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Sorptive stabilization of organic matter in soils by hydrous iron oxides

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Abstract

Strong correlations between iron oxides (FeOx) and organic matter (OM) in soils have implied the importance of the former in stabilizing the latter. One mechanism thought to be important in this stabilization is sorption. We tested this possibility by reductively dissolving FeOx in a wide variety of soils and measuring the organic carbon (OC) that was solubilized. The OC dissolved from non-FeOx phases via anion exchange was corrected for by parallel control extractions. The resultant pool, reductively soluble OC, made up a minor amount of total soil OC in all but one of these soils, indicating that simple sorption reactions do not stabilize the bulk of soil OC in most mineral soils. OC:Fe ratios in the extracts from 2/3 of these soils were less than 0.22 (wt/wt), consistent with a sorbed state for this OC and showing that OC sorption by FeOx in these soils is limited by the amount of FeOx. The remaining soils had low pH and high OM concentrations; their higher OC:Fe ratios indicate inclusion of precipitated organo-Fe complexes in the extracts, which are likely only partially extracted by our method. The high volumetric ratios of OM to FeOx found in correlations between them from the literature are inconsistent with a dominant sorption control and point instead to stabilization to other mechanisms such as organo-Fe complexes or ternary associations among FeOx, OM and other minerals.

1. Introduction

Soil organic matter (OM) represents an important carbon reservoir in the global carbon cycle. Significant amounts of soil OM appear to be protected against biological oxidation by its mineral matrix (Baldock and Skjemstad, 2000). Yet specific mineral phases or the mechanisms responsible for the mineral protection of OM remain unclear (Sollins et al., 1996; Krull et al., 2003). Iron and aluminum oxides, hydroxides, and oxyhydroxides (FeOx and AlOx) influence soil OM stabilization, as evidenced by (a) positive correlations between metal and total organic carbon (OC) concentrations among a range of field soils (Hughes, 1982; Johnson and Todd, 1983; Adams and Kassim, 1984; Tiessen et al., 1984; Evans and Wilson, 1985; Skjemstad et al., 1989; Kaiser and Guggenberger, 2000), (b) inverse correlations between soil OC turnover rates and metal concentrations (Veldkemp, 1994; Torn et al., 1997; Masiello et al., 2004), (c) their high sorption capacity (Tipping, 1981), and (d) their ability to retard microbial/enzymatic mineralization of OM (Boudot et al., 1989; Jones and Edwards, 1998). Three types of association between iron and OM have been considered to account for this stabilization.

Extensive and reactive surfaces of FeOx and AlOx are often presumed to account for sorption and stabilization of soil OM. Maximum sorption capacities of FeOx phases for naturally occurring OC are 110–140 mg-OC g^{-1} oxide (Tipping, 1981; Kaiser and Guggenberger, 2006), at least one order of magnitude higher than that of common aluminosilicate clays (e.g., Jardine et al., 1989; Chorover and Amistadi, 2001). Based on the OC–FeOx correlations and this reactivity, sorption has been suggested to account for the protective association between bulk OM and FeOx (Kaiser and Guggenberger, 2000; Kaiser et al., 2002; Kiem and Kögel-Knabner, 2002; Eusterhues et al., 2003; Wiseman and Püttmann, 2005).

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Complexation of Fe(III) ions with dissociated functional groups on OM can occur in soil (micro)environments with high supply of dissolved Fe(III) and humic material (Schwertmann et al., 1986). Precipitation of these complexes is an important stabilization mechanism in volcanic and acid-leached subsurface soils (e.g., Petersen, 1976; Wada, 1995) and possibly other types of soils (Masiello et al., 2004).

Physical protection of OM via microaggregation induced by metal oxides (especially FeOx) is another possible mechanism of SOM stabilization. Both OM and extractable phases of FeOx positively correlate with aggregate stability in soils (Krisnamurti and Huang, 1987; Duiker et al., 2003). The importance of AlOx and FeOx for OM stabilization in soil aggregates has been shown in two tropical soils (Shang and Tiessen, 1998).

More direct assessment of the OM association with FeOx would help clarify the mechanism by which this protection is accomplished. We focus here on determining the amount of OM adsorbed onto FeOx. To measure this pool, we assume that reductive dissolution of FeOx will allow redissolution of OM that was originally adsorbed from solution. To allow measurement of this OM, we developed an inorganic version of the well-known dithionite-based approach to reductively dissolve Fe and co-precipitated Al. Dithionite is considered to have little impact on other soil mineral phases (Borggaard, 1982). Dissolution of OC from organo-Fe(III) complexes by dithionite extraction is less clear but likely. Dithionite extraction almost fully dissolved precipitated, organically complexed Fe from a peat soil (Schwertmann and Murad, 1988). While dithionite effectively disperses Fe-cemented microaggregates (Pinheiro-Dick and Schwertmann, 1996), insoluble organic matter (e.g., plant detritus) in these aggregates will not appear in the dithionite-extractable phase. Therefore, the OC extractable by our dithionite method represents the potentially soluble OC that is bound to reducible FeOx (and, to a limited extent, AlOx) phases via sorption and, to some extent, precipitation mechanisms, and will hereafter be called reductively soluble OC.

Using this approach, we examined 34 mineral soil horizons, including eight soil orders that account for most soil OC storage of the world (Eswaran et al., 1993). We also report organo-aluminum relationships in the extracts.

