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Authors

Agnelli, A
Trumbore, SE
Corti, G
[et al.](#)

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The dynamics of organic matter in rock fragments in soil investigated by ^{14}C dating and measurements of ^{13}C

A. AGNELLI^a, S. E. TRUMBORE^b, G. CORTI^a & F. C. UGOLINI^a

^aDipartimento di Scienza del Suolo e Nutrizione della Pianta, Università degli Studi di Firenze, Piazzale delle Cascine 28, 50144 Firenze, Italy, and ^bEarth System Science Department, University of California, Irvine, CA 92697-3100, USA

Summary

Rock fragments in soil can contain significant amounts of organic carbon. We investigated the nature and dynamics of organic matter in rock fragments in the upper horizons of a forest soil derived from sandstone and compared them with the fine earth fraction (<2 mm). The organic C content and its distribution among humic, humin and non-humic fractions, as well as the isotopic signatures ($\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$) of organic carbon and of CO_2 produced during incubation of samples, all show that altered rock fragments contain a dynamic component of the carbon cycle. Rock fragments, especially the highly altered ones, contributed 4.5% to the total organic C content in the soil. The bulk organic matter in both fine earth and highly altered rock fragments in the A1 horizon contained significant amounts of recent C (bomb ^{14}C), indicating that most of this C is cycled quickly in both fractions. In the A horizons, the mean residence times of humic substances from highly altered rock fragments were shorter than those of the humic substances isolated in the fine earth. Values of $\Delta^{14}\text{C}$ of the CO_2 produced during basal respiration confirmed the heterogeneity, complexity and dynamic nature of the organic matter of these rock fragments. The weak ^{14}C signatures of humic substances from the slightly altered rock fragments confirmed the importance of weathering in establishing and improving the interactions between rock fragments and surrounding soil. The progressive enrichment in ^{13}C from components with high- ^{14}C (more recent) to low- ^{14}C (older) indicated that biological activity occurred in both the fine and the coarse fractions. Hence the microflora utilizes energy sources contained in all the soil compartments, and rock fragments are chemically and biologically active in soil, where they form a continuum with the fine earth.

Introduction

Soil is the major reservoir of carbon (C) in the terrestrial environment. The total amount of organic C in the upper metre of soil has been estimated to be about 1500 Pg (Eswaran *et al.*, 1993; Batjes, 1996). This is large relative to the C stored in biomass and atmosphere (Schlesinger, 1991).

Estimates of the C in soil are based on the measurements in the fine earth (the <2-mm fraction), which is considered representative of the whole soil. In soils derived from sedimentary rocks, the fraction coarser than 2 mm, known as rock fragments or the soil skeleton, may contain considerable amounts of organic C (Rivard & De Kimpe, 1980; Ugolini *et al.*, 1996; Corti *et al.*, 1998; Agnelli *et al.*, 2000). For example, in the upper horizons of soils derived from sandstone in the northern Apennines of Italy, Ugolini *et al.* (1996) found that the concentration of organic C in rock fragments was close to that of the fine earth.

The organic C content of the soil skeleton is a function mainly of lithology and degree of weathering (Rivard & De Kimpe, 1980; Ugolini *et al.*, 1996; Corti *et al.*, 1998). Generally, the amount of organic carbon increases with the degree of alteration in rock fragments. Weathering of the fragments tends to increase their porosity and hence the possibility of exchanges between them and the rest of the soil (Ugolini *et al.*, 1996). In addition, Agnelli *et al.* (2001) have shown that highly altered rock fragments host an active microbial population.

Stony soils, that is those composed of more than 40% rock fragments by mass or 35% by volume, cover much of the world's land surface. They occupy about 30% of the land in Western Europe, more than 60% of the Mediterranean basin (Poesen, 1990), entire regions of North Africa, and 16% of the agricultural lands in the USA (Miller & Guthrie, 1984). Quantification and characterization of the organic matter present in rock fragments could improve our understanding of the soil's carbon cycle, and these tasks can be aided by using C isotopes.

