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Mean residence time of soil organic matter associated with kaolinite and smectite

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Summary

To gain insight into the effect of clay mineralogy on the turnover of organic matter, we analysed the ¹⁴C activity of soil organic matter associated with clay in soils dominated by kaolinite and smectite in natural savanna systems in seven countries. Assuming that carbon inputs and outputs are in equilibrium in such soils, we took the ¹⁴C age as mean residence time of the organic matter. We corrected the ¹⁴C activity for the Suess effect, Bomb effect and difference between date of sampling and date of ¹⁴C measurement. Organic matter associated with kaolinite turned over fast (360 years on average). Organic matter associated with smectite turned over relatively slowly, with an average mean residence time for the whole clay-size fraction of 1100 years. Multiple linear regression indicates that clay mineralogy is the main factor explaining differences in the mean residence time of the organic matter extracted.

Introduction

In the global carbon cycle, soil organic matter (SOM) is a major source and sink of atmospheric C. The organic matter is highly heterogeneous and consists of numerous components, ranging from easily mineralizable sugars to recalcitrant aliphatic compounds. Residence times of C in these compounds in the soil vary from a few minutes to thousands of years (Trumbore, 1993; Lichtfouse *et al.*, 1995; Torn *et al.*, 1997).

Models that describe the carbon cycle usually differentiate between at least two pools of SOM, for example a labile and a stable pool, but there is no method available to separate these physically and to quantify them. Turnover times are usually estimated on the basis of ¹⁴C dating of fractions (e.g. Buyanovsky *et al.*, 1994), modelling (e.g. Parton *et al.*, 1988), changes in ¹³C signatures (e.g. Balesdent *et al.*, 1988), or a combination of these. Labile pools of soil organic matter have a mean residence time (MRT) from a few minutes to decades, and stable pools have an MRT of hundreds to thousands of years (Hsieh, 1992).

The large variations in turnover times of the stable pool, which makes up 35–90% of all SOM, are partly related to climate. The MRT of the stable pool is estimated to be 250–380 years in tropical soils, and 850–3000 years in temper-

ate soils (Hsieh, 1996). Furthermore, it is widely assumed that the variations in turnover times of stable organic matter are related to interactions with mineral soil material, via physical and chemical stabilization (Martin & Haider, 1986; Theng *et al.*, 1992; Hsieh, 1996; Parfitt *et al.*, 1997; Torn *et al.*, 1997; Römken *et al.*, 1998).

In an earlier paper (Wattel-Koekkoek *et al.*, 2001), we described the effect of clay mineralogy on the chemical composition of clay-associated SOM. We showed that organic matter associated with kaolinite was to a large extent free or bound to the aluminium-hydroxide surface, and that smectitic clay minerals preferentially bind organic matter through cationic bridges. Furthermore, we found that organic matter associated with kaolinite was rich in polysaccharide products, whereas smectite-associated SOM contained more aromatic compounds of many kinds. These differences suggest there is a difference in the dynamics of the organic matter between the two clay minerals.

Here, we focus on the effect of mineralogy on the residence time of this SOM. We define *clay-associated organic matter* as all organic matter present in the clay-size separate, both free and bound. We restrict ourselves to the organic matter associated with two of the most common clay minerals in soil: kaolinite and smectite. We compared the mean residence time of kaolinite- and smectite-associated SOM in natural systems, using six kaolinite and six smectite-dominated soils from old savannas.

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Materials and methods

Samples

We selected the soils (Tables 1 and 2) from the collection of the International Soil Research and Information Centre (ISRIC, Wageningen). We used the surface horizons only because these contain much carbon and yield large amounts of carbon during the extraction. The samples were air-dried and passed through a 2-mm sieve. The pH, organic carbon content, and particle size distribution were measured previously by ISRIC.

The clay mineralogy was measured by X-ray diffraction (relative peak area of diffractograms in %). The specific surface area (SSA) of the clay-size fraction after removal of organic carbon by H₂O₂ was measured using ethylene glycol monoethyl ether (EGME) (van Reeuwijk, 1992).

We did not use a dispersing agent such as NaOH while separating the (whole) clay-size fractions, so that the ECEC of the fractions could be determined (Table 2) (BaCl₂ method; van Lagen, 1996). The sum of exchangeable bases was taken as ECEC measured as cmol₊ kg⁻¹, because exchangeable Al³⁺ was expected to be negligible at the soil pH (4.5–7.9). To get the ECEC of the mineral phase only (ECEC_{min}), we corrected the ECEC of the whole clay-size fraction for the ECEC of the organic matter as follows.

First we obtained values for SOM in the fraction concerned by multiplying the measured carbon content, *C*, by 2, i.e. SOM = 2*C*. Van Breemen & Buurman (1998) had found the ECEC of organic matter in such soil to be approximately 200 cmol kg⁻¹, and we assumed this value here. This led to our correction:

$$\text{ECEC}_{\text{min}} = \text{ECEC} - 200 \times 2C, \quad (1)$$

where *C* is in kg C kg⁻¹ of the fraction.

