

Poorly crystalline mineral phases protect organic matter in acid subsoil horizons

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Summary

Soil minerals are known to influence the biological stability of soil organic matter (SOM). Our study aimed to relate properties of the mineral matrix to its ability to protect organic C against decomposition in acid soils. We used the amount of hydroxyl ions released after exposure to NaF solution to establish a reactivity gradient spanning 12 subsoil horizons collected from 10 different locations. The subsoil horizons represent six soil orders and diverse geological parent materials. Phyllosilicates were characterized by X-ray diffraction and pedogenic oxides by selective dissolution procedures. The organic carbon (C) remaining after chemical removal of an oxidizable fraction of SOM with NaOCl solution was taken to represent a stable organic carbon pool. Stable organic carbon was confirmed as older than bulk organic carbon by a smaller radiocarbon (¹⁴C) content after oxidation in all 12 soils. The amount of stable organic C did not depend on clay content or the content of dithionite–citrate-extractable Fe. The combination of oxalate-extractable Fe and Al explained the greatest amount of variation in stable organic C ($R^2=0.78$). Our results suggest that in acid soils, organic matter is preferentially protected by interaction with poorly crystalline minerals represented by the oxalate-soluble Fe and Al fraction. This evidence suggests that ligand exchange between mineral surface hydroxyl groups and negatively charged organic functional groups is a quantitatively important mechanism in the stabilization of SOM in acid soils. The results imply a finite stabilization capacity of soil minerals for organic matter, limited by the area density of reactive surface sites.

Introduction

Minerals exert control over soil organic matter (SOM) content through mechanisms that protect either organic inputs or their decomposition products against biological attack. Models of SOM turnover, while incorporating soil texture (i.e. clay content) as a key element in carbon (C) dynamics, generally treat the impact of clay on C stabilization as being independent of clay mineralogy (Paustian *et al.*, 1997). However, more than five decades ago Allison *et al.* (1949) showed that the amount of organic C surviving in a decomposition experiment depended on the type of clay mineral present. Recent research also indicates a differential capacity of minerals to adsorb and protect organic matter as a result of mineral-specific properties such as surface area, charge characteristics and porosity (Krull *et al.*, 2003).

Schnitzer & Kodama (1992) emphasized the importance of poorly crystalline minerals for C retention and turnover in

soils. Jahn *et al.* (1992) and Torn *et al.* (1997) showed that the ability of volcanic soils to store organic C is a function of their content of poorly crystalline minerals, and declines with the accumulation of more-crystalline minerals in the course of pedogenesis. Similar results were obtained by Percival *et al.* (2000) for 167 pedons from 12 soil orders in New Zealand: they found that clay content explained little ($R^2=0.01$) of the variation in soil C while significant linear relationships were observed with parameters representative for poorly crystalline minerals (R^2 of 0.37, 0.50 and 0.60 for oxalate-extractable Si (Si_o), oxalate-extractable Al (Al_o) and pyrophosphate-extractable Al (Al_p), respectively).

Abundant evidence suggests the mechanism of ligand exchange between carboxyl groups of organic matter and hydroxyl groups at the surfaces of mineral phases to be the most important control on the formation of stable organic–mineral matter complexes under acid conditions (e.g. Kaiser & Guggenberger, 2000). Hydroxyl-bearing phases, such as Fe (hydr)oxides and poorly crystalline aluminosilicates, should therefore control the amount of SOM that might be stabilized by interaction with a mineral matrix in acid soils.

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Processes that stabilize SOM, such as organic–mineral interactions, reduce decay rates. Hence, other conditions being equal, the relative stability of two soil fractions can be assessed by their rate of decay or by the age of the organic C they contain. Soil organic matter resistant to chemical degradation procedures has been shown to be older than bulk organic C before treatment (Balesdent, 1996) and to comprise more refractory organic carbon structures (Cuypers *et al.*, 2002).

Since chemical oxidative degradation induces changes in SOM composition similar to those observed during biodegradation, the residual organic C could reflect a C fraction relatively (i.e. compared with what was oxidized) resistant to biodegradation as well (Cuypers *et al.*, 2002).