2. Method

2.1. Sample source and handling

Surface mineral horizons and OC-enriched, acid-leached subsurface horizons were sampled from a range of soil types and geographic areas (Table 1). Deeper samples low in OC were also taken from two weathered tropical soils for the comparison with surface samples. Soil samples were either air-dried at room temperature or freeze-dried, passed through a 2-mm sieve, and stored at room temperature (for air-dried samples) or in a freezer (for freeze-dried samples) for less than 3 years. Alfisols, Mollisols, and Ultisols from the US were obtained from a soil archive (USDA, Soil Survey Center, Nebraska).

2.2. Extraction procedure

2.2.1. Overview

Our FeOx extraction is based on the original dithionite method (Deb, 1950) from which evolved the commonly used approach of incorporating citrate, an organic complexing agent, and pH buffer to minimize precipitation of iron sulfide (Mehra and Jackson, 1960). This method with the citrate included has been used to assess organic matter associated with iron oxides, but residual citrate makes quantitative interpretation problematic (Filimonova et al., 2006). In our fully inorganic dithionite extraction, we eliminated the citrate to allow measurement of liberated OC, which we compensated by a weak acid rinse of residues following dithionite extraction to redissolve Fe precipitated as acid-volatile sulfides and associated OC. We used a soil-to-solution ratio (mg mL^{-1}) of 4.3 for Fe-rich soils and 7.1 for Fe-poor soils, with dithionite concentration of 0.049 M. We mixed fresh sodium dithionite with pre-weighed soil, adding deionized water (Milli-Q) immediately and double-sealing each tube with Parafilm to minimize decomposition of dithionite (Gan et al., 1992). All dithionite extractions were done at room temperature for 16 h on a rotational shaker, followed by centrifugation at 40,000*g* for 40 min (which was shown to be effective by 0.45-μm filtration). The pH of dithionite extracts was measured immediately after the centrifugation step. After removing the supernatant, residues were extracted with 0.05 M HCl for 1 h.

For five randomly chosen samples, OC recoveries (the sum of OC dissolved by the dithionite and acid extractions, plus residual OC) were 107 ± 12.8% of total OC concentrations of bulk samples. The precision of the OC and Fe measurements in dithionite and acid extractions assessed from the replicates of 17 randomly chosen samples was <6.4% (coefficient of variation). Sodium dithionite (Fisher Scientific, laboratory grade) contained 0.3% OC. This OC was accounted for by subtracting the OC concentrations in dithionite controls (dithionite plus water without soil) in each set of dithionite extractions.

Some of the OC in soils is soluble in water and ion-exchangeable by oxysulfur anions, such as oxidation products of dithionite (Lyons and Nickless, 1968), and thus not all of the OC dissolved by our dithionite and acid extractions is attributable to sorption onto FeOx. Therefore, control extractions of all samples were performed for 16 h using a 0.049 M sodium sulfate solution, after adjusting the pH with HCl to the level found at the end of the dithionite extraction for each sample. Sulfate-extractable Fe was minimal (1.0 ± 0.2% of dithionite-extractable Fe) across all samples, and sulfate is very poor at displacing OC from adsorption sites on FeOx (Kaiser

Table 1
Sample source information and soil chemical characteristics

Soil order	Location	Altitude (m)	Horizon: depth (cm)	Total OC (mg g^{-1})	Bulk soil C:N	OC_{HF} (mg g^{-1})	Bulk soil pH_{H_2O}
Entisol	Hawaii Island	<500	A: 0–2	165	17	NA	5.4
Inceptisol	Massachusetts	<500	E: 6–12	29.5	39	NA	4.5
			Bw: 12–22	30.3	25	NA	4.0
Inceptisol	Massachusetts	<500	Ap: 0–18	28.9	12	NA	5.0
Inceptisol	Washington	625	A: 0–10	45.7	42	NA	5.3
Inceptisol	Oregon	180	A: 0–10	105	17	NA	5.2
Inceptisol[a]	Kinabalu, Malaysia	2700	A: 0–10	93.9	28	60.2	4.5
Incept/Alf	Kinabalu, Malaysia	1700	A: 0–10	22.4	17	14.5	4.6
Inceptisol	Kinabalu, Malaysia	2700	A: 0–10	126	19	62.8	4.9
Alfisol	New Jersey	<500	A: 0–6	79.7	16	NA	4.3
Alfisol	New Jersey	<500	Ap: 0–13	10.1	9	NA	6.0
Alfisol	Mississippi	<500	Ap: 0–8	14.1	10	NA	6.0
Alfisol[a]	Kinabalu, Malaysia	1700	A: 0–10	43.1	19	33.0	5.3
Mollisol	North Dakota	<500	A: 0–5	23.8	11	NA	5.8
Mollisol	Indiana	<500	Ap: 0–28	26.3	12	NA	5.7
Ultisol	Virginia	<500	Ap: 0–20	44.8	14	NA	5.2
Ultisol	Maryland	<500	Ap: 0–13	41.6	12	NA	4.9
Ultisol	Virginia	<500	Ap: 0–20	60.9	11	NA	6.2
Ultisol	Kinabalu, Malaysia	700	A: 0–10	27.6	13	20.3	4.4
Oxisol	Puerto Rico	<500	A: 0–5	66.2	18	NA	5.2
Oxisol	Puerto Rico	<500	A: 0–5	64.7	14	NA	5.6
Oxisol	Parana, Brazil	<500	A: 0–2	38.5	12	NA	6.2
Oxisol[a]	Kinabalu, Malaysia	700	Ac: 0–10	29.9	12	25.7	4.8
Spodosol	Massachusetts	<500	E: 10–15	15.7	26	NA	4.7
			Bhs: 15–18	72.6	21	NA	4.2
Spodosol	Maine	<500	B1: 0–5[b]	60.9	23	48.7	4.5
			B2: 5–25[b]	39.3	21	35.4	4.6
Spodosol	Maine	<500	B1: 0–5[c]	86.8	23	69.4	4.7
			B2: 5–25[c]	92.1	24	82.9	4.9
Andisol	Hawaii Island	500	A: 0–2	151	15	NA	5.1

More detail information is found in Wagai (2005).