Radiocarbon (^{14}C), the radioactive isotope of C, is much used in studying carbon cycling in soil. The ^{14}C is produced in

Correspondence: A. Agnelli. E-mail: agnelli@iges.fi.cnr.it

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the stratosphere and it is rapidly oxidized to $^{14}\text{CO}_2$. The ^{14}C content of the atmosphere depends on the exchange of $^{14}\text{CO}_2$ between its site of production and the ocean and terrestrial reservoirs. Because of the rapid cycling of carbon between the atmosphere and living organisms, plants maintain a ^{14}C specific activity (or $^{14}\text{C}/^{12}\text{C}$ ratio corrected for a mass-dependent isotopic fractionation) that equals that of atmospheric CO_2 . The ^{14}C in the tissues of plant debris is no longer replenished, and decays with a half-life of 5730 years; the $^{14}\text{C}/^{12}\text{C}$ ratio can thus be used to indicate the time since the death of the organisms (Trumbore, 1996). The $^{14}\text{C}/^{12}\text{C}$ ratio of organic matter that resides in the soil long enough for significant radioactive decay reflects the mean age of C in soils. During the 1950s and early 1960s, the ^{14}C content of atmospheric CO_2 sharply increased as a result of the production of ^{14}C during atmospheric testing of nuclear weapons (bomb ^{14}C). This isotopic spike has made radiocarbon a tracer of processes in the C cycle on timescales of years to decades.

The stable isotope ^{13}C is present in natural systems at about 1.1% relative to ^{12}C . Processes such as photosynthesis discriminate against the heavier ^{13}C , though the degree of this discrimination depends on the photosynthetic pathway. Average $\delta^{13}\text{C}$ values (‰ deviation of the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample from that of the standard) are -27‰ for C3 plants and -13‰ for C4 plants (Boutton *et al.*, 1998). Since the $\delta^{13}\text{C}$ of soil organic matter reflects the $\delta^{13}\text{C}$ of the vegetation from which it was derived, ^{13}C has been used to trace carbon dynamics in the soil when one type of vegetation has been replaced by another (e.g. Balesdent *et al.*, 1987; Follet *et al.*, 1997; Boutton *et al.*, 1998). If the vegetation has not changed over time, enrichment in ^{13}C occurs with the progress of decomposition and humification of organic matter in soil (Kalbitz *et al.*, 2000).

Soil organic matter is heterogeneous, containing materials with different turnover rates, and its dating should yield the average age of the different pools of C in it. To separate that average into more active (rapidly cycling) and passive (slowly cycling) pools, methods have been developed to measure the mean age of separated components of soil organic matter. Soil carbon has been separated in several ways: chemical fractionation (Paul *et al.*, 1997), physical fractionation (Gaudinski *et al.*, 2000; Puget *et al.*, 2000), or isolation of specific compounds (Bol *et al.*, 1996; Huang *et al.*, 1999). In addition, radiocarbon measurements of CO_2 produced during decomposition of soil organic matter can furnish information about the pool of C with the shortest mean residence time and the seasonal variation in soil respiration (Trumbore, 2000).

We have tried to assess the amount and the nature of the organic matter in both rock fragments and fine earth of a forest soil derived from sedimentary parent rock. In particular we wanted to determine whether carbon in rock fragments is an active pool of C with an average age of less than 1 year to decades, or a passive pool of stable organic matter that persists over several thousands of years (Townsend *et al.*, 1995; Trumbore, 1997). For this purpose we measured both the bulk organic

C content and its distribution in different fractions (humic C, non-humic C and non-extractable C), and determined the $\Delta^{14}\text{C}$ and the $\delta^{13}\text{C}$ of humic and fulvic acids, bulk organic matter, and CO_2 produced during incubation of the samples.

Materials and methods

The area chosen for this study is at 1100 m above sea level in the Vallombrosa National Forest, on the west flanks of the Apennine mountains in Italy. The mean annual precipitation is 1340 mm and the mean annual air temperature is 10.2°C. The soil of the forest developed from an Oligocene sandstone, made of coarse turbidites of quartz, feldspars and phyllosilicates, intercalated with thin siltstone beds.