The main objective of this study was to test the hypothesis that the extent to which an acidic soil can protect organic C against chemical attack depends on the amount of poorly crystalline minerals. We further hypothesize that the stabilizing effect of poorly crystalline minerals towards soil C might not be restricted to allophanic soils, but could operate to an unknown extent in any acidic soil.

To test these hypotheses, we compared the relations between organic carbon contents and some variables representing poorly crystalline mineral phases before and after the isolation of a stable organic carbon fraction with NaOCl. To approximate its general applicability, we used 12 acid subsoils of different mineralogical composition, including soils containing various amounts of phyllosilicates, short-range order minerals, and Al and Fe (hydr)oxides.

Materials and methods

Sample selection and pretreatment

Sample selection was based on the underlying assumption that a protection mechanism depending on mineral surface reactivity must be effective regardless of geographical site location, climate regime, vegetation type, or horizon depth. Therefore, sampling was designed to maximize (i) differences in surface reactivity and (ii) mineralogical variability. Accordingly, the 12 soils sampled represent a gradient from low (siloxane-type) to high (short-range order-type) mineral surface reactivity as expressed by fluoride reactivity (Table 1).

The phyllosilicate mineral assemblage was intended to represent all major phyllosilicate species (Figure 1) in order to avoid a bias towards a single mineralogical class. Soils containing allophane were not the focus of this study and thus were intentionally omitted, as were calcareous soils. The absence of allophane from samples with large Si_o values (Soils 9–11) was verified in previous work (Kleber *et al.*, 2003, 2004a). For each soil, subsurface horizons were chosen to minimize the amount of particulate organic matter not associated with mineral surfaces. The samples were air-dried and sieved to < 2 mm.

Fluoride reactivity

Fluoride reactivity was proposed as a differential criterion between well- and poorly ordered minerals by Bracewell *et al.* (1970). The fluoride reactivity of the samples was determined according to Perrott *et al.* (1976), who showed that the increase in pH when a NaF solution is added to a soil reflects the reactivity of the mineral surfaces. Briefly, 20 ml of a 0.85 M NaF solution prepared with CO₂-free water and adjusted to pH 6.8 was added to a 100 mg soil sample. The suspension was kept at a constant pH by titrating the OH⁻ released under a continuous argon flow at 25°C with 0.2 M HCl from a micro-syringe burette using an automatically recording Titrigraph.

Physical soil properties

Basic soil properties, including particle-size distribution and specific surface area (SSA), were measured according to Siregar *et al.* (2004). Phyllosilicate mineralogy was determined by X-ray diffraction on oriented specimens of clay fractions as described in Kleber *et al.* (2004b).

Chemical properties and selective dissolution

Soil pH, cation exchange capacity (CEC), organic C, total N as well as dithionite–citrate-, oxalate- and pyrophosphate-extractable elements were determined as detailed by Siregar *et al.* (2004). Selective dissolution data were interpreted according to Wada (1989): dithionite–citrate-extractable Fe (Fe_d) is taken to represent both crystalline and poorly crystalline Fe oxides, and dithionite–citrate-extractable Al (Al_d) represents Al substituted in Fe oxides and from the partial dissolution of poorly ordered Al (oxy)hydroxides. Acid oxalate is supposed to extract Al, Fe and Si from poorly crystalline aluminosilicates, ferrihydrite, and Al- and Fe-humus complexes, but not from gibbsite, goethite and haematite, or from layer silicates. Pyrophosphate is used for estimation of Fe and Al associated with organic matter. The Fe activity ratio (Fe_o/Fe_d) reflects the poorly crystalline fraction of total Fe oxides. Thus, $Fe_d - Fe_o$ represents crystalline Fe oxides, while $Al_o + 0.5Fe_o$ is a diagnostic criterion employed to distinguish subtypes of andic properties in soil taxonomy (Shoji *et al.*, 1996).