Fractionation

We used a combination of physical and chemical fractionation. Though clay minerals also occur in other size fractions, the largest part, with its associated organic matter, is in the clay size (< 2 μm) fraction. We collected the clay-size fractions of all samples, using ultrasonic (full) dispersion and sedimentation. The ultrasonically dispersed clay-size fraction was shaken in 0.5 M NaOH under N₂ for 24 hours (0.51, clay:solution = 1:10).

We centrifuged the suspension for 60 minutes, shook the residue with demineralized water for 2 hours, centrifuged again, and acidified the combined supernatants to pH = 1 with concentrated HCl. Thereafter concentrated HF was added until a concentration of 0.3 M HF was reached. To remove salts, the acidified supernatant was dialysed against demineralized water (pH = 6). Thereafter the supernatant (= NaOH extract) was freeze-dried. Next, the NaOH residue was shaken for 24 hours with 0.1 M Na₄P₂O₇ under nitrogen (clay:solution = 1:10). The solution was centrifuged for 60 minutes, and the residue was shaken with demineralized water for 2 hours, centrifuged again, and the combined supernatants

were acidified again to pH = 1 with concentrated HCl. Thereafter concentrated HF was added until a concentration of 0.3 M HF was reached. Both the supernatant (= Na₄P₂O₇ extract) and the pyrophosphate residue were dialysed and freeze-dried. The amounts of carbon in the total clay-size fractions, the freeze-dried extracts, and the residues were measured on an Interscience elemental analyser EA1108 (Table 3).

¹⁴C analysis

Hydrolysis of soil samples with 6 M HCl prior to isotope measurements is part of the standard pretreatment in the Centre for Isotope Research (Groningen, The Netherlands) for isotope analysis. The purpose of this procedure is to obtain the oldest fraction. Acid hydrolysis removes the potentially most labile, rapidly cycling carbon into solution, leaving a more refractory, slower cycling residue (Scharpenseel & Schiffmann, 1977; Anderson & Paul, 1984; Trumbore *et al.*, 1989). Since we were not interested in the fraction with the smallest possible ¹⁴C concentration, but in the 'true' mean age of the total SOM in the extracts and the residues, we omitted hydrolysis. This also allowed us to link directly in a multiple regression the ¹⁴C results to NMR analyses performed earlier on the same samples (Wattel-Koekkoek *et al.*, 2001). One kaolinite and one smectite sample, LABEX6 and LABEX17, were measured with and without hydrolysis.

The clay-size fractions, NaOH extracts, Na₄P₂O₇ extracts and residues were combusted at 850°C under a continuous flow of oxygen. The CO₂ was purified by CuO and Ag using standard methods. Values of ¹³C were measured by mass spectrometry. Following ¹³C analysis, the CO₂ was trapped cryogenically and converted to graphite for subsequent AMS analysis (van der Plicht *et al.*, 2000). The amount of ¹⁴C in SOM relative to the ¹⁴C concentration in the atmosphere was used to calculate the age of the material. The measured relative ¹⁴C activity (¹⁴*a*_m) is

$${}^{14}a_m = \frac{{}^{14}A}{{}^{14}A_0}, \quad (2)$$

where *A*₀ is the original specific ¹⁴C activity defined by the 1950 standard and *A* is the measured specific ¹⁴C activity of the sample. The measured relative ¹⁴C activity was corrected for isotopic fractionation with ¹³C according to Mook & van der Plicht (1999).

Correction of ¹⁴C analyses

To correct for the interval between soil sampling and analysis (Table 4), the ¹⁴C activity in the year of sampling (¹⁴*a*_s) was calculated according to

$${}^{14}a_s = \frac{{}^{14}a_m}{\exp(-\lambda\Delta t)}, \quad (3)$$

Table 1 Site characteristics and soil analyses

ISRIC key for sites ^a	Country, site	Latitude and longitude	Parent rock	Temperature °C	Rainfall /mm year ⁻¹	Vegetation	Soil type ^b	Clay /g kg ⁻¹	Organic C /g kg ⁻¹	pH (H ₂ O)	pH (KCl)	CEC _{soil} /cmol kg ⁻¹	Base saturation /%
BR1	Brazil, Itaguaí	22°45'S; 43°41'W	Residual from gneiss	22.9	1317	Grassland	Haplic Lixisol	150	10	4.5	4.1	3.7	49
BR2	Brazil, Aparibé	21°38'S; 42°7'W	Pre-Cambrian rocks	22.8	1234	Grassland	Haplic Lixisol	260	10	5.7	4.5	4.4	66
LABEX6	Kenya, Nairobi	1°15'N; 36°41'E	Residual from intermediate igneous rocks	18	973	Grassland	Humic Nitisol	660	26	5.7	6.8	19	61
ML1	Mali, Koulikoro	12°5'N; 8°24'W	Alluvial clay	26.9	1087	Woodland	Ferric Acrisol	230	9	6.2	4.9	5.9	87
ML8	Mali, N'Tentou	11°25'N; 7°53'W	Colluvium from lateritic hill	27.3	1337	Grassland	Ferric Acrisol	130	9	6.5	5.6	3.5	97
MOC4	Mozambique, Montepuez	13°9'S; 38°37'E	Residual from basic igneous rock	24.2	932	Grassland (<i>Oxytenanthera abyssinica</i>)	Ferric Acrisol	270	23	5.9	5.3	15.9	95
IN25	Indonesia, East Java	7°37'S; 112°50'E	Residual from tuff	26.8	1316	Grassland	Pellic Vertisol	860	11	7.6	6.4	92.5	100
KE66	Kenya, Kajjado	1°49'S; 36°49'E	Residual from tuff	17.5	504	Grassland	Pellic Vertisol	600	14	7.3	6.0	55.6	100
LABEX17	Kenya, Sultan Hamud	2°8'S; 37°28'E	Undifferentiated sediment	22.6	611	Grassland	Pellic Vertisol	860	18	7.9	6.6	86	100
NI9	Nicaragua, Timal	12°15'N; 86°2'W	Alluvium from tuff	27.3	1184	Grassland	Pellic Vertisol	790	11	6.4	4.7	77.2	100
ZA8	South Africa, north of Pietermaritzburg	29°22'S; 30°24'E	Residual from intermediate igneous rocks	18.5	928	Shrub (<i>Acacia</i> spp.)	Pellic Vertisol	460	24	6.3	5.0	42.0	63
ZA9	South Africa, north of Pietermaritzburg	29°22'S; 30°24'E	Residual from intermediate igneous rocks	18.5	928	Shrub (<i>Acacia</i> spp.)	Pellic Vertisol	570	16	6.8	5.3	45.2	87