Soil profiles were opened at Cavalla, on a 5% slope with a northeast exposure. They exposed a modern soil developed in soliflucted material, probably deposited during the last glaciation, resting on a buried palaeosol (Ugolini *et al.*, 1996). The vegetation is a plantation of *Abies alba* Mill. about 70 years old. The soil was classified as a Humic Cambisol, in the FAO classification.

In this work we considered only the upper part (42 cm) of the soil (A1, A2 and Bw1 horizons). A profile description is given in Table A1 (Appendix).

Samples were collected during early November 1996. Sampling was done on a volume basis using the 'irregular hole' method (Blake & Hartge, 1986). The samples were separated into rock fragments and fine earth by dry- and wet-sieving at 2 mm. The rock fragments were ranked according to type (sandstone and siltstone) and degree of alteration (Corti *et al.*, 1998). The clasts were sorted into three classes according to degree of weathering: highly altered, moderately altered and slightly altered. The size limits for the three classes differed with soil horizons and are shown in Table 1. To obtain clean rock fragments, the skeletal material was wet-sieved repeatedly. During this operation we recovered another fraction, here referred to as 'washings', consisting of the material <2 mm that firmly adhered to the surfaces of the rock fragments.

The organic C content was determined in triplicate on all the fractions, after crushing them to less than 0.5 mm in size and washing with 0.2 M HCl solution, by a Carlo Erba NA 1500

Table 1 Size limits of highly, moderately and slightly altered rock fragments from the Cavalla profile

Horizon	Rock fragments		
	Highly altered /mm	Moderately altered /mm	Slightly altered /mm
A1	2–8	8–12	> 12
A2	2–8	8–12	> 12
Bw1	2–6	6–12	> 12

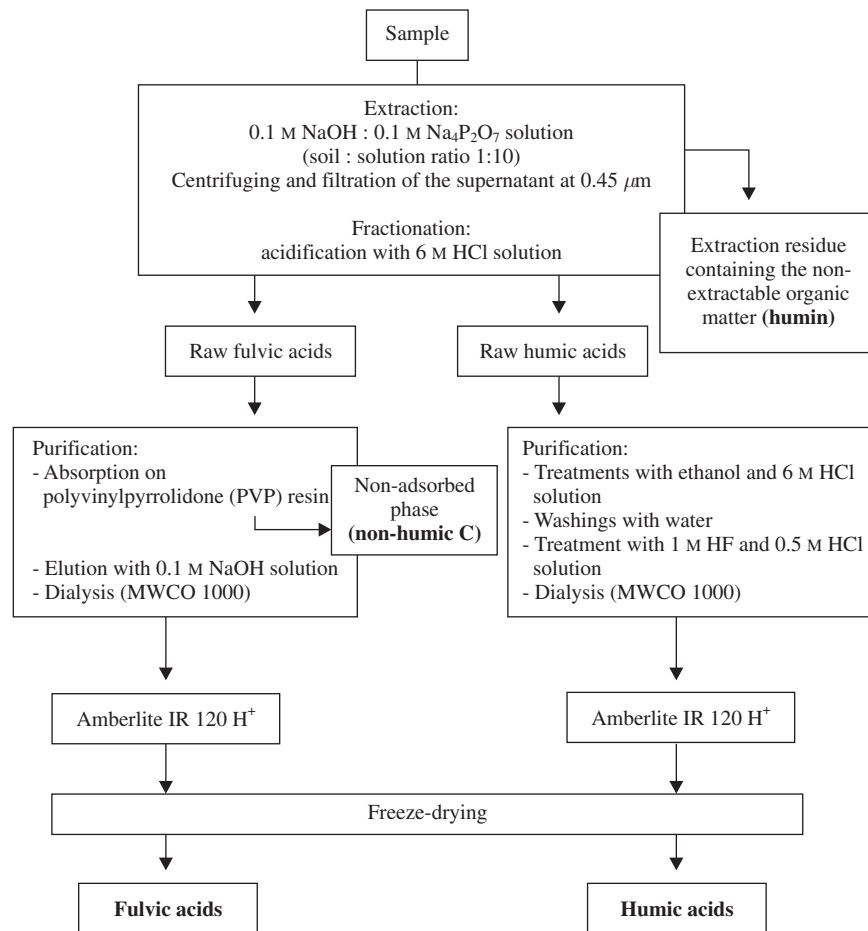


Figure 1 Scheme of extraction, fractionation and purification of the humic substances.

combustion analyser. Vegetable matter (rootlets, seeds, etc.) was removed before analysis.