Isolation of stable organic C

An oxidation-resistant organic C fraction was isolated by means of a NaOCl treatment as described by Siregar *et al.* (2004). Radiocarbon content of organic matter before and after oxidation was measured by accelerator mass spectrometry at the Lawrence Livermore National Laboratory on targets prepared by zinc reduction. Before target preparation, samples were held under an atmosphere of HCl overnight to avoid possible contamination with inorganic carbon and were

Table 1 Site description

Sample ID	Soil designation	Classification ^a	Horizon	Depth /cm	Parent rock	Vegetation	MAT ^b /°C	MAP ^c /mm	Fluoride reactivity /mol OH ⁻ kg ⁻¹	pH (KCl)
1	Rottleberode	Dystric Cambisol	Bw	5–23	Schist	Deciduous forest	7.0	750	0.19	3.8
2	Kyffhäuser	Haplic Luvisol	E	5–15	Loess	Deciduous forest	7.5	600	0.27	3.4
3	Kyffhäuser	Haplic Luvisol	Bt	40–80	Loess	Deciduous forest	7.5	600	0.42	3.6
4	La Selva	Humic Ferralisol	Bws	75–100	Andesite	Neotropical rainforest	25.8	3960	0.58	4.1
5	Bärenthal	Chromic Cambisol	Bw	16–36	Limestone	Coniferous forest	6.5	800	0.42	5.1
6	Hewenegg	Vitric Phaeozem	AB	5–35	Basalt	Deciduous forest	7.0	800	0.54	5.8
7	Wildmoos	Chromic Cambisol	Bw	10–30	Gneiss	Coniferous forest	6.0	1600	0.82	3.9
8	Oberwarsteinach	Haplic Podzol	Bhs	10–35	Phyllite	Coniferous forest	5.3	1310	0.36	3.6
9	Köhlerwald	Andic Luvisol	Bt	13–33	Basalt and loess	Coniferous forest	5.5	1200	1.59	4.1
10	Köhlerwald	Andic Luvisol	2Bw	87–107	Basalt and loess	Coniferous forest	5.5	1200	1.58	4.1
11	Lausche	Umbric Andosol	Bw	40–70	Phonolite	Mixed deciduous forest	5.5	900	2.32	4.1
12	Wuelfersreuth	Dystric Cambisol	Bw	7–22	Phyllite	Coniferous forest	5.7	1190	0.51	3.3

^aAccording to FAO (1994).

^bMAT, mean annual air temperature.

^cMAP, mean annual precipitation.



Figure 1 X-ray diffraction scans of oriented specimens (Mg-saturated, glycerolated) from the clay (<math><2\mu\text{m}</math>) fractions of the 12 subsoil horizons, arranged by identification number (Table 1). Dotted vertical lines represent d-spacings in nm. All scans are normalized to the 0.71 nm peak to facilitate comparison of relative phase abundance.

subsequently dried at 105°C. Radiocarbon content is expressed as $\Delta^{14}\text{C}$, the deviation of the $^{14}\text{C}/^{12}\text{C}$ ratio in the sample from that of an oxalic acid standard, with decay and ^{13}C corrections according to Stuiver & Polach (1977). In the late 1950s to early 1960s, above-ground nuclear weapons testing caused a large increase in atmospheric $^{14}\text{CO}_2$. The $\Delta^{14}\text{C}$ unit is normalized such that the pre-1950 atmosphere was roughly $\Delta^{14}\text{C}=0$. A negative $\Delta^{14}\text{C}$ indicates that radioactive decay of older material has occurred, and positive values of $\Delta^{14}\text{C}$ indicate the presence of bomb-produced ^{14}C .

Analytical precision

All chemical analyses were done in triplicate and the mean values are reported. The standard errors were less than 1% of the means throughout, with few minor deviations, and are therefore not represented in Tables 1–3 for clarity.

Data analysis

We examined the relationship between soil C content in untreated and NaOCl-treated samples and physical soil properties and selective dissolution data with single variable linear regression. All regression analyses were carried out with PlotIT for Windows.