^aInternational Soil Reference and Information Centre.^bAccording to FAO.

Table 2 Mineralogical analyses of the clay-size fraction. Specific surface areas (SSA) are means with standard errors in parentheses

Sample	Kaolinite /%	Mica /%	Smectite /%	SSA /m ² g ⁻¹	Exchangeable cations				ECEC sum	ECEC _{min}
					Ca	Mg	Na	K		
					/cmol kg ⁻¹					
Kaolinitic										
BR1	92	8	0	169.4 (3.3)	3.8	2.4	0.0	0.1	6.3	0
BR2	98	2	0	170.0 (3.2)	3.3	0.0	0.0	0.0	3.4	0
LABEX6	95	5	0	ND	5.9	1.7	0.0	0.3	8.0	2.4
ML1	96	4	0	245.2 (5.5)	6.7	7.5	0.0	0.1	14.5	6.1
ML8	99	0	1	154.4 (4.8)	7.1	4.8	0.0	0.1	12.0	0
MOC4	100	0	0	177.0 (2.4)	7.3	5.8	0.0	0.0	13.1	1.1
Smectitic										
IN25	1	0	99	801.7 (11.9)	57.1	16.0	2.0	0.0	75.2	70.6
LABEX17	20	0	80	ND	52.5	32.5	0.1	0.1	85.3	80.1
NI9	0	0	100	721.5 (3.7)	44.6	29.5	0.1	0.0	74.2	68.6
KE66	1	0	99	727.8 (8.6)	71.2	23.5	13.2	0.1	107.9	98.3
ZA8	21	0	79	498.7 (5.4)	32.1	23.3	0.1	0.0	55.5	38.7
ZA9	21	0	79	582.1 (0.6)	26.4	29.5	0.1	0.0	56.1	46.9

ND, not determined.

where $^{14}a_m$ is the measured ^{14}C activity, Δt is the time (years) between the year of soil sampling and the year of the measurements, and λ is the decay constant ($121 \times 10^{-6} \text{ year}^{-1}$, based on the half-life of 5730 years).

The soil samples were taken after the 1960s, and therefore influenced by both the 'Suess effect' (decrease in atmospheric ^{14}C activity due to the burning of fossil fuels starting around

1850) and the 'Bomb effect' (increase in atmospheric ^{14}C activity due to nuclear bomb tests).

Before 1850 anthropogenic effects on the atmospheric ^{14}C activity can be neglected, and the ^{14}C activity of carbon in a uniformly mixed pool at year t can be expressed as

$$^{14}a_t = ^{14}a_{\text{atm}} \exp(-\lambda T), \quad (4)$$

where $^{14}a_{\text{atm}}$ is the natural ^{14}C activity in the atmosphere, from the 'single year curve' from Stuiver & Braziunas (1993), and T is the mean ^{14}C age of the carbon pool. We realize that the assumption that soil is a uniformly mixed pool is a simplification, but this model is our best guess. A model with multiple pools (e.g. a 'labile' and a 'stable' pool) would require assumptions about the distribution of the carbon over the slow and fast pools, for which data are lacking.