Most of the rock fragments in the soil derive from sandstone, and we therefore restricted our study to these, disregarding those from the siltstone. The separates then considered for further analyses were fine earth, washings, highly altered and slightly altered sandstone fragments.

Total porosity was calculated by

$$P\% = \left(1 - \frac{D_b}{D_s}\right) \times 100,$$

where D_b is the bulk density and D_s is the specific density. The procedure for the determination of D_b and D_s is reported in detail in Corti *et al.* (1998).

Microporosity in the range 10–100 nm of pore diameter was determined on rock fragments by adsorption of N_2 at -196.15°C (Brunauer *et al.*, 1938) with a Carlo Erba Sorptomatic 1900 apparatus.

Humic substances were extracted from three aliquots of each sample, then fractionated and purified following the procedure outlined in Figure 1.

Carbon contents of the humic and fulvic acids and of the non-extractable organic matter (humins) in the extraction residue were also measured with the Carlo Erba NA 1500 combustion analyser. Each sample was run in triplicate. We obtained the non-humic C, lost during the purification of the humic substances, by subtracting the C of humic and humin materials from the total organic C content.

Because of the non-normal distribution of the data, the statistical significance of the differences in organic C content among the soil fractions and their humic, humin and non-humic components was assessed by a non-parametric test, the Mann–Whitney U -test. This test extends to a probability level of $P < 0.1$ the limit at which the null hypothesis is rejected (Rohlf & Sokal, 1995).

Radiocarbon of humic and fulvic acids and of whole samples was determined by accelerator mass spectrometry (AMS) at the Centre for AMS, Lawrence Livermore Laboratory, Livermore, California. Briefly, samples were combusted at 900°C in evacuated, sealed quartz tubes in the presence of CuO wire (Buchanan & Corcoran, 1959). The CO_2 produced during the combustion was cryogenically purified and converted to graphite targets for AMS using the zinc reduction methods

(Vogel, 1992). The targets were then analysed for ^{14}C . Radiocarbon analyses were also made on the CO_2 obtained from the basal respiration of fine earth and highly altered rock fragments incubated in sterile glass jars for 14 days at 25°C and at 50% of their total water-holding capacity. The CO_2 produced during the respiration was cryogenically purified and reduced to graphite for the AMS targets. Radiocarbon data were expressed in $\Delta^{14}\text{C}$, ‰ deviation from the $^{14}\text{C}/^{12}\text{C}$ ratio of oxalic acid standard in 1950 (Modern), corrected to a $\delta^{13}\text{C}$ of -25‰ , to correct for mass-dependent isotopic fractionation effects (Stuiver & Polach, 1977). Positive values of $\Delta^{14}\text{C}$ indicate the presence of ^{14}C produced by nuclear weapons testing, meaning that a considerable amount of the C in the analysed material was fixed by plants since 1950; negative values indicate that the C in the material has resided in the soil long enough for significant radioactive decay of ^{14}C (half-life 5730 years). The instrument error for the radiocarbon analyses, determined on repeated measurements of secondary standards, was $\pm 6\text{‰}$, on the absolute value.

We calculated mean residence time (MRT) for C in each fraction based on its radiocarbon content (Trumbore, 1993; Gaudinski *et al.*, 2000). For a homogeneous carbon reservoir, the balance of carbon and radiocarbon with time is given, respectively, by

$$\frac{dC(t)}{dt} = I - kC(t) \quad (1)$$

and

$$\frac{d\{F_m(t)C(t)\}}{dt} = IF_{\text{atm}}(t) - (k + \lambda)F_m(t)C(t), \quad (2)$$