[a] Developed on ultramafic rock.

[b] Top 0–5 and 5–25 cm of spodic horizon under a conifer forest.

[c] Top 0–5 and 5–25 cm of spodic horizon under a deciduous forest.

and Zech, 1999; Kaiser and Guggenberger, 2000). Thus, this control should account for OC not adsorbed on FeOx but displaceable by non-reductive chemical solution conditions similar to the dithionite extraction. The difference in dissolved OC released between dithionite extractions and control extractions ($\Delta OC = [DOC_{dithionite} + DOC_{HCl}] - [DOC_{control} + DOC_{control\text{–}HCl}]$) was operationally defined as reductively soluble OC. Similarly, the difference in dissolved Fe ($\Delta Fe = [Fe_{dithionite} + Fe_{HCl}] - [Fe_{control} + Fe_{control\text{–}HCl}]$) represents the amount of reducible Fe.

2.2.2. *Extraction conditions*

2.2.2.1. Centrifugation. We centrifuged at 40,000*g* to maximize the recovery of all suspended solids in dithionite and sulfate extracts for the subsequent acid rinse step. Slower centrifugation (7800*g*) had little effect on $DOC_{dithionite}$ concentrations for four random samples tested.

2.2.2.2. pH. Mitchell and MacKenzie (1954) and Mitchell et al. (1971) conducted a fully inorganic dithionite extraction, reporting suggestive but inconclusive data with respect to the effect of pH on iron extractability. We therefore examined the effect of pH using three soils of contrasting mineralogy. Dissolution of OC was not significantly different among pH treatments over the range 3.2–7.1 except for an FeOx-rich sample where an unbuffered treatment released the most. Dithionite extraction without pH buffer was, therefore, adopted. Further discussion of pH and of the possible role of ionic strength on extraction efficiency is found in Electronic Annex (EA-1).

2.2.2.3. Dithionite–citrate. Iron extraction by our method averaged 98 ± 4% (mean ± SD) of the conventional dithionite–citrate (DC) method (Loeppert and Inskeep, 1996) for all the soils studied (EA-2). Comparison of OC extraction efficiency is obviously impossible because of the citrate in the DC method, so instead we examined nitrogen extraction by the dithionite–HCl method compared to that of the DC, as well as the ascorbate–citrate (AC) extraction which has been shown to selectively dissolve less-crystalline FeOx phases (Reyes and Torrent, 1997). None of these extraction tests used the sulfate control step. Among six soil samples of a range of soil types, four samples showed similar amounts of nitrogen extracted by dithionite–HCl compared to those by DC or AC (EA-3). To the extent that similar fractions of total carbon and nitrogen in soil OM are bound to FeOx, this result indicates that our dithionite–HCl method compares well with the DC approach. The other two soils (volcanic and spodic samples), however, showed roughly twofold higher N in the DC and AC extractions compared to dithionite–HCl extraction. We believe this discrepancy in the latter two soils to be due to high levels of precipitated organo-metal complexes typically found in these soil types (Petersen, 1976; Wada, 1995). The DC and AC methods each contain complexing agents that should enhance dissolution of OM precipitated by metals, agents which are absent in the dithionite–HCl approach. We therefore believe that our dithionite–HCl method likely underestimates the amount of OC precipitated as metal complexes. Nevertheless, the dithionite–HCl extraction fully dissolves reducible FeOx phases and the OC sorptively associated with those FeOx phases. Further discussion is presented in EA-3 and Section 3.

2.3. Density separations

To quantify the OC tightly associated with soil minerals, particulate organic materials having loose association with soil minerals were removed from bulk soil for selected samples by density separation (Golchin et al., 1994). Samples were mixed with 1.6 g cm^{-3} sodium polytungstate solution and treated with ultrasound (656 J mL^{-1}) using a Fisher-Artek-Dynatech Model 300 sonicator with 19-mm diameter tip. Settled materials in the sodium polytungstate solution after sonication were rinsed with deionized water and centrifuged repeatedly, and then freeze-dried for total OC and N analysis.

2.4. Other analyses

Dried bulk soil samples (2-mm sieved) were measured for soil pH in deionized water after 1-h equilibration. Total OC and N in dried samples were analyzed using a Perkin-Elmer 2400 CHN analyzer (Perkin-Elmer, Norwalk, CT, USA) after removal of carbonate by fuming with hydrochloric acid (Mayer, 1994). Total Fe concentrations were measured by ICP after dissolution by a sodium peroxide fusion method (detection limit = 0.05%, ALS Chemex, Sparks, NV, USA).

3. Results and discussion

3.1. Reductively soluble OC

The net mass of solubilized OC derived from FeOx reduction (ΔOC) ranged from below detection to 22 mg g^{-1} (EA-2). The fraction of total soil OC explained by reductively soluble OC was always low (<25%) except for one FeOx-rich Oxisol (37%, Fig. 1). Thus, direct association of soluble OC to reducible iron had only a minor role in total OC storage for virtually all the soil samples examined here.