Table 3 Carbon distribution in the clay-size fraction, its extracts and residues

Sample	Clay-size fraction	NaOH extract	Na ₄ P ₂ O ₇ extract
	/g C 100 g ⁻¹ clay		
Kaolinite			
BR1	3.8	1.9	0.4
BR2	2.3	1.0	0.2
LABEX6	2.1	0.9	0.1
ML1	2.1	0.7	0.3
ML8	3.0	1.0	0.4
MOC4	3.0	1.5	0.5
Average	2.7	1.2	0.3
Standard error	0.3	0.2	0.1
Smectite			
IN25	0.9	0.02	0.5
KE66	2.4	0.4	1.2
LABEX17	1.6	0.1	0.7
NI9	1.4	0.2	0.5
ZA8	4.2	0.9	1.2
ZA9	2.3	0.7	0.4
Average	2.1	0.4	0.7
Standard error	0.5	0.1	0.1

Table 4 Years of sampling and year of ^{14}C analysis

Sample	Years of sampling	Year of analysis	Δt /years
Kaolinite			
BR1	1984, 1985	1998	14
BR2	1984, 1985	1998	14
LABEX6	1976	1997	21
ML1	1988	1998	10
MOC4	1982, 1983	1998	16
Smectite			
KE66	1985	1998	13
LABEX17	1985	1997	12
NI9	1992	1998	6
ZA8	1975	1998	23
ZA9	1975	1998	23

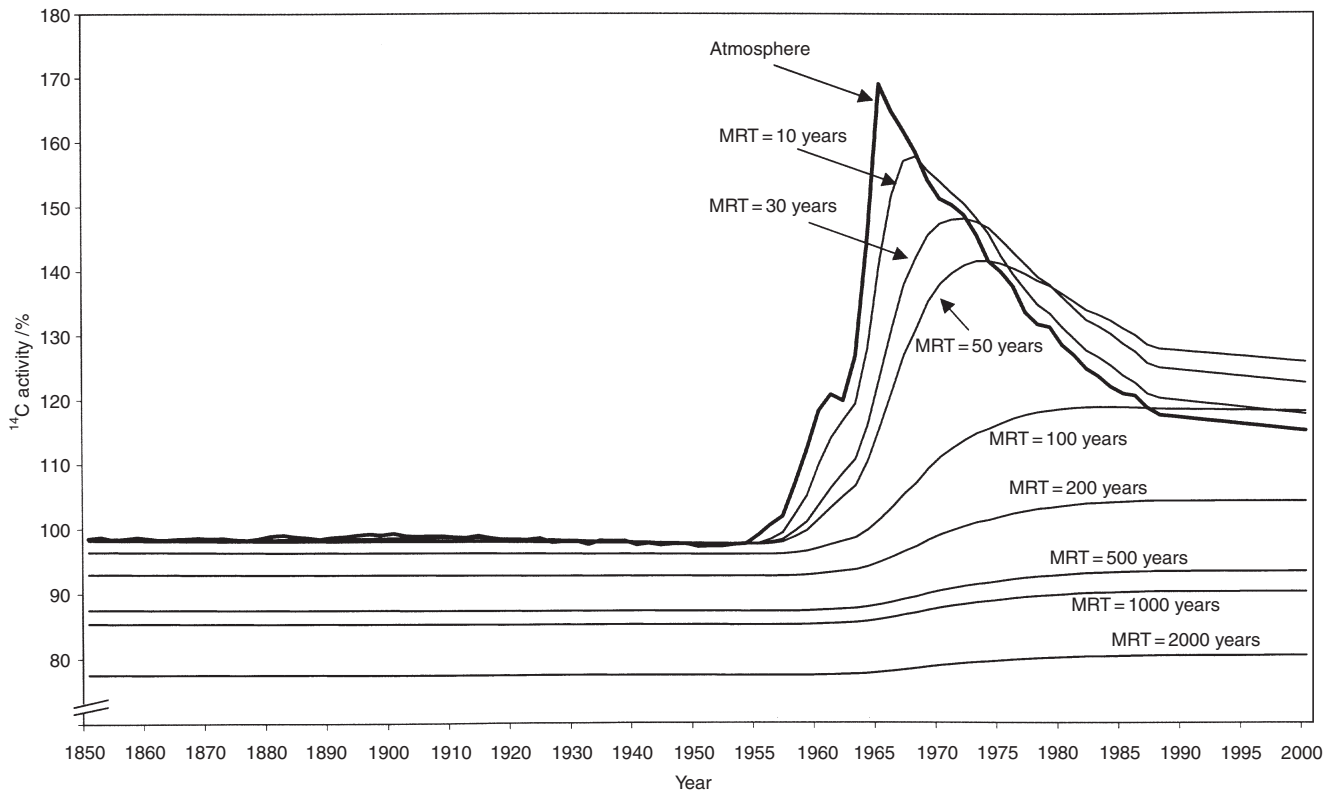


Figure 1 Distribution of atmospheric ^{14}C activity measured in the southern hemisphere for the past 150 years, compared with the theoretical curves calculated for specific MRTs.

After 1850, with a steady-state pool of SOM, the carbon decomposed is replaced by depleted (Suess) or enriched (Bomb) carbon from the atmosphere. If at $t-1$ the activity of the total carbon pool is $^{14}a_{t-1}$, then at time t the activity is given by

$$^{14}a_t = ^{14}a_{t-1} + ^{14}a_{\text{in}} - ^{14}a_{\text{out}}, \quad (5)$$

where $^{14}a_{\text{in}}$ is the ^{14}C activity 'gained' between $t-1$ and t , and $^{14}a_{\text{out}}$ is the ^{14}C activity lost by decomposition of SOM and ^{14}C radioactive decay. As the soils are from old savannas in which carbon inputs and outputs are in equilibrium, we can assume steady-state turnover of SOM at a decomposition rate k (year^{-1}). Then

$$^{14}a_{\text{in}} = ^{14}a_{\text{atm},p} \{1 - \exp(-k)\}, \quad (6)$$

where $^{14}a_{\text{atm},p}$ is the (input) ^{14}C activity of the atmospheric CO_2 during the preceding year p , and

$$^{14}a_{\text{out}} = ^{14}a_{t-1} \{1 - \exp(-k - \lambda)\}, \quad (7)$$

so that

$$^{14}a_t = ^{14}a_{t-1} \exp(-k - \lambda) + ^{14}a_{\text{atm},p} \{1 - \exp(-k)\}. \quad (8)$$

