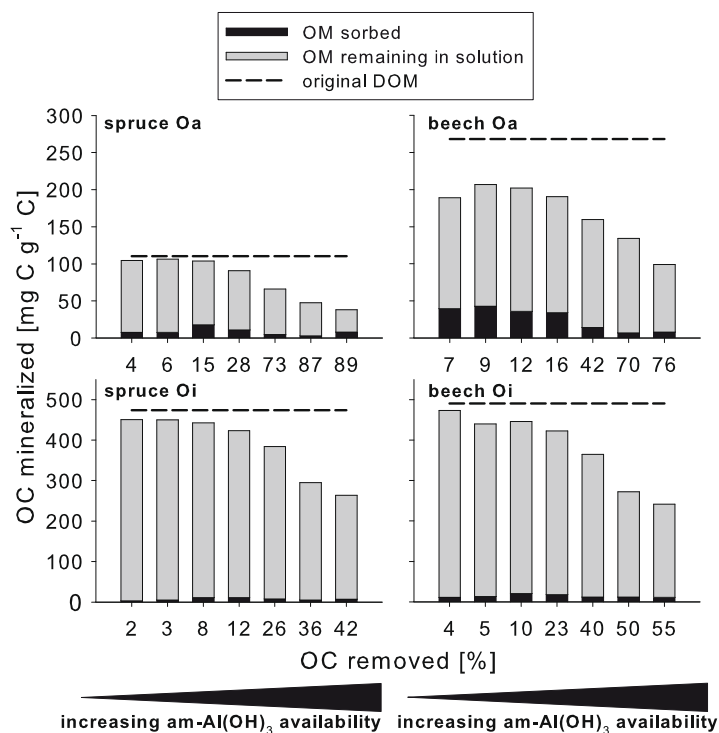


Fig. 4. Overall carbon mineralization during 60 days of incubation at 20 °C, as related to the portion of organic carbon sorbed from solution by amorphous Al(OH)₃. Overall mineralization is the sum of mineralization from the sorbed and non-sorbed organic matter (OM). Dashed lines show the mineralization of the original dissolved organic matter (DOM) solution.

and should be preferentially sorbed by am-Al(OH)₃ (Kaiser and Guggenberger, 2000; Kaiser, 2003; Kalbitz et al., 2005). Indeed, we observed larger sorption of OM from Oa than from Oi solutions. The differences in OM composition would imply a higher mineralization of sorbed OM derived from Oi than from Oa horizons. However, at low mineral availability (i.e., low SSR), sorbed OM derived from Oa horizons was more readily mineralized than that from Oi horizons. Spectroscopic measurements indicated that beech Oa-derived OM sorbed under such conditions had the lowest aromatic C content but the highest ON content among all treatments (Fig. 2, Table 3). The sorption of N-rich, easily mineralizable components was accompanied by low mineralization of the respective non-sorbed OM (Fig. 3). The general assumption of aromatic and carboxylic moieties to be sorbed preferentially to variable-charge minerals is, therefore, not true if the availability of surfaces is low. The effect of chemical fractionation of OM as imposed by mineral availability warrants further attention.

At higher availability of am-Al(OH)₃, when larger portions of OC were removed from solution (Table 2), the more complex and aromatic moieties were preferentially sorbed, which matches well with previous studies (Chorover and Amistadi, 2001). The relationship between composition and sorption of OM to minerals is not as straightforward as previously assumed; nevertheless, aromatic compounds were most stable as indicated by the inverse linear relationship between the aromaticity of sorbed OM and C mineralization, e.g., for OM derived from the Oa horizons ($r^2 = 0.64\text{--}0.78$; data not shown). However, this relation-

ship cannot explain all observations: at sorption of >6–12% of the solution OC, the aromatic content of sorbed OM leveled off (Fig. 2) while the mineralization of sorbed OM decreased (up to an OC sorption of at least 30%; Fig. 3). Despite the similar aromatic content of OM sorbed at higher SSR (Table 3), the mineralization of the different samples varied (Fig. 3). This supports that bonds between OM and am-Al(OH)₃ became stronger with increasing mineral availability, resulting in higher resistance against mineralization.