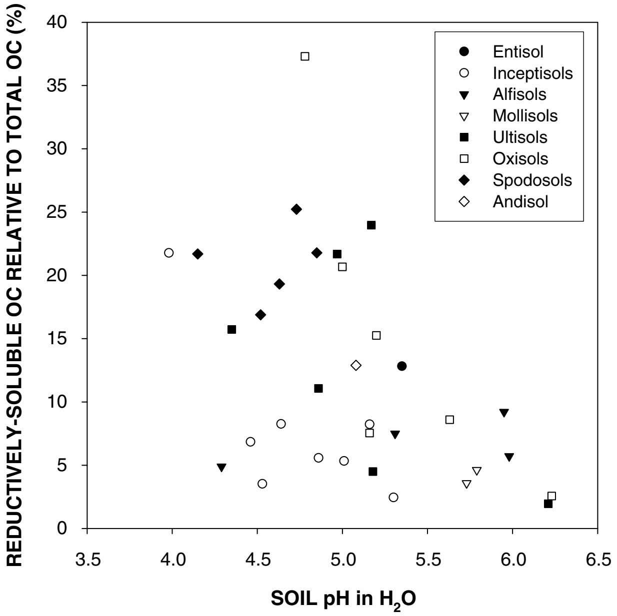

Fig. 1. Fraction of total soil OC that is reductively soluble vs. bulk soil pH in deionized water.

The sulfate and subsequent acid treatments released up to 23 mg-OC g^{-1}, representing 12–73% of the OC extracted by the dithionite plus acid treatments (EA-2). These significant fractions illustrate the importance of control extractions to accurately estimate the amount of OC attributable to the association with reducible FeOx.

We assume that a single dithionite extraction was sufficient to remove all reducible iron and associated OC from the samples. Repeated extractions for selected samples verified almost complete extraction by the single treatment except for highly weathered Oxisols. For the two Oxisols tested, OC release dropped significantly while iron dissolution rate continued strongly over three extractions (Table 2), suggesting that the most easily reducible FeOx phase (i.e., first extract) was enriched in OC. The Puerto Rican Oxisol released only a minor fraction (18%) of total OC during the three extractions. The Kinabalu Oxisol, however, released half of the total OC (Table 2). The high proportion of reductively soluble OC in the Kinabalu Oxisol is reasonable as this soil, developed from ultramafic rock, consists of essentially pure FeOx. For the other Oxisols, total Fe concentrations were used to extrapolate a potential upper limit for the reductively soluble OC. Assuming that all iron was in an FeOx form and had a similar OC:Fe ratio as the single dithionite-extractable fraction, only a minor fraction of total OC (4–18%) could be bound to these iron phases. Only in the Kinabalu Oxisol could total Fe account for more than a minor fraction of total soil OC.

Bulk soil includes mineral-free particulate OC as well as mineral-associated OC. Does the reductively soluble OC account for a major fraction of mineral-associated OC, the fraction of soil OM likely representing long-term storage (e.g., Baisden et al., 2002)? After adjusting total OC for the light-density fraction (plant detritus and possi-

Table 2
Repeated dithionite and acid extractions of two Oxisol samples

Sample ID # of extraction	Fe_{dith} (mg g^{-1})	Fe_{HCl} (mg g^{-1})	OC_{dith} (mg g^{-1})	OC_{HCl} (mg g^{-1})	$OC_{dith+HCl}$ (mg g^{-1})	$OC_{control}$[a] (mg g^{-1})
Puerto Rican Oxisol (Ox-1 in EA-2)						
First extraction[b]	70	20	4.1	3.4	7.5	3.0
Second extraction	69	15	0.72	2.5	3.2	NA
Third extraction	37	7.1	0.16	0.82	1.0	NA
Sum	176	42	4.9	6.7	11.7	NA
Kinabalu ultramafic Oxisol (Ox-4 in EA-2)						
First extraction[b]	103	48	5.2	4.5	9.8	1.5
Second extraction	101	33	0.64	3.4	4.0	NA
Third extraction	45	7.6	1.8	2.1	3.9	NA
Sum	249	88	7.7	10.0	17.7	NA

[a] Sum of control extractions (i.e., sulfate and HCl).

[b] The difference in the OC and Fe concentrations here and those in EA-2 likely resulted from sub-sampling error.

bly charred material), and excluding the Kinabalu Oxisol, only 10–32% of remaining, mineral-associated OC was reductively soluble for the 12 samples for which density separation data are available (Table 1). The light fractions typically have much higher C:N ratios (>25–30) than mineral-associated fractions (10–20) and account for a minor fraction of total OC except in some volcanic or organic soils. Most of the samples for which density separation data are unavailable had relatively low C:N ratios, and those with high C:N (>25) contained <4% of total OC associated with FeOx. Thus, our conclusions likely apply to the mineral-associated OC for all of our samples except for the Kinabalu Oxisol.

The highest contributions of reductively soluble OC were found in low pH soils (Fig. 1), especially weathered Oxisol and Ultisol samples. The OC-enriched, subsurface horizons of acid soils (all spodic horizons and the most acidic Inceptisol sample) also showed consistently high, reductively soluble OC relative to total OC. Reductively soluble OC thus accounted for higher fractions of total OC in the highly weathered or strongly leached soil end-members where base elements are largely leached via acidification, an important pedogenic process under humid regimes (Chesworth, 1992).