Because the samples originated from close to the equator and from the southern hemisphere to 29°S , we used the ^{14}C activity in the atmosphere, $^{14}a_{\text{atm},p}$, of the southern hemisphere meas-

ured by Manning *et al.* (1990). Knowing the sampling year and $^{14}a_s$, we used the model to calculate k from Equation (8) and the mean residence time (MRT) from Equation (9). In Figure 1 the distribution of atmospheric ^{14}C activity measured for the past 150 years is compared with the theoretical curves calculated for specific MRTs:

$$\text{MRT} = \frac{1}{k}. \quad (9)$$

We used the MRT to calculate the ^{14}C activity the sample would have had, had there been no changes in atmospheric ^{14}a , according to

$$^{14}a_{\text{corr}} = \exp(-\lambda \text{MRT}), \quad (10)$$

where $^{14}a_{\text{corr}}$ is the ^{14}C activity corrected for the Bomb effect, Suess effect and the difference in time between sampling and measurement.

Scanning electron microscopy

To check for the presence of unhumified, recognizable cell fragments, scanning electron microscope (SEM) analyses were done on the pyrophosphate extracts and residues of BR2, ML1 (both kaolinitic), KE66 and ZA8 (both smectitic), with a Philips 515 SEM.

Results

MRTs of non-hydrolysed clay separates

Table 5 lists the measured ^{14}C activity, the MRT calculated with Equations (8) and (9) and corrected ^{14}C activity with Equation (10) for the whole clay-size fractions, NaOH extracts, $\text{Na}_4\text{P}_2\text{O}_7$ extracts and residues. The averages and standard deviations concern the non-hydrolysed fractions only.

The average MRT of kaolinite-associated organic matter was 357 years with a standard error of 121 years. The ^{14}C activities of the four fractions of the kaolinitic soils (clay-size fraction, NaOH extract, $\text{Na}_4\text{P}_2\text{O}_7$ extract, residues) did not differ significantly. Of all kaolinitic clay-size fractions, ML1 has the fastest turnover, and LABEX6 and MOC4 the slowest.

The average MRT of smectite-associated SOM is 1089 years with a standard error of 157 years. The pyrophosphate extracts appear to have a significantly smaller ^{14}C activity than the hydroxide extracts. Of all smectite-dominated samples, NI9 has a relatively short MRT and LABEX17 a relatively long MRT.

Overall, clay-size SOM of smectite-dominated soils has a significantly smaller ^{14}C activity than that in the soils dominated by kaolinite. Also, NaOH- and $\text{Na}_4\text{P}_2\text{O}_7$ -extracted SOM of smectite-dominated soils has a significantly smaller ^{14}C activity than NaOH- and $\text{Na}_4\text{P}_2\text{O}_7$ -extracted SOM of kaolinite-dominated soils. The residues of the kaolinite and smectite clays were not significantly different.

We tested differences for significance using the distribution-free Mann–Whitney test. According to this test, the clay-size, NaOH- and $\text{Na}_4\text{P}_2\text{O}_7$ -extracted SOM of smectite-dominated soils has a significantly smaller ^{14}C activity than clay-size, NaOH- and $\text{Na}_4\text{P}_2\text{O}_7$ -extracted SOM of soils dominated by kaolinite. The residues of the kaolinite and smectite clays were not significantly different.

To indicate the accuracy of this experiment, we calculated the weighted ^{14}C activity of the clay-size fraction based on the carbon distribution (Table 3) and the measured (corrected) ^{14}C activity of the NaOH extracts, $\text{Na}_4\text{P}_2\text{O}_7$ extracts and residues (Table 5). Furthermore, we calculated the difference (Δ) between the corrected ^{14}C activity of the whole clay-size fraction and the calculated weighted ^{14}C activity (Table 6). The large Δ for KE66 and ZA9 suggests that the mass balance or the ^{14}C data or both are inaccurate for KE66 and ZA9.