4.2. Unreacted mineral surfaces and the organic carbon loading as controls of carbon stabilization

The range of OC loadings achieved for the am-Al(OH)₃ (0.1–1.2 mg OC m⁻²) was comparable to those observed in soils and sediments (Keil et al., 1994; Mayer, 1994; Kögel-Knabner et al., 2008). The large range of OC loadings allows for testing the dependence of sorptive OM stabilization on the mineral's OC loading. Combining all sorption and mineralization data it appears that the mineralization of sorbed OM increased with increasing OC loadings (Fig. 5a). This relationship was particularly strong for the beech Oa sample ($r^2 = 0.81$) and weaker for the other three test OM ($r^2 = 0.18\text{--}0.59$), where the OC loadings did not decrease proportionally with increasing mineral availability. The highest OC loading was obtained for OM from the beech Oa (1.2 mg C m⁻²), which was paralleled by the most intense OC mineralization (Fig. 5a). Basically, all of these results support the idea that decreasing

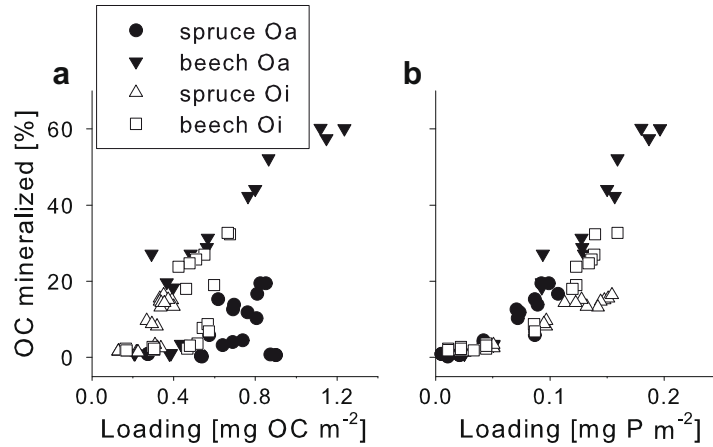


Fig. 5. Mineralization from sorbed organic matter (OM) as related to the organic carbon loadings (a) and to the P loadings (b) of the amorphous Al hydroxide surface.

OC loadings of the mineral phase increase the stability of OM against microbial decay (Podoll et al., 1987; Kaiser and Guggenberger, 2003).

However, this concept may not be generally valid. For example, the mineralization of sorbed OM from the spruce Oa solution was low and statistically not different over a wide range of am-Al(OH)₃ availability (0.3–1.2 g L⁻¹), thus OC loadings (0.27–0.89 mg C m⁻²). Similar observations were made for the other OM solutions. Mineralization was highest at the lowest SSR where a high, but not necessarily the highest, OC loading occurred. The generally higher OC loadings of am-Al(OH)₃ achieved with OM from Oa than from Oi horizons also contrasts with the generally lower mineralization of Oa-derived sorbed OM. It seems that the source of OM affects its sorptive stabilization to a larger extent than the loading of the mineral.

We do not think that concentration effects are responsible for differences in C mineralization. Firstly, assuming a first order decay kinetic of the mineralization process (Kalbitz et al., 2005), the C mineralization rates would be proportional to the amount of the substrate (Plante and Parton, 2007). Thus, mineralization should be higher at a high SSR, where larger amounts of C were sorbed than at

low SSRs. However, we observed the opposite. Furthermore, the total amounts of C in the incubation vessels were in the same range for sorbed OM and for the original DOM. Nevertheless, we observed large differences in C mineralization. Secondly, the sum of C mineralization from sorbed and non-sorbed OM never exceeded the mineralization of DOM, even at low SSRs where small amounts of highly mineralizable C were sorbed. Under such conditions, the amounts of OM did not affect mineralization, supporting the idea that concentration effects were not responsible for differences in C mineralization.