Results

Organic C removal

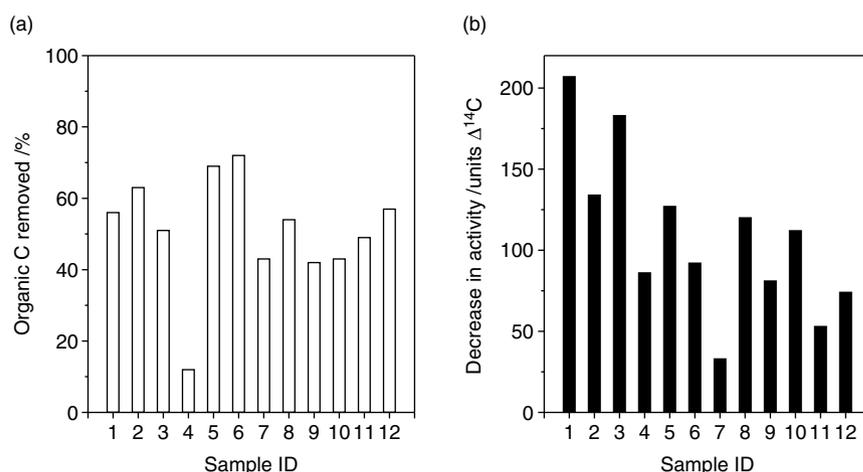
Treatment with NaOCl removed different amounts of organic matter (Figure 2a). This indicates that, within the sample population, there is either a varying degree of recalcitrance of SOM, or a different degree of protection exerted by the mineral matrix, or both. The NaOCl treatment also changed the C/N ratios of SOM, with a greater relative N loss in soils containing larger amounts of poorly crystalline Fe and Al (Figure 3); this indicates less mineral protection for N-containing organic compounds.

Chemical degradation and sample properties

The decline in organic C contents following NaOCl treatment was accompanied by a concomitant decline in CEC (except Ferralsol No. 4). The observed increase of SSA after chemical oxidation of SOM has been frequently reported and was attributed to the removal of organic coatings from mineral surfaces (Siregar *et al.*, 2004).

The NaOCl treatment did not significantly alter the contents of dithionite–citrate- and oxalate-extractable Fe, Al, and Si (Tables 2 and 3), supporting the idea that NaOCl leaves poorly crystalline mineral components largely intact (Siregar *et al.*, 2004).

Figure 2 Relative decline in organic matter concentration (a) and decrease in radiocarbon activity (b) after treatment with NaOCl. $\Delta^{14}\text{C}$ is the deviation in parts per thousand from the activity of an oxalic acid standard measured in 1950, corrected for the radioactive decay of the standard thereafter. The decrease of $\Delta^{14}\text{C}$ values corresponds to an increase in radiocarbon ages of 75–1880 years. Sample IDs are as given in Table 1.



Isolation of stable organic C

Radiocarbon age of the untreated samples was between modern and nearly 5000 years before present (Table 2). Sodium hypochlorite treatment decreased the ^{14}C activity in all samples, with differences in $\Delta^{14}\text{C}$ spanning a range of 53 to 207 units (Figure 2b). Thus, in all 12 samples, the NaOCl procedure left behind organic C with a greater radiocarbon age than in the untreated samples. The content of stable organic C was not related to mean horizon depth, SSA or clay content. Fluoride reactivity explained 45% ($P < 0.05$) of the variability of stable organic C (Table 4).

Linear regression analysis – untreated samples

Organic matter contents in the untreated samples were independent of most of the parameters obtained by selective dis-

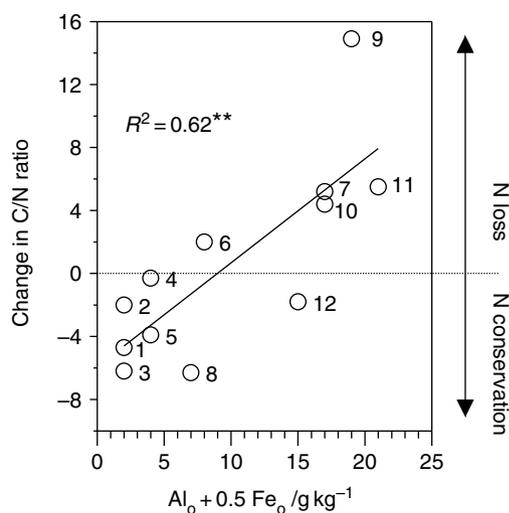


Figure 3 Change in C/N ratio after treatment of organic matter with NaOCl solution as a function of concentrations of poorly crystalline components represented by $\text{Al}_0 + 0.5\text{Fe}_0$. Numbers indicate sample ID (Table 1). $**P < 0.01$.