MRTs of hydrolysed clay separates

Hydrolysis generally removed relatively young carbon, resulting in a decrease in the ^{14}C activity. Hydrolysed fractions of LABEX6 and LABEX17 were invariably older than the non-hydrolysed fractions, except for the NaOH extract of smectite (1202 BP with hydrolysis and 1419 BP without hydrolysis). The age difference between the hydrolysed and the non-hydrolysed samples was especially large for the residues. The organic matter in the residue of LABEX6 (kaolinite) had an MRT of

Table 5 Measured and corrected ^{14}C activity and mean residence time (MRT) of the clay-size fractions, extracts and residues, with standard errors in parentheses. LABEX6H and LABEX17H are the hydrolysed fractions of LABEX6 and LABEX17, respectively

Sample	Clay (< 2 μm)			NaOH extract			$\text{Na}_4\text{P}_2\text{O}_7$ extract			Residue		
	$^{14}a_m$ /%	MRT /years	$^{14}a_{\text{corr}}$ /%	$^{14}a_m$ /%	MRT /years	$^{14}a_{\text{corr}}$ /%	$^{14}a_m$ /%	MRT /years	$^{14}a_{\text{corr}}$ /%	$^{14}a_m$ /%	MRT /years	$^{14}a_{\text{corr}}$ /%
Kaolinite												
BR1	116.40 (0.60)	225	97.2	122.45 (0.63)	153	98.1	119.30 (0.62)	188	97.7	115.87 (0.60)	232	97.2
BR2	109.58 (0.59)	341	95.8	117.57 (0.61)	209	97.4	114.23 (0.60)	256	96.9	96.57 (0.54)	782	90.7
LABEX6H	96.17 (0.71)	739	91.2	99.21 (0.50)	600	92.8	96.86 (0.65)	705	91.6	89.30 (0.90)	1153	86.6
LABEX6	ND			106.09 (0.37)	378	95.4	101.39 (0.37)	516	93.8	94.90 (0.37)	805	90.5
ML1	121.49 (0.62)	158	98.1	123.40 (0.63)	136	98.3	119.06 (0.62)	188	97.7	120.25 (0.62)	173	97.9
MOC4	98.88 (0.55)	712	91.5	103.80 (0.56)	485	94.1	98.79 (0.54)	671	92.0	101.83 (0.55)	551	93.4
Average		357	95.7		273	96.7		360	95.6		502	93.9
Standard error		121	1.5		68	0.8		96	1.2		131	1.6
Smectite												
KE66	90.69 (0.53)	1124	86.9	103.64 (0.56)	498	94.0	77.89 (0.50)	2162	76.4	96.93 (0.54)	767	90.9
LABEX17H	58.36 (0.63)	4409	57.8	89.54 (0.58)	1202	86.1	55.75 (0.62)	4779	55.2	52.23 (0.57)	5306	51.7
LABEX17	ND			86.53 (0.32)	1419	83.8	62.61 (0.25)	3848	61.9	72.69 (0.29)	2679	71.6
NI9	96.45 (0.54)	803	90.5	106.54 (0.57)	421	94.9	90.96 (0.53)	1120	87.0	107.75 (0.58)	390	95.3
ZA8	92.83 (0.53)	906	89.3	100.04 (0.56)	550	93.4	88.30 (0.51)	1208	86.0	93.31 (0.53)	877	89.7
ZA9	84.14 (0.51)	1532	82.6	94.29 (0.56)	821	90.3	79.43 (0.50)	1946	78.5	85.80 (0.51)	1397	84.0
Average		1089	87.3		733	91.3		2000	78.0		1184	86.3
Standard error		157	1.7		174	2.0		437	4.5		362	4.1

ND, not determined.

Table 6 Comparison of corrected and weighted MRT of the total clay-size fraction, with standard error in parentheses

Sample	Corrected		Weighted average		Δ (Corrected – Weighted) ¹⁴ a
	¹⁴ a /%	MRT /years	¹⁴ a /%	MRT /years	
Kaolinite					
BR1	97.2 (0.60)	225	97.7 (1.85)	187	-0.5
BR2	95.8 (0.59)	341	94.1 (1.75)	487	1.7
ML1	98.1 (0.62)	158	98.0 (1.87)	162	0.1
MOC4	91.5 (0.55)	712	93.4 (1.65)	545	-1.9
Smectite					
KE66	86.9 (0.53)	1124	84.3 (1.60)	1368	2.6
NI9	90.5 (0.54)	803	92.5 (1.68)	629	-2.0
ZA8	89.3 (0.53)	906	89.4 (1.60)	903	-0.1
ZA9	82.6 (0.51)	1532	85.0 (1.57)	1302	-2.4

1153 BP with hydrolysis and 805 BP without hydrolysis. The SOM in the residue of LABEX17 (smectite) had an MRT of 5306 BP with hydrolysis and 2679 BP without hydrolysis. As a consequence, the residues contain the oldest fraction, followed by the pyrophosphate extracts and the hydroxide extracts, respectively (Table 5).

Scanning electron microscopy

Images obtained by SEM (not shown) were used to determine whether the measured isotopic data reflect the ¹⁴C activity of recognizable plant remnants or of completely humified, i.e. unrecognizable amorphous, material. The images of Na₄P₂O₇-extracted SOM of smectitic samples KE66 and ZA8 are dominated by 'amorphous' organic components, i.e. without recognizable cell structures. The pyrophosphate extract of kaolinitic samples BR2 and ML1 contained plant tissue fragments. Both contained some amorphous material, though less than in the Na₄P₂O₇ extracts from smectites. The pyrophosphate residues of smectitic samples KE66 and ZA8 and kaolinitic samples BR2 and ML1 are dominated by plant fragments and hollow spheres (approximately 2 µm in diameter) probably originating from microbes. We did not obtain SEM images from the NaOH extracts.