3.2. Soil depth series

Soil OC storage generally decreases with depth, but greater fractions of total OC are likely stabilized by minerals in subsurface horizons (e.g., Kaiser et al., 2002). Thus, we selected three soil types with high pedogenic FeOx contents to examine organo-iron associations at depth. From

Table 3
Soil depth trends in the dithionite + HCl and control extractions

Depth (cm) or horizon	Soil pH in H_2O	$Fe_{dith+HCl}$ (mg g^{-1})	$Fe_{control}$[a] (mg g^{-1})	$OC_{dith+HCl}$ (mg g^{-1})	$OC_{control}$[a] (mg g^{-1})	ΔOC (mg g^{-1})	ΔOC relative to TOC (%)	ΔOC:ΔFe (g:g)
Highly weathered, iron-rich Kinabalu Oxisol (Ox-4)								
0–10	4.8	185	0.12	12.6	1.5	11.2	34	0.06
20–40	5.0	212	NA	2.3	0.28	2.0	21	NA
80–100	5.2	257	NA	0.48	0.08	0.40	15	NA
Moderately weathered, kaolinitic Kinabalu Ultisol (Ult-4)								
0–10	4.4	25	0.43	6.4	2.0	4.3	16	0.18
20–40	5.0	26	NA	3.1	0.96	2.2	22	NA
60–80	5.2	29	NA	1.8	0.55	1.3	24	NA
Highly leached acid subsoils								
E[b]	4.7	1.5	0.02	0.4	0.7	−0.3	~0	~0
Bhs[b]	4.2	23	1.9	22.0	6.40	16.0	22	0.74
B1[c]	4.3	23	2.0	22	12	10	17	0.48
B2[c]	4.5	21	1.46	14	6.9	7.6	19	0.40
B1[d]	4.6	32	1.73	39	17	22	25	0.73
B2[d]	4.6	20	0.62	43	23	20	22	1.02
E[e]	4.5	8.5	0.53	3.1	2.0	1.0	3	0.13
Bw[e]	4.0	48	2.2	12	5.8	6.6	22	0.14

[a] Sum of control extractions (i.e., sulfate and HCl).

[b] Spd-1E and Spd-1Bhs in EA-2.

[c] Spd-2B1 and 2B2.

[d] Spd-3B1 and 3B2.

[e] Inc-1E and 1Bw.

the surface to 1-m depth of the Kinabalu Oxisol, progressively smaller fractions of total OC were released by a single dithionite extraction (Table 3). The amount of reductively soluble OC at depth in this Oxisol is perhaps underestimated, however, because repeated dithionite extractions were not performed.

On the other hand, a single dithionite treatment fully dissolved pedogenic FeOx from a kaolinitic Kinabalu Ultisol which showed increasing, albeit minor (<25%), contributions of reductively soluble OC to total OC with increasing depth (Table 3). While leached horizons of Spodosols and an Inceptisol contained little reductively soluble OC, their underlying horizons with high Fe accumulations contained much more, accounting for 17–25% of the total OC (Table 3). These results are consistent with well-known importance of organo-metal associations in subsurface OM accumulation in podzolic soils (Petersen, 1976, and see below).

3.3. *OC:Fe ratios and the nature of the association*

The ratios of OC to iron in the extracts (ΔOC:ΔFe) provide insight into the potential nature of the organo-iron associations if compared to these ratios from reported sorption and complexation studies. The maximum sorption of natural OC onto FeOx phases at pH 4–7 is 0.22 g-OC g-Fe^{-1} (Kaiser and Guggenberger, 2006) where freshly precipitated ferrihydrite (specific surface area = 224 m^2 g^{-1}) was used as the sorbent and dissolved OM from a temperate forest O-horizon as the sorbate. This value is at least 25% greater than other maximum values reported (e.g., Kavanagh et al., 1977; Tipping, 1981; Murphy et al., 1990; McDay et al., 1994; Gu et al., 1995; Kaiser et al., 1997; Wang et al., 1997; Chorover and Amistadi, 2001). Two-thirds of our samples showed OC:Fe ratios below this maximum sorption capacity (Fig. 2). Sorption of OM onto FeOx is thus a plausible mechanism for the association in these samples, consistent with inferences drawn from correlation studies (Kaiser and Guggenberger, 2000; Kaiser et al., 2002; Kiem and Kögel-Knabner, 2002; Eusterhues et al., 2003, 2005; Wiseman and Püttmann, 2005). The limited contribution of this sorption mechanism to total OC storage in our soil samples (Fig. 1) thus appears limited by the amount of FeOx. This inference is emphasized by the dominant role of FeOx in OM storage in the surface horizon of the Kinabalu Oxisol, which is composed of essentially pure FeOx.

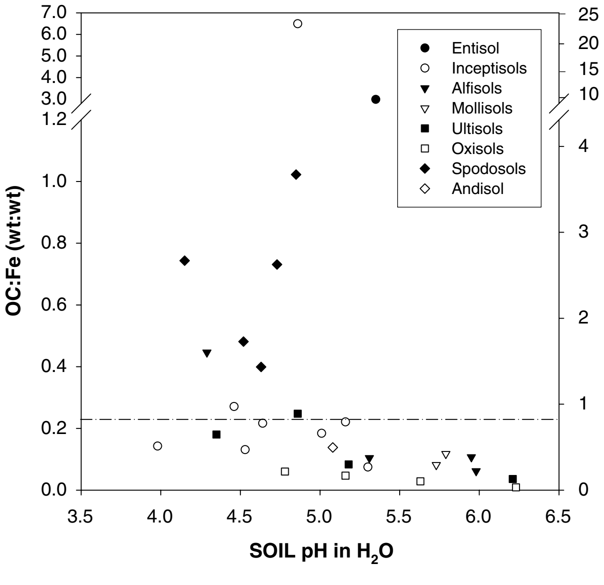

Fig. 2. The mass ratio of OC to Fe (left axis) and volumetric ratio of organic matter to FeOx (right axis) of the reductively soluble OC bound to reducible Fe vs. soil pH in deionized water. These ratios were calculated from ΔOC and ΔFe in EA-2. The horizontal line represents the maximum sorptive capacity of FeOx phases: 0.22 g-OC g-Fe^{-1} = 0.8 mm^3 OM (mm^3 FeOOH)$^{-1}$ from sorption experiments (Kaiser and Guggenberger, 2006).