solution with a few notable exceptions. Oxalate-extractable Fe explained 40% ($P < 0.05$) of the variability of organic C contents in the untreated samples (Table 4). Slightly more variability (42%, $P < 0.05$) is explained when Fe_0 and Al_0 are combined in a single parameter. In soil taxonomy, an Al plus 0.5 Fe concentration ($\text{Al}_0 + 0.5\text{Fe}_0$) of $\geq 20 \text{ g kg}^{-1}$ indicates the presence of andic soil properties, implying that the exchange complex in these horizons is dominated by X-ray amorphous compounds of Fe, Al, Si and humus. The 12 subsoils investigated are non-allophanic throughout, so it seems plausible that Fe_0 should be of similar or even greater predictive power than Al_0 . In fact, when all Fe_0 is added to Al_0 (Table 4), 48% of the variability of C contents in the untreated subsoils is explained ($P < 0.05$).

The results suggest that organic C contents in untreated, acid subsoils are positively and linearly related to the content of poorly crystalline minerals. This perception is supported by the observation that 41% ($P < 0.05$) of the variability of organic C is explained by pyrophosphate-extractable C, i.e. such C that can be released by alkaline pyrophosphate from organic–mineral associations by displacing bound organic compounds from sorption sites.

Linear regression analysis – stable organic C

Neither the amount of dithionite–citrate–extractable Fe nor crystalline Fe oxides ($\text{Fe}_d - \text{Fe}_0$) explained the contents of stable organic C in either untreated or NaOCl-treated samples. This indicates that better-crystalline Fe oxides are of minor importance for C protection although those minerals were abundant in some of our samples (Soils 4 and 5). However, a highly significant relation ($R^2 = 0.89$, $P < 0.001$) between pyrophosphate-soluble C (C_p) and stable organic C suggests that the majority of stable organic C is protected by (i) attachment to mineral surfaces or (ii) complexed hydroxy-metal species, or both, since the strongly adsorbing pyrophosphate anion specifically and effectively displaces organic ligands

Table 2 Chemical properties, selective dissolution data and C and N concentrations of untreated samples

Soil	SSA ^a /m ² g ⁻¹	CEC ^b (pH 7) /cmol _c kg ⁻¹	Bsat ^c /%	Dithionite			Oxalate			Pyrophosphate				Total			C/N	Δ ¹⁴ C /units	¹⁴ C age /years BP
				Fe	Al	Si	Fe	Al	Si	Fe	Al	Si	C	C	N				
1	6.1	11.5	16	22.0	1.4	0.6	2.3	1.0	0.2	1.6	1.4	1.3	2.5	10.8	0.7	14.9	-1.1	> Modern	
2	7.6	22.6	36	6.4	1.1	1.1	1.1	1.5	0.3	2.1	4.0	5.7	3.1	11.5	0.7	17.4	27.3	> Modern	
3	33.4	30.3	50	10.1	1.6	2.8	1.1	1.8	0.3	2.6	4.9	7.4	1.9	4.9	0.3	14.5	-124.2	1015	
4	74.7	8.1	6	101.8	21.2	1.1	2.3	3.3	0.4	16.1	11.4	6.1	11.1	10.0	0.9	11.0	-463.2	4945	
5	32.9	36.9	55	52.6	4.9	1.4	2.9	2.5	0.3	2.2	1.3	0.7	4.9	19.7	1.6	12.6	23.9	> Modern	
6	23.0	75.3	64	23.7	2.9	4.5	8.8	3.4	1.4	1.4	0.8	0.8	6.1	38.2	2.3	16.5	77.2	> Modern	
7	37.3	38.3	1	35.0	8.8	0.5	18.9	7.3	0.3	19.3	9.2	3.6	18.0	36.0	1.9	19.2	-57.5	425	
8	10.7	19.3	2	20.1	3.2	0.3	9.3	2.6	0.2	7.7	3.1	1.6	6.8	13.8	1.0	13.8	-48.2	345	
9	35.0	34.1	2	32.4	11.1	2.3	12.8	12.7	2.3	14.2	21.4	16.6	12.7	30.7	1.6	19.1	-80.9	625	
10	24.8	29.5	1	31.1	9.1	3.1	10.0	11.5	3.7	6.4	9.2	5.8	7.1	15.7	1.4	10.9	-377.8	3760	
11	16.0	52.1	4	10.2	10.7	2.3	4.8	18.8	5.6	5.1	13.0	7.8	15.3	27.7	2.0	13.8	-224.6	1990	
12	18.4	31.4	1	35.9	5.1	0.5	20.5	4.4	0.2	17.3	6.2	4.3	12.2	23.2	1.3	17.5	-37.8	260	