where

- $C(t)$ is the carbon inventory in year t ;
- I is the amount of C added to the soil per year;
- $F_m(t)$ is the $^{14}\text{C}/^{12}\text{C}$ ratio in the soil organic pool in year t , normalized to an internationally agreed standard, 1895 wood;
- $F_m = (\Delta^{14}\text{C}/1000 + 1) \exp\{(y - 1950)/8267\}$, where y is the year of sampling, 1996;
- $F_{\text{atm}}(t)$ is the $^{14}\text{C}/^{12}\text{C}$ ratio (divided by the standard, which is 1895 wood) of fresh litter added to the soil in year t ; $F_{\text{atm}}(t) = 1.0$ for $t < 1950$, but has variable values for 1950 to the date of collection, reflecting changes in atmospheric $^{14}\text{CO}_2$ since atmospheric weapon testing;
- λ is the radioactive decay constant for ^{14}C , equal to $1/8267 \text{ year}^{-1}$;
- k is the decay constant for organic matter (year^{-1}).

The MRT is defined as $1/k$.

For soil carbon pools collected before 1950, $F_{\text{atm}}(t) = 1.0$, and considered to be at steady state, Equations (1) and (2) can both be set equal to zero:

$$I - kC(t) = IF_{\text{atm}}(t) - (k + \lambda)F_m(t)C(t). \quad (3)$$

Solving for $F_m(t)$ we find

$$F_m(t) = \frac{k}{(k + \lambda)}. \quad (4)$$

For example, a soil organic matter fraction with MRT of 400 years collected in 1950 will have $\Delta^{14}\text{C}$ of -47.4‰ .

For soils collected since 1950, the $^{14}\text{C}/^{12}\text{C}$ of C inputs to the soil, $F_{\text{atm}}(t)$, is not constant, and a time-dependent model to determine the changes in $F_m(t)$ in the soil fraction of interest must be used. Following Trumbore *et al.* (1996), we used the equation

$$F_m(t)C(t) = IF_{\text{atm}}(t) + (1 - k - \lambda)F_m(t-1)C(t-1). \quad (5)$$

If the pools of C are at steady state, $I = kC(t)$ and $C(t) = C(t-1)$ then Equation (5) is reduced to

$$F_m(t) = kF_{\text{atm}}(t) + (1 - k - \lambda)F_m(t-1). \quad (6)$$

The same pool of soil organic matter with a mean residence time of 400 years (which had $\Delta^{14}\text{C}$ of -47.4‰ in 1950) would thus have a $\Delta^{14}\text{C}$ of -18.5‰ in 1996.

We used data for the $\Delta^{14}\text{C}$ of northern hemisphere air for the period 1900–96 published by Levin & Heshshaimer (2000) to determine $F_{\text{atm}}(t)$ and calculated $F_m(t)$ for the period 1900–96, assigning different values for k ($1/\text{MRT}$) until the 1996 $F_m(t)$ reproduced the observed $\Delta^{14}\text{C}$ values in our fractions of organic matter. In some instances, when $\Delta^{14}\text{C} > 100\text{‰}$, two different mean residence times will yield identical values of F_m (1996) (Figure 2). To distinguish between these values, we either have ^{14}C data for samples collected at a different time, or we must know something about the magnitude of C fluxes into or out of the organic matter fraction (for details see Gaudinski *et al.*, 2000). Since no further information was available to constrain the estimates of the mean residence time, we have presented both possible values.

Note that the MRT we calculated from ^{14}C depends on the assumptions that the pool of carbon we are analysing is homogeneous and at steady state. If the pool is instead composed of a mixture of materials, some of which decompose more rapidly than others, then the MRT we calculate will represent the average.

Stable carbon isotope (^{13}C) values were determined on aliquots of purified CO_2 obtained from both combustion and respiration samples used for the ^{14}C analyses. The ^{13}C was measured by dual injection stable isotope mass spectrometry at the Woods Hole Oceanographic Institute, Massachusetts, and the UCI Department of Earth System Science.

The values were expressed in

$$\delta^{13}\text{C} = ({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}} - {}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}) / {}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}} \times 10^3$$

relative to the Pee Dee Belemnite standard (PDB). The instrument error for the ^{13}C analyses, determined on repeated measurements of secondary standards, was $\pm 0.02\text{‰}$, on the absolute value.