Exceptions to this trend all had low pH, including all of the spodic horizons, the Entisol, an uncultivated Alfisol and a tropical-forest Inceptisol. Each had an OC:Fe ratio higher than reported maximum sorption capacities (Fig. 2). The solubility of FeOx increases with decreasing pH below 6–7 (Lindsay, 1979), leading to the trend that lower pH favors complexation and precipitation of Fe with OM while higher pH favors adsorptive association between FeOx and organic materials (Tipping et al., 2002). Field observations from a range of surface soils (Skjemstad et al., 1989) and suspended river materials (Allard et al., 2004) support this pH trend in organo-iron association mechanisms. The fact that all of our spodic samples positioned above the sorption maximum adds confidence to our inference of precipitated organo-Fe complexes from high Fe:OC ratios. Of course, the dissolved materials that make up the OC:Fe ratio do not necessarily derive from such organo-Fe complexes or include all of the precipitated organo-Fe complexes present in the soil (see EA-3). Complexation may protect OM via a mechanism analogous to metal tanning, in which monomers and oligomers of metals, especially trivalent metals, form extensive cross-links among organic molecules that prevent enzymatic attack on the organic moieties. Both iron and aluminum have been used in commercial tannages. OC:Fe ratios for organo-metal complexes have been calculated to be at least 1.3–2.2 (wt:wt), based on assumptions on charge balance and organo-metal stoichiometry (Wada and Higashi, 1976; Oades, 1989). Our samples with OC:Fe ratios >0.22 thus likely contained organo-iron associations in the form of precipitated complexes, either alone or in combination with other types of associations.

Most of the low pH (<4.5) samples with OC:Fe ratios below the maximum sorption capacity (Fig. 2) had low total OC concentration (<30 mg g^{-1}), while all of the samples with high OC:Fe ratios were found in soils with higher OC concentrations (Fig. 3). Thus, our results support the conceptual model (Schwertmann et al., 1986) that the dominant form of iron in soil environment shifts from FeOx to precipitated organo-Fe complexes with increasing OC supply. High soil OM concentration resulting from inefficient microbial decomposition promotes organic acidity. Low pH, in turn, retards microbial degradation of OC

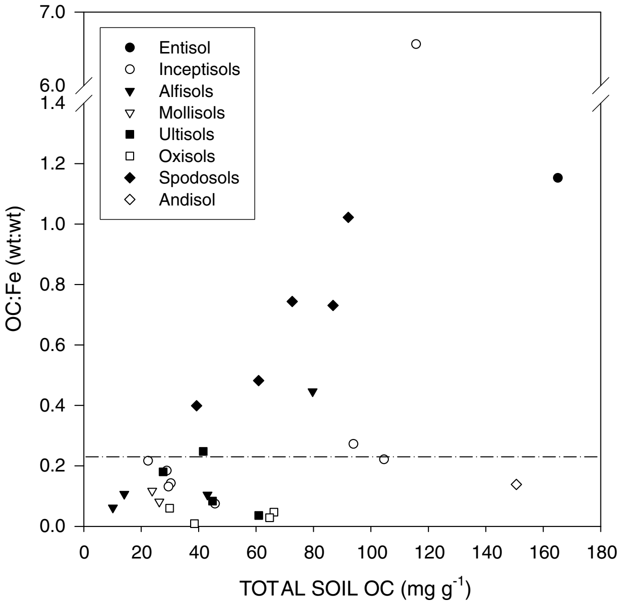

Fig. 3. The mass ratio of OC to Fe of the reductively soluble OC bound to reducible Fe vs. total soil OC concentration. The horizontal line represents the maximum sorptive capacity of iron oxide phases (see Fig. 2 for detail).

(e.g., Motavalli et al., 1995), obscuring the causality between high OC and low pH. Nevertheless, our data imply that both low pH and high total OC concentration are prerequisites for organo-Fe(III) precipitation among our soil samples.

Our measurements of soil OC:Fe ratios in reducible FeOx phases allow comparison with other environments. Ratios of total OC to dithionite-extractable Fe for iron-rich precipitates in spring water and small streams ranged from 0.03 to 0.19 (Carlson and Schwertmann, 1980, 1981; Rhoton et al., 2002), consistent with sorption. Similarly, OC:Fe ratios of suspended materials from the lower Mississippi river (unpublished data—using our current method) ranged from 0.10 to 0.17, consistent with the soils sampled from its catchment for this study (Alf-3 and Mol-2 in EA-2). In Amazon river tributaries, Allard et al. (2004) found an abundance of organo-Fe(III) complexes only in acidic, organic-rich water, which reflected the dominance of podzolic soil types in the catchments. Thus, both sorptive and complexation associations exist in aquatic systems as well as in soils.