4.3. Impact of sorbed phosphate and pH on carbon stabilization

Fig. 6a suggests that phosphate contained in the DOM solutions had a pronounced impact on the uptake of OC. Sorption of OC decreased exponentially at high P/am-Al(OH)₃ ratios, i.e., with decreasing am-Al(OH)₃ availability at low SSRs. Despite constant molar P/C ratios for each DOM sample, decreasing the SSR resulted in a larger sorption of P than of OC as indicated by increasing molar ratios of sorbed P and C (Table 2). The small change in sorbed

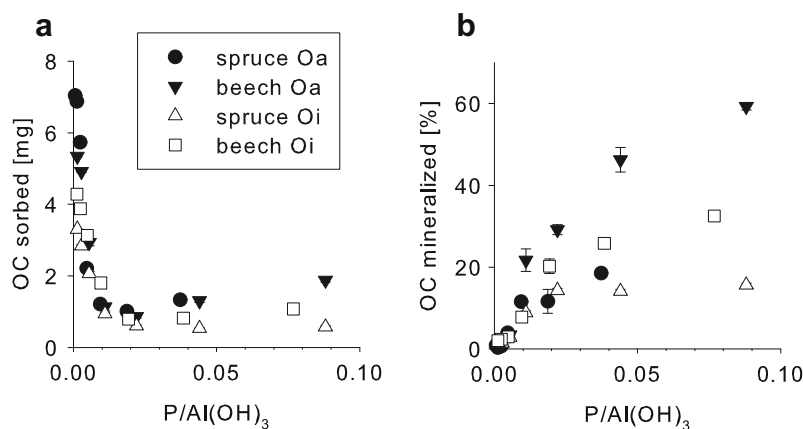


Fig. 6. Organic carbon (OC) sorption (a) and mineralization of sorbed organic matter (b) with increasing initial P/Al(OH)₃ ratios (wt./wt.).

OC when the initial mass-based P/am-Al(OH)₃ ratios exceeded ~ 0.01 (Fig. 6a) underlines the high affinity of phosphate for surface hydroxyl sites of the am-Al(OH)₃. Similarly, Borggaard et al. (2005) showed that phosphate sorption by am-Al(OH)₃ was not affected even at high concentrations of humic acids, thus highlighting the strong competitiveness of phosphate compared with OM.

Obviously, solution phosphate can become a major factor in determining the microbial stability of sorbed OC if few mineral sites are available (Figs. 5b and 6b). The linear positive relationship between mineralization of sorbed OC and site occupancy by phosphate (Fig. 5b) directly reflects the sorptive competition between OM and phosphate. The highest P loadings were observed for OM derived from the beech Oa horizon ($6.1 \mu\text{mol P m}^{-2}$) and from the spruce Oi horizon ($4.8 \mu\text{mol P m}^{-2}$), having the highest initial phosphate concentrations (Table 1). At such P loadings, the surfaces of am-Al(OH)₃ are largely occupied by phosphate (Borggaard et al., 2005). Thus, at low SSR, with the phosphate competition being maximal, sorbed OM may be less strongly bound due to fewer ligands directly attached to the mineral surface. The higher mineralization of OM sorbed under strong competition with phosphate conditions agrees with the higher mineralization of OM sorbed to goethite ($\alpha\text{-FeOOH}$) at pH 4 in the presence of phosphate (Mikutta et al., 2007). At high availability of am-Al(OH)₃, decreasing P loadings and molar (P/C)_{sorbed} ratios (Table 2) indicate less competition between phosphate and OM; formation of strong mineral–organic bonds is, therefore, not hindered. At SSRs > 0.3 , P loadings ($\sim 0.3\text{--}1.6 \mu\text{mol P m}^{-2}$) were less than what can be assumed to be necessary to achieve complete surface occupation ($3.5\text{--}4.5 \mu\text{mol P m}^{-2}$; Borggaard et al., 2005). Therefore, weaker mineral–organic bonds become predominant at low am-Al(OH)₃ availability, where competition is more crucial.

In a previous study, we showed that increasing pH values during incubation promoted desorption, thus microbial utilization of OM, especially of OM that is more weakly bound (Mikutta et al., 2007). During the 60-day incubation, the pH increased by up to 2 units for mineral–organic asso-

ciations formed at lower SSR, with presumably weaker bonds involved (Fig. 7a). As a result, more OM should have been desorbed. Although the data are somewhat scattered, the plot of final pH values versus $\text{OC}_{\text{dissolved}}/\text{OC}_{\text{sorbed}}$ ratios (Fig. 7b), suggests that the pH increase during incubation caused a partial desorption of OM. This finding implies that the mineralization of sorbed OM also depends on the pH shifts, which in turn affect the desorption of OM. At lower am-Al(OH)₃ availability (lower SSRs), with more P present at the mineral surfaces and with weaker mineral–organic bonds involved, the increase in pH was highest, as was the release of OM (Fig. 7a and b). Mineralization was consequently higher. In contrast, at higher mineral availability, favouring stronger bonds (less competition with phosphate), the pH during incubation varied less, thus causing less desorption and mineralization.