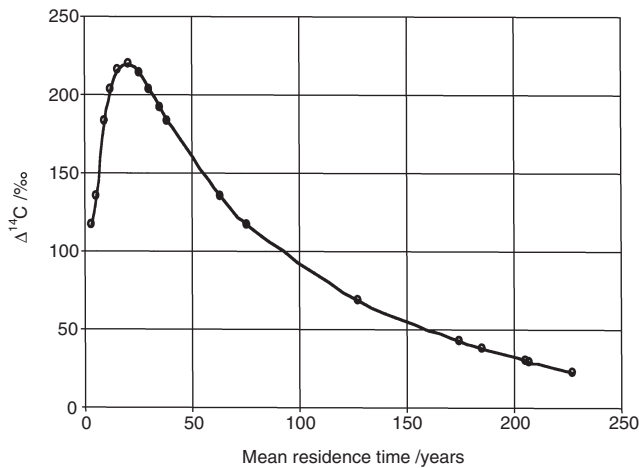


Figure 2 Positive values of $\Delta^{14}\text{C}$ and estimated mean residence time of C for samples collected in 1996.

Results

Distribution of the soil fractions, organic C content and porosity

The proportion of rock fragments (by volume) increased with depth in the soil, from about 9% in the A horizons to about 13% in the Bw1 horizon (Table 2). The largest percentage of highly altered rock fragments, both of sandstone and of siltstone, was in the A horizons. In the Bw1, slightly altered sandstone was the most abundant. The quantity of washings ranged from about 7 to 17%, with most in the A2 horizon.

Since fine earth and rock fragments have different bulk densities, the data on the organic C are reported on a volume basis. These values can be converted to a mass basis by means of the bulk density values reported in Table A2 (Appendix). Organic C content (Table 3) decreased with increasing depth for all the fractions, except for the moderately altered siltstone fragments, where it appeared similar in the A1 and A2 horizons. In each horizon the fine earth contained the most organic C, from 39.2 g dm⁻³ in the A1 to 10.9 g dm⁻³ in the Bw1 horizon. Highly altered rock fragments contained

relatively large concentrations of organic C, especially in the A horizons, where those derived from sandstone contained 14.2–24.2 g dm⁻³ and those from siltstone 6.3–10.7 g dm⁻³. The washings had values from 27.3 to 6.0 g dm⁻³, which are similar to those of the fine earth and highly altered clasts. Slightly altered rock fragments contained the least organic C, while the moderately altered ones had contents intermediate between those of the highly and slightly altered rock fragments.

In each horizon the total porosity of the fine materials was larger than that of the rock fragments (Table 4). The highly altered rock fragments were more porous than the slightly altered ones. Total porosity of all fractions increased from the A1 to A2 horizon, to decrease in the Bw1. In the rock fragments, the proportion of pores with a diameter between 10 and 100 nm tended to increase with increasing depth, and the same was true for the ratio between microporosity and total porosity (Table 4).

Distribution of organic C in humic, humin and non-humic form

The amount of C associated with humic substances (fulvic acids C + humic acids C) decreased with increasing depth (for a probability level of at least $P < 0.1$). Within each horizon the humic C content was similar among the fine earth, washings and highly altered rock fragments (Figure 3a). The smallest amount of humic C was found in each horizon in the slightly altered rock fragments (at least $P < 0.005$).

In the A horizons, fine earth and washings had similar concentrations of humin C (Figure 3b); both were larger than those of the two classes of rock fragments ($P < 0.001$). In the Bw1 horizon, the differences among the fractions became less pronounced.

The non-humic C (Figure 3c) was more abundant in the fine earth than in the other fractions in the A1 and Bw1 horizons, whereas in the A2 horizon it was similar in fine earth, washings and highly altered rock fragments. Similar values of non-humic C were also found in the washings and highly altered rock fragments of the A1 horizon.