3.4. Aluminous phases

AlOx and amorphous aluminosilicate phases provide other reactive sorbents for soil OM, and are often considered with FeOx phases (e.g., Torn et al., 1997; Kaiser and Guggenberger, 2000). Lack of specific inorganic extractants, analogous to dithionite for iron, prevented similar test of their potential role in soil OM stabilization. Co-dissolution of aluminum upon the reductive dissolution of FeOx phases, on a molar basis, accounted for 20 ± 15% of reducible (Fe + Al) for all the samples and 37 ± 16% for spodic horizons (EA-2). Similar levels of Al substitution in FeOx, particularly in goethite, have been reported (Schwertmann, 1988). Silica dissolution was low (<1.3 mg g^{-1}), implying negligible allophanic and imogolitic material in our spodic samples.

The acid rinse treatments (pH 1.3 for 1 h) should cause significant dissolution of AlOx. The acid-dissolution of Al from both dithionite- and sulfate-extraction residues correlated very strongly with OC dissolution across all of our samples (e.g., for sulfate residues, $[\mathrm{OC}]_{\mathrm{HCl}} = 1.60 * [\mathrm{Al}]_{\mathrm{HCl}} - 0.23$, $R^2 = 0.87$, $p < 0.001$, on weight basis). These correlations suggest organo-aluminum associations in our samples. Similarly, in spodic horizons of Australia, weak acid extractions (0.01–0.5 M HCl) led to a significant co-dissolution of OC and Al but not Fe (Skjemstad et al., 1992), which was mainly attributed to hydrolysis of precipitated organo-Al complexes. We made a liberal assumption that all the acid-extracted OC from the sulfate residues was bound to acid-labile AlOx phases to assess the maximum extent of its sorptive accumulation of OC in the same way that we did for reducible iron phases. The resultant OC:Al ratios mostly exceeded the maximum sorptive capacity of amorphous AlOx phases from sorption experiments, 0.82 g-OC g-Al^{-1} (Kaiser et al., 1997) (Fig. 4). Similar to the relationship between the OC:Fe ratio of dithionite-reducible phases with pH (Fig. 2), lower soil pH generally led to higher OC:Al ratio (Fig. 4). As with iron, the solubility of AlOx phases and activity of Al^{3+} are greater at lower pH (Lindsay, 1979). Together with the fact that low pH generally corresponds to high soil OM and supply of organic acids (e.g., Fig. 2

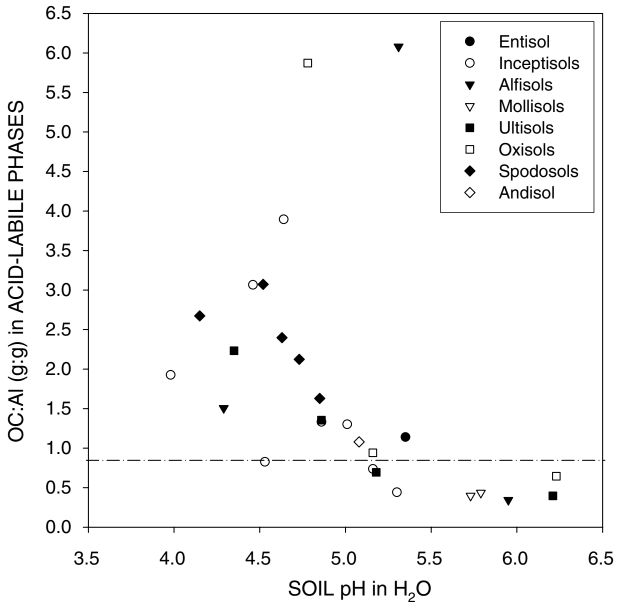

Fig. 4. The mass ratio of OC to Al of the material extracted by the acid rinse treatment of the sulfate-control residue from each sample vs. soil pH in deionized water. The horizontal line represents the maximum sorptive capacity of AlOx phases (0.82 g-OC g-Al^{-1}) from sorption experiments (Kaiser et al., 1997).

and 3), the observed OC:Al ratios above the maximum sorption range imply dominance of precipitated organo-aluminum complexes over sorptive associations.

For all of our samples except for the spodic horizons, the acid–labile OC accounted for <4% of the total OC. For the spodic horizon samples, in contrast, 5–35% of the total OC was explained by the acid-labile phase, in accordance with the well-known importance of organo-aluminum associations in spodic horizons (e.g., Petersen, 1976; Skjemstad et al., 1992).

3.5. Implications for OC:Fe Correlations in Soils

The maximum sorption capacity of 0.22 g-OC:g-Fe (Kaiser and Guggenberger, 2006) corresponds to a volumetric ratio of 0.8 OM:FeOx assuming that OM is 50% C, the density of soil OM is 1.4 g cm^{-3} (Mayer et al., 2004), and FeOx consists of FeOOH with a density of 4.0 g cm^{-3}. In other words, laboratory experiments indicate that FeOx phases can sorb only up to approximately their own volume in OM, consistent with the notion that adsorbates are generally smaller than adsorbents.

Similarly, we calculated the volumetric ratios of OM to FeOx and AlOx for soils in the literature from regression slopes where OC-metal correlations were reported (Table 4). These ratios, for the vast majority of the reported soils and their physical fractions, indicate organic matter volumes that are many times greater than the FeOx and AlOx contents, either individually or summed together (Table 4). These patterns support our conclusion that simple OC sorption to FeOx phases accounts for only a minor fraction of total OC storage. Guggenberger and Kaiser (2003) suggested limited sorptive capacities of these phases in some temperate acid soils to store OC based on the extrapolation of the sorption maxima measured using field soil horizons, consistent with the conclusion we draw using a different approach.