^aSSA, specific surface area (BET-N₂).^bCEC, cation exchange capacity (NaOAc).^cBsat, base saturation.

from mineral binding sites, including amorphous Al species (Kaiser & Zech, 1996; Table 4). This is corroborated by the dependence of C_p on oxalate-extractable Fe and Al compounds ($R^2=0.80$, $P<0.001$), which are here taken to represent the main providers of hydroxylated surfaces.

Stable organic C is significantly and positively related to the number of mineral surface hydroxyls released by NaF ($R^2=0.45$, $P<0.05$), supporting the view that reactive hydroxyl groups on mineral surfaces are mechanistically involved in C stabilization.

If examined individually, both Fe_o and Al_o explain significant amounts of stable organic C (Table 4). If combined (Al_o+0.5Fe_o or Al_o+Fe_o) to a parameter indicative of amorphous mineral matter as a whole, they explain the majority of the variability of stable organic C ($R^2=0.72$ for Al_o+0.5Fe_o and $R^2=0.78$ for Al_o+Fe_o, both significant at $P<0.001$). These results strongly suggest a contribution of oxalate-extractable Fe and Al to the protection of SOM, giving ample reason to accept our hypothesis for the pool of subsoil samples investigated.

Table 3 Chemical properties, selective dissolution data and C and N concentrations after NaOCl treatment

Soil	Fluoride reactivity /mol OH ⁻ kg ⁻¹	SSA ^a /m ² g ⁻¹	CEC ^b (pH 7) /cmol _c kg ⁻¹	Dithionite			Oxalate			Pyrophosphate				Total			C/N	Δ ¹⁴ C /units	¹⁴ C age /years BP
				Fe	Al	Si	Fe	Al	Si	Fe	Al	Si	C	C	N				
1	0.22	7.1	9.4	22.7	1.3	0.7	2.2	0.8	0.1	0.6	0.6	0.4	1.2	4.8	0.5	10.2	-207.9	1820	
2	0.27	12.7	16.8	5.6	0.9	0.9	1.0	1.2	0.1	0.5	0.9	0.9	1.3	4.2	0.3	15.4	-106	850	
3	0.47	35.0	26.0	9.4	1.4	2.3	1.0	1.5	0.2	0.3	0.6	0.6	0.8	2.4	0.3	8.3	-306.9	2895	
4	0.74	75.4	18.9	94.8	19.7	1.2	1.8	2.8	0.3	0.2	0.8	0.1	2.7	8.7	0.9	10.7	-549.4	6350	
5	0.38	32.2	26.4	50.3	4.9	1.1	3.0	2.1	0.1	1.0	1.0	0.3	1.9	6.1	0.7	8.7	-103	820	
6	0.56	41.1	61.5	24.8	3.3	4.1	9.5	3.6	0.9	1.6	1.4	1.1	2.3	10.7	0.6	18.5	-15.5	75	
7	1.30	25.0	29.0	36.4	8.7	0.9	18.7	6.8	0.3	10.4	5.0	0.8	12.5	20.6	0.8	24.4	-90.6	710	
8	0.47	11.7	11.5	20.1	2.8	0.5	9.3	2.2	0.1	2.1	1.5	0.7	2.1	6.3	0.9	7.5	-168.2	1430	
9	2.01	38.9	27.6	34.7	12.1	2.5	12.5	11.4	1.7	5.9	7.9	4.4	8.3	17.7	0.5	34.0	-162.5	1375	
10	1.92	30.7	26.3	31.5	10.2	3.5	9.6	10.6	2.5	4.3	6.6	3.9	5.0	9.0	0.6	15.3	-489.5	5350	
11	2.86	15.0	40.0	10.1	11.5	2.7	4.9	17.1	4.4	3.1	8.4	3.7	8.4	14.2	0.7	19.3	-278.1	2565	
12	0.71	23.5	19.9	35.8	4.6	0.5	15.7	3.0	0.1	3.3	1.6	0.5	4.8	10.0	0.6	15.7	-112.3	905	