4.4. Controls of the overall stabilization of OM after sorption to amorphous Al hydroxide

Preferential sorption of *a priori* intrinsically stable OM constituents, as observed at increasing am-Al(OH)₃ availability, results in a high mineralization of the OM remaining in solution. Likewise, selective sorption of easily mineralizable OM, as observed at low SSR, led to decreased mineralization of the respective non-sorbed OM. The sum of mineralized OC of sorbed and non-sorbed OM would have consequently been equal to that of the original DOM, if sorption did not lead to stabilization. In most cases, however, the sorption of DOM to am-Al(OH)₃ induced an overall decrease in mineralization.

The extent of overall stabilization strongly depends on the availability of am-Al(OH)₃, hence, on the extent of the OC sorption (Fig. 8a and b). At low mineral availability, the small amounts of OC removed from solution were highly mineralizable. As result, the overall stabilization was low or even negligible (spruce Oa) and is mainly based on the low mineralization of the non-sorbed OM. The preferential sorption of easily mineralizable, N-rich compounds could be responsible for the low mineralization of

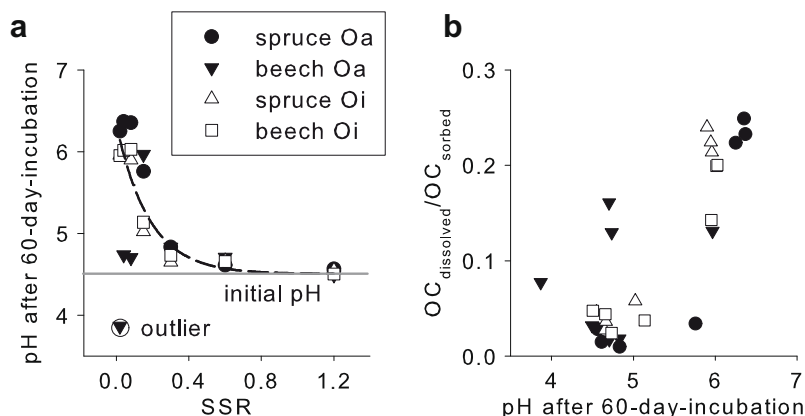


Fig. 7. Relationship between the pH measured at the end of incubation (60 days, 20 °C) and the solid-to-solution ratio (SSR, in g L^{-1}). The grey line represents the pH value at the beginning of the incubation; the stacked exponential line serves as guide to the eyes only (a). Relationship between the $\text{OC}_{\text{dissolved}}/\text{OC}_{\text{sorbed}}$ ratio on the pH measured after incubation, where $\text{OC}_{\text{dissolved}}$ is the solution organic carbon (OC) concentration at the end of incubation and $\text{OC}_{\text{sorbed}}$ the OC content of the solid prior to incubation (b).