We therefore need to consider more complex mechanisms, besides simple sorption to metal oxide phases, to enable the storage of a several-fold greater volume of OM per unit volume of metal oxides. If adsorbed OM undergoes humification reactions after sorption that renders it insoluble, then our method would not detect it. It is possible that significant volumes of OM could accumulate in this manner, perhaps via post-sorption tanning reactions (see above). Metal–organic complexes provide another alternative, especially for low-pH and high-OM soils. Last, we suggest that ternary OM–FeOx–clay associations provide

Table 4
The volumetric ratios of OM to metal oxides calculated from the previous reports

General soil type	Horizon or depth	*N*	Physical fraction of soil analyzed[a]	Extractant used for metal[b]	OM:FeOx (vol:vol)	OM:AlOx (vol:vol)	OM:(FeOx + AlOx) (vol:vol)	Ref.
Eight soil orders	A–B	168	Bulk	DC	**3.7**	15	2.9	(1)
Nine soil orders	A	167	Bulk	DC	**14.7**	NA	NA	(2)
			Bulk	Oxalate	NA	**2.8–17.4**	NA	(2)
			Bulk	Pyrophos	NA	**11–32**	NA	(2)
A range of NE Australian soils	A	36	Bulk	DC	3.3	**16.0**	2.7	(3)
			Bulk	Oxalate	17.5	**12.0**	7.2	(3)
			Bulk	Pyrophos.	64.0	**32.0**	22.0	(3)
Three soil orders from California	Top 1 m	7	Bulk	DC	**9–73**	**10–374**	**8–44**	(4)
			Bulk	Pyrophos.	**32–50**	**7–19**	**6–13**	(4)
Five soil orders, Hawaii	Top 1 m	35	Bulk	Oxalate	NA	NA	**0.4–3.3**[d]	(5)
Volcanic soils	A	25	Pyrophos.	Pyrophos.	**4.6–11**[d]	**1.5–3.5**[d]	**1.1–2.6**[d]	(6)
Acidic temperate soils	A–B	59	Sonic, >1.6 g cm^{-3}	DCB	**5.7–14**	NA	NA	(7)
Acidic temperate soils	A–C	14	>1.6 g cm^{-3}	Oxalate, DCB	**19, 11**	NA	NA	(8)
Acidic temperate soils	A	12	Size fractions	Oxalate, DCB	**5.4, 6.8**	NA	NA	(9)
Two acidic forest soils	A–C	6	Bulk	DCB	**6.0–6.3**[e]	NA	NA	(10)
Two acidic forest soils	Bh,s,w	2	<2 μm, >2.0 g cm^{-3}	DCB	**3.2–6.9**	2.5–9.9	1.8–3.2	(11)
			<2 μm, >2.0 g cm^{-3}	Oxalate	**5.5–15.6**	4.0–12.6	2.8–5.8	(11)
Spodosols	B	54	Pyrophos.	Pyrophos.	**22**	**4.4**	**3.7**	(12)
			Pyrophos.	DCB	**5.4**	**2.1**	**1.6**	(12)
Weathered tropical soils	A	13	Sonic, <2 μm	Oxalate	**18–103**	**5–52**	**4–35**	(13)
Weathered tropical soils	A	2	2–50 μm[f]	Oxalate	**82–123**	**34–42**	**24–31**	(14)

The ratios where significant positive correlations were found are shown in bold.

Reference: (1) Tiessen et al. (1984), (2) Percival et al. (2000), (3) Skjemstad et al. (1989), (4) Masiello et al. (2004), (5) Torn et al. (1997), (6) Wada (1995), (7) Kaiser and Guggenberger (2000), (8) Kaiser et al. (2002), (9) Kiem and Kögel-Knabner (2002), (10) Eusterhues et al. (2003), (11) Eusterhues et al. (2005), (12) Evans and Wilson (1985), (13) Hughes (1982), and (14) Shang and Tiessen (1998).

[a] Sonic, sonication; pyrophos., pyrophosphate-extraction.

[b] DC, dithionite–citrate; DCB, dithionite–citrate-bicarbonate.

[c] Maximum sorptive capacity was calculated as 0.80 and 0.95 (vol:vol) for FeOx and AlOx.

[d] Fe and Al were assumed to account for half of the extractable Fe + Al reported.

[e] Three to four density fractions of 20–50 μm size aggregates separated from two soils.

[f] Three to four density fractions were separated from two soils. NA, data not available.

another mechanism. Extractable FeOx and AlOx phases in soil matrices are often found associated with phyllosilicate clays, helping to glue these clays together. Ternary OM–FeOx–clay associations have been considered important for soil microaggregate formation (Oades, 1984; Krisnamurti and Huang, 1987; Shang and Tiessen, 1998; Vrdoljak and Sposito, 2002; Wiseman and Püttmann, 2006). Despite the significantly lower sorptive capacity of phyllosilicate clays compared to FeOx and AlOx phases, clay minerals are planar and have high surface-to-volume ratios, effective traits to physically reduce enzyme and oxygen accessibility to OM. Thus, the combination of highly reactive metal oxides with less sorptive but more abundant clays may physically protect larger volumes of insoluble OM. This protective mechanism could explain why only minor fractions of total OC were found to be associated with FeOx by our direct measurement despite the significant OC–FeOx correlations often found in the literature. If true, then multiple mechanisms are likely responsible for the OC-Fe correlations, with the organo-metal precipitates particularly important for low pH, organic-rich soils and the ternary OM–FeOx–clay associations for other soils. Thus, FeOx may be critical for OC storage, but likely not via a direct sorption mechanism.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.08.047.

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