^aSSA, specific surface area (BET-N₂).^bCEC, cation exchange capacity (NaOAc).

Table 4 Coefficients of determination (R^2 values) for single linear regressions of the C concentrations (g kg^{-1}) in untreated and NaOCl-treated samples as a function of other soil variables (g kg^{-1})

Variable ($n = 12$)	Untreated	Oxidized
Depth ^a	0.12	0.01
Fluoride reactivity	0.16	0.45*
Clay content	0.04	0.01
Fe _d	0.01	0.05
Al _d	0.01	0.28*
Si _d	0.09	0.03
Fe _o	0.40*	0.57**
Al _o	0.22	0.44*
Si _o	0.10	0.17
Fe _p	0.10	0.78***
Al _p	0.08	0.54**
Si _p	0.01	0.24
C _p	0.41*	0.89***
Al _o + 0.5Fe _o	0.42*	0.72***
Al _o + Fe _o	0.48*	0.78***

^aDepth measured at mid-horizon.

*, **, *** Significant at $P < 0.05$, $P < 0.01$, and $P < 0.001$, respectively.

Discussion

Treatment of soil with NaOCl solution preferentially removed a younger C fraction and allowed the isolation of an older and thus more stable organic matter pool. A similar effect has been observed by Eusterhues *et al.* (2003) using $\text{Na}_2\text{S}_2\text{O}_8$ as an oxidant in forest soils, and Balesdent (1996) who also reported an enrichment of old organic matter after treating particle-size fractions from arable soils with H_2O_2 . This was interpreted as 'compatible with a relation between resistance to H_2O_2 and resistance to biodegradation' (Balesdent, 1996). Cuypers *et al.* (2002) observed that compositional changes of organic matter upon persulfate treatment were similar to the compositional changes upon humification.

Clay content was not a good predictor for stable organic C contents in our sample pool. Many studies have reported a positive relation between fine soil texture and soil C content, while other studies have observed poor or no correlations between clay content and soil C. Our data do not support the existence of a functional relationship between clay content and organic matter stabilization.

The SSA (BET-nitrogen adsorption) of mineral phases has been advocated as a promising predictor of the potential of soils and sediments for C storage. Kiem & Kögel-Knabner (2002) found SSA to be correlated with the accumulation of refractory organic C in soils from long-term agroecosystem experiments. The existence of surface-bound organic matter was corroborated by Mayer (1994), who observed a direct proportionality between organic matter contents and mineral SSA in marine sediments. The SSA determined by nitrogen adsorption was not a good predictor for stable C in our sample

set. This suggests that it is not the size of mineral surfaces that is decisive for C stabilization, but their reactivity, i.e. the ability of mineral surfaces to interact with organic compounds. Mayer & Xing (2001) found that the extent of surface coverage in acid soils depends on pH, with greater coverage (close to $1 \text{ mg organic C m}^{-2}$) at low pH. This is consistent with the view that organic matter sorption is facilitated by protonation of hydroxylated mineral surfaces, which, in turn, are likely to be more abundant under the conditions of great weathering intensity often encountered in acid soils.