Discussion

MRTs of non-hydrolysed clay separates

The fast turnover of organic matter associated with kaolinite (357 years with a standard error of 121 years) suggests that the bulk of the organic matter is not, or is only weakly, bound to the mineral surfaces, such as iron oxides and the edges of the octahedral sheets of kaolinites, in such soils.

Our findings agree with those of Shang & Tiessen (1997), who found that the most stable organic fraction in an Oxisol

had a ¹⁴C age of only 100 years, i.e. the OM in this soil was labile with no slow pool (as defined by Parton *et al.*, 1987).

Previously, Wattel-Koekkoek *et al.* (2001) showed that NaOH- and pyrophosphate-extracted SOM from kaolinite is rich in sugars. Sugars readily decompose, so their presence suggests that kaolinite-associated SOM has a fast turnover. This is confirmed by the short mean residence time of the NaOH and Na₄P₂O₇ extracts of kaolinite.

The residues consist mainly of aliphatic components (Wattel-Koekkoek *et al.*, 2001), which are fairly resistant to decomposition (de Leeuw & Largeau, 1993; Lichtfouse *et al.*, 1995). Our ¹⁴C data, however, indicate that the aliphatic residues associated with kaolinite, despite their inherent recalcitrance, do not turn over significantly more slowly than the NaOH and Na₄P₂O₇ extracts.

Of all kaolinitic soils, ML1 had the fastest turnover. This could be because the soil is warmer than the other soils. The SOM associated with clay in LABEX6 and MOC4 turned over more slowly. For LABEX6 this could also be because it is cooler than the other soils. The slow turnover of MOC4 could be related to its large content of aromatic C, which resists decomposition.

Smectite-associated SOM had a relatively slow turnover (1089 years with a standard error of 157 years), which agrees with earlier studies on 2:1 clay minerals. Buyanovsky *et al.* (1994) used data from Balesdent *et al.* (1988) on montmorillonitic soils to calculate the turnover of various size fractions. They found MRTs for the clay-size fraction in the range of 1000–1600 years. Slower turnover was observed by Theng *et al.* (1992), who reported a ¹⁴C age of 5680 years for the C in the clay-size fraction of a mica-beidellite from a Spodosol.

The pyrophosphate extracts of the smectitic clays had a long MRT. This agrees with previous results which indicated that this fraction is bound by cation bridges, contains many aromatic components, and is therefore difficult to decompose.

The SEM images of the pyrophosphate extracts of kaolinite and smectite also indicated a difference in type of SOM. Smectites showed mostly amorphous organic matter, indicating an advanced stage of humification, and thus slow turnover. The pyrophosphate extracts of kaolinites contained many more recognizable plant remnants, suggesting incomplete humification, and a fast turnover.

There are large variations in residence time of the pyrophosphate residues of the smectite-dominated soils (from 250 to 2560 years). These may be related to the amount of debris from plant and microbial cells present in the residues, as shown by the SEM. Because of its slow sedimentation, non-complexed SOM will end up in the clay-size fraction (even when larger than 2 µm) during the separation. As these plant remnants hardly dissolve in NaOH or Na₄P₂O₇, they remain behind in the residues. Thus, the more debris there is, the younger is the ¹⁴C age. However, we could not test this hypothesis by SEM for lack of sufficient residual material and the limited number of samples studied.

Of all smectite-dominated samples, NI9 had the shortest turnover time. This material comes from an area with a high mean annual temperature, which may encourage decomposition. Sample LABEX17 had a relatively large MRT. We do not know what causes the slow turnover.

In an attempt to explain the ^{14}C activity we regressed $^{14}a_{\text{corr}}$ of the extracts on the following independent variables, either singly or in combination:

- effective cation exchange capacity of the mineral phase of the clay-size fraction (ECEC_{min}), as a variable characteristic of clay mineralogy;
- specific surface area (SSA), another characteristic of clay mineralogy;
- temperature (mean annual), to represent the climate;
- type of extract (1 for NaOH extracts and 0 for $\text{Na}_4\text{P}_2\text{O}_7$ extracts), as a measure for the binding mechanisms on the assumption that NaOH loosens different bonds from those that $\text{Na}_4\text{P}_2\text{O}_7$ loosens; and
- percentage of alkyl C, O-alkyl C, aromatic C and carbonyl C (based on NMR analyses) in the extracts as a characteristic for the chemical composition of the organic matter.