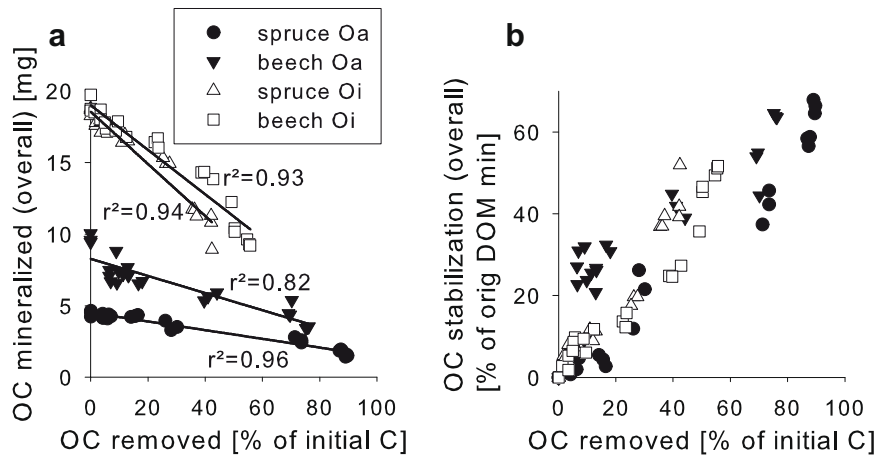


Fig. 8. Overall amount of mineralized carbon (a) and overall carbon stabilization (b), as related to the portion of organic carbon sorbed. Overall carbon mineralization represents the sum of mineralization from sorbed and non-sorbed organic matter; overall carbon stabilization is given as the relative reduction in overall carbon mineralization as compared to the mineralization of the original dissolved organic matter solution.

non-sorbed OM and the high mineralization of the respective sorbed OM. In addition, enzymes initially present in the DOM (beech Oa) and subsequently sorbed to am-Al(OH)₃ could still remain active, in particular at low SSR, and thus could have assisted in the mineralization of sorbed OM (Scheel et al., 2008b). In contrast, the high overall stabilization of OM at moderate to high availability of am-Al(OH)₃ (SSR >0.15) was mainly caused by the strong sorption of OM rich in aromatic structures, with little competition with phosphate for sorption sites.

The effect of sorption on overall OC stabilization is reflected by the linear relationship between the portion of OC sorbed and the OC mineralization of the different DOM types (Fig. 8a). This pattern becomes more apparent when the overall stabilization of OM is normalized to the mineralization of the original solution OM (Fig. 8b). The relationship applies to all DOM samples, but the regression slopes varied significantly for the different OM types. In general, the higher overall stabilization of OM derived from Oa horizons relative to that from Oi horizons seems to relate to the higher aromaticity and the stronger sorption. The steeper slopes observed for OM from Oi horizons, however, indicate that intrinsically less stable OM is gaining the most stability by sorbing when the mineral availability increases.

5. IMPLICATIONS

We were able to provide experimental evidence that (i) sorption to amorphous Al hydroxide results in an overall stabilization of DOM and that (ii) the stabilization cannot be solely ascribed to preferential accumulation of recalcitrant OM. These findings stress the importance of sorptive interactions as a major mechanism of OM stabilization in soils. The extent of the resulting stabilization strongly depends on the availability of reactive mineral surfaces.

Our results have important consequences for the assessment of long-term OM stabilization in acidic soil environ-

ments and more generally in all soils with higher contents of poorly crystalline allophane- and imogolite-type mineral phases. Poorly crystalline allophane- and imogolite-type mineral phases can be expected to be abundant in soils characterized by intensive weathering and the formation of secondary minerals, such as acidic forest soils (e.g., Podzols, Gustafsson et al., 1999) and volcanic soils rich in allophanes (Andosols) (Kleber and Jahn, 2007). Compared to their relatively low density, amorphous Al hydroxides, which were used here as surrogates for poorly crystalline allophane- and imogolite-type mineral phases, exhibit high specific surface area which allows for large amounts of OM to sorb per unit mass. Little was known about the stabilizing effect of OM sorption to amorphous Al hydroxides until now.

Under conditions where mineral surfaces become limited and competitive anions are present, such as in soil A horizons, newly formed mineral-organic associations are relatively weak and the OM is more susceptible to desorption and microbial decay. In contrast, once the availability of mineral surfaces increases, e.g., after DOM has been leached to deeper soil horizons, the stabilization of OM upon sorption will increase. The concept that lower surface OC loadings of minerals favour the stability of sorbed OM strictly applies only to situations where the mineral availability is low. When the mineral availability is higher, this causal relation is not necessarily valid. Hence, determining the surface OC loading of the soil's mineral phase will not help in assessing the potential stabilization of OM unambiguously. Instead, batch sorption experiments with C-labelled DOM can be used to determine the effects of sorption on OM stabilization. Such experiments need to consider the availability of mineral surfaces, thus the solid-to-solution ratios, in relation to the fraction of DOM that can be sorbed. For site-specific estimates of OM stabilization, solid-to-solution ratios should be chosen with great care because of their decisive influence on C stabilization. Ratios should reflect the natural conditions in terms of soil water fluxes and mineral stocks in the soil.

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