Phyllosilicate mineralogy (Figure 1) did not reveal a pattern suggestive of a functional relationship with stable organic C contents. A number of authors have presented experimental evidence that phyllosilicates are much weaker sorbents for dissolved organic C (DOC) than Fe oxides, especially under acid conditions (e.g. Chorover & Amistadi, 2001). Subsoil clay fractions exhibited only a weak adsorption of DOC once Fe oxides were removed (Kaiser & Zech, 2000). The reactivity of siloxane surfaces is restricted by charge dispersion over a limited surface area as created through isomorphous substitution. Thus, electrostatic interactions with organic adsorbates at basal mineral surfaces of clay minerals are presumably less stable compared with single molecular charges (surface hydroxyl groups) at hydroxyl-bearing mineral surfaces ((hydr)oxides, edges of clay minerals).

Aluminium and Fe (hydr)oxides occur in almost any acid soil as products of soil formation. Iron oxides play an important role in the preservation of organic matter as indicated by a greater DOC sorption with increasing contents of Al and Fe oxides in forest soils and a positive correlation between Fe oxide content and organic C in bulk samples and particle-size fractions of various soils (Kaiser & Guggenberger, 2000). Kiem & Kögel-Knabner (2002) found that organic C content increased linearly with increasing dithionite-extractable Fe fraction in some particle-size fractions, but not in others.

Neither total free Fe (Fe_d) nor crystalline Fe oxides ($\text{Fe}_d - \text{Fe}_o$) were good predictors of stable organic C contents in our data set. A similar observation was published by Kiem & Kögel-Knabner (2002), who found that organic C content in C-depleted plots from an illitic Mollisol varied independently of Fe oxide contents. They found significant and positive relationships of organic C with Fe oxides in soils where contents of poorly crystalline Fe oxides outmatched those of well-ordered Fe oxides ($\text{Fe}_o/\text{Fe}_d > 0.7$). It seems therefore that Fe_d is of predictive power only in situations where most of the Fe oxides present are poorly crystalline ($\text{Fe}_o \approx \text{Fe}_d$).

This combined evidence supports our hypothesis that the abundance of poorly crystalline minerals determines the ability of a mineral matrix to preserve organic C and simultaneously points to the most probable bonding mechanism. The strong dependence of DOC sorption on pH, the competition of DOC with specifically binding inorganic anions such as SO_4^{2-} and PO_4^{3-} for sorption sites, and the release of OH^- during DOC sorption suggest that surface complexation of functional

groups via ligand exchange is the most important process in the sorption of organic matter on mineral phases (Kaiser & Guggenberger, 2000). Ligand exchange involves the exchange of a singly coordinated, inorganic hydroxyl group with an organic functional group (mostly carboxylic groups). The mechanism is of particular importance in acid soils, because protonation renders surface hydroxyl groups more exchangeable (Sposito, 1984). The mechanism is also promoted by the abundance and extension of hydroxylated mineral surfaces, which are a characteristic of poorly crystalline minerals. Consequently, any mineral phase supplying singly coordinated hydroxyl groups must be regarded as a potential contributor to C stabilization in an acid soil. The acid oxalate procedure happens to extract the majority of such phases, yielding a parameter ($Al_o + Fe_o$) with the potential to describe quantitatively the potential of acid soils for C stabilization.

Conclusions

Treatment of organic matter with NaOCl solution preferentially removed young organic C from our samples. The fraction remaining after oxidation thus represents a stable organic matter pool. Variables representative of poorly crystalline mineral phases explained much more variability of organic C contents after treatment with NaOCl solution than when related to organic C contents of the untreated samples.

Mean horizon depth, clay content, Fe_d and SSA were not good predictors of stable organic C contents. The majority of stable organic C was attached to mineral surfaces or complexed by hydroxy-metal species. Parameters indicative of poorly crystalline minerals and hydroxy-metal species ($Al_o + Fe_o$) explained 78% of the variability of stable organic C, rendering crystalline phyllosilicates and crystalline pedogenic oxides less important for C stabilization in the acid subsoils studied.

A significant and positive relationship between stable organic C content and the amount of hydroxyl ions released after reaction with NaF solution supports the hypothesis that ligand exchange between protonated surface hydroxyl sites and organic functional groups is the main mechanism of C stabilization in these acid subsoils. The results suggest that the capacity of a given mineral matrix to protect SOM in acid subsoils against decomposition can be expressed as a function of its content of poorly crystalline mineral phases. As this depends on density of reactive surface sites, this capacity will be limited and subject to saturation.

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