With only one of the NMR components as predictor (O-alkyl, alkyl, carbonyl, or alkyl C), O-alkyl is the best for explaining the variance ($R^2_{\text{adj}} = 0.34$) in ^{14}C activity (Table 7). Furthermore, we see a negative regression coefficient between aromatic C and ^{14}C activity. It seems plausible that aromatic C diminishes ^{14}C activity, and thus gives a slower turnover, because it is relatively resistant to decomposition. Carbonyl C

Table 7 The adjusted coefficient of determination (R^2_{adj}) and the regression coefficients after (multi) linear regression analyses using different combinations of independent variables to predict the corrected ^{14}C activity of the NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ extracts

Independent variables	R^2_{adj}	Regression coefficient	
O-alkyl /%	0.34		0.32
Aromatic C /%	0.30		-0.35
Alkyl C /%	0		0.46
Carbonyl C /%	0.25		-0.72
ECEC_{min} / cmol kg^{-1}	0.43		-0.14
SSA / $\text{m}^2 \text{g}^{-1}$	0.50		-0.02
Temperature / $^{\circ}\text{C}$	0.23		1.09
Extract type	0.17		6.85
O-alkyl /%	0.21	O-alkyl	0.42
Aromatic C /%		Aromatic C	0.14
Alkyl C /%		Alkyl C	0.07
Alkyl C /%	0.70	Alkyl C	0.57
SSA / $\text{m}^2 \text{g}^{-1}$		SSA	-0.02
Temperature / $^{\circ}\text{C}$		Temperature	0.76
Extract		Extract	3.68
Alkyl C /%	0.67	Alkyl C	0.62
ECEC_{min} / cmol kg^{-1}		ECEC_{min}	-0.10
Temperature / $^{\circ}\text{C}$		Temperature	0.74
Extract		Extract	3.98

also has a negative regression coefficient. Carbonyl C may diminish the decomposition rate because it can form bonds with exchangeable cations at the clay surface, thereby restricting decomposition.

The type of extract has a positive regression coefficient, indicating that the NaOH extract contains young, easily decomposable SOM. As suggested previously, temperature has a positive regression coefficient, explaining 23% of the variance.

The best factors for explaining the variance in ^{14}C activity were the SSA ($R^2_{\text{adj}} = 0.50$) and ECEC ($R^2_{\text{adj}} = 0.43$). Both have negative regression coefficients. This supports our hypothesis that clay mineralogy affects SOM decomposition. Clay minerals with a large ECEC, such as smectites, have relatively slow SOM turnover as the exchangeable cations enable the clays to bind SOM, whereas clay minerals with a small ECEC, such as kaolinites, have relatively fast SOM turnover, as the ability to bind SOM is much less. Clay minerals with a large surface area have plenty of space to bind SOM, for example by van der Waals forces, whereas clays with little SSA have less space to bind SOM.

The NMR data are not completely independent: they are relative peak areas and therefore always sum to 100%. We therefore calculated several regressions omitting one of the NMR components at a time, using the other three components as independent variables. We found that the combination of three components that gave the best explanation of variance was O-alkyl, aromatic C, alkyl C ($R^2_{\text{adj}} = 0.21$). The principal factor was again O-alkyl, which is present mainly in polysaccharides, and easy to decompose, probably therefore resulting in a large ^{14}C activity.

With all available independent variables, 48% of the variance in ^{14}C activity of the extracts can be explained. We tried all possible combinations of the independent variables and found that the optimal explanation was reached when using SSA, alkyl C, temperature, and extract type as input variables ($R^2_{\text{adj}} = 0.70$), of which SSA is by far the most important factor explaining the variance in ^{14}C . The second best set of variables ($R^2_{\text{adj}} = 0.67$) was ECEC_{min} , alkyl C %, temperature, and extract type (Table 7).

When SSA or ECEC_{min} are used as independent variables, the percentage of alkyl C, and not O-alkyl, is the best predicting factor in the chemical data available. Addition of any other NMR-based variable diminishes the percentage of variance explained. This suggests there is a relation between clay mineralogy and % alkyl C associated with the clay. Theng *et al.* (1986) found that aliphatic components are intercalated in the interlayers of smectites. However, it seems improbable that the aliphatic components that we found in the extracts were intercalated, as intercalation is a very strong type of bond that is unlikely to be dissolved by NaOH or $\text{Na}_4\text{P}_2\text{O}_7$.

It is remarkable that the percentage of alkyl C shows a positive regression coefficient with ^{14}C activity. Aliphatic components are fairly resistant to decomposition (de Leeuw & Largeau, 1993; Lichtfouse *et al.*, 1995), and therefore we

expected a negative regression coefficient with ^{14}C activity. A possible explanation for the positive correlation is that the extracts contain 'free' plant remains. These remains may be mainly cuticles and roots, which contain aliphatic polymers such as cutan and suberan (Nip *et al.*, 1986; de Leeuw & Largeau, 1993; Nierop, 1999).

MRTs of hydrolysed clay separates

In general, hydrolysed samples had smaller ^{14}C activities than non-hydrolysed samples. This agrees with previous research that indicated hydrolysis removes labile, rapidly cycling carbon, leaving behind a more refractory, slower cycling residue (Trumbore *et al.*, 1989; Trumbore & Zheng, 1996). We cannot explain why hydrolysis apparently rejuvenated the hydroxide extract of LABEX17.

Conclusion

By comparing the ^{14}C activity of organic matter present in the NaOH extracts, $\text{Na}_4\text{P}_2\text{O}_7$ extracts and residues of the clay-size fractions ($< 2\ \mu\text{m}$) of kaolinite- and smectite-dominated soils from seven countries, we showed that (i) kaolinite- and smectite-associated SOM have significantly different turnover times, and (ii) clay mineralogy is the most important factor in explaining variance in the mean residence time of the NaOH- and $\text{Na}_4\text{P}_2\text{O}_7$ -extracted organic matter.

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