Table 2 Percentage distribution, by volume, of fine earth, washings and rock fragments, according to lithology and degree of alteration, from the Cavalla profile. Values in parentheses are standard errors

Horizon	Fine earth	Washings	Rock fragments						Total
			Sandstone			Siltstone			
			Highly altered	Moderately altered	Slightly altered	Highly altered	Moderately altered	Slightly altered	
A1 (0–11 cm)	83.6 (0.2)	7.2 (0.2)	5.6 (0.3)	0.8 (0.0)	1.0 (0.1)	1.5 (0.1)	0.3 (0.1)	0.1 (0.0)	9.2 (0.1)
A2 (11–23 cm)	74.0 (0.5)	16.9 (0.6)	4.3 (0.5)	0.6 (0.1)	1.3 (0.3)	2.3 (0.1)	0.3 (0.1)	0.3 (0.1)	9.1 (0.1)
Bw1 (23–42 cm)	76.4 (0.3)	10.7 (0.5)	1.6 (0.2)	1.2 (0.3)	6.1 (0.6)	1.7 (0.3)	0.6 (0.0)	1.7 (0.9)	12.9 (0.2)

Table 3 Organic C content (in g dm⁻³) of fine earth, washings and rock fragments, according to lithology and degree of alteration, from the Cavalla profile. Values in parentheses are standard errors

Horizon	Fine earth	Washings	Rock fragments					
			Sandstone			Siltstone		
			Highly altered	Moderately altered	Slightly altered	Highly altered	Moderately altered	Slightly altered
A1	39.23 (2.09)	27.30 (1.58)	24.24 (1.67)	10.52 (0.75)	5.79 (0.47)	10.71 (0.54)	7.65 (0.51)	6.52 (0.30)
A2	18.44 (1.80)	15.96 (1.65)	14.23 (1.00)	7.83 (0.43)	2.56 (0.17)	6.30 (0.16)	7.92 (0.32)	3.21 (0.24)
Bw1	10.88 (0.56)	6.03 (0.28)	4.36 (0.25)	4.03 (0.17)	1.90 (0.04)	3.22 (0.22)	3.84 (0.09)	2.04 (0.33)

Table 4 Total porosity (TP) and microporosity (mp) in the range between 10 and 100 nm pore diameter, in % by volume, of fine earth, washings and rock fragments from the Cavalla profile. Values in parentheses are standard errors

Horizon	Fine earth and washings TP	Rock fragments						
		TP	Highly altered			Slightly altered		
			mp	mp/TP	TP	mp	mp/TP	
A1	68.2 (1.5)	38.3 (3.1)	4.7 (0.2)	12.3	18.4 (2.3)	2.6 (0.3)	14.1	
A2	73.2 (2.0)	43.3 (2.2)	4.7 (0.1)	10.9	21.0 (1.6)	3.3 (0.2)	15.7	
Bw1	67.2 (1.6)	32.8 (2.0)	6.0 (0.2)	18.3	18.4 (1.3)	3.3 (0.3)	17.9	

$\Delta^{14}C$ and $\delta^{13}C$

The mean residence time (MRT) derived from ¹⁴C measurements for humic substances of all the horizons ranged from 170 to 13 900 years (Table 5), and increased with depth, as generally observed in soils. In the A1 and A2 horizons, the humic acids with the largest ¹⁴C content (shortest MRT) were those extracted from the washings and the highly altered rock fragments. Furthermore, in the A1 horizon, the humic acids extracted from these two fractions had positive $\Delta^{14}C$ values, +30.0‰ for the washings and +43.4‰ for the highly altered rock fragments, corresponding to mean residence times of 210 and 170 years, respectively (Table 5). The fulvic acids extracted from highly altered rock fragments also had the largest $\Delta^{14}C$ values in the A1 and A2 horizons: +30.9‰ (MRT of 200 years) and -69.9‰ (MRT of 760 years), respectively. The positive $\Delta^{14}C$ values indicated that most of the carbon from these samples was derived from plants grown since 1963 (subsequent to the rapid increase in atmospheric ¹⁴C from weapon testing). Fulvic and humic acids in the Bw1 horizon have much smaller $\Delta^{14}C$ values (longer MRT) than those in the A horizons, in agreement with the concept that the amount of passive organic matter increases with soil depth (O'Brien & Stout, 1977; Scharpenseel *et al.*, 1989). In each horizon the humic substances of slightly altered rock fragments had the smallest ¹⁴C signatures, with the exception of the fulvic acids

from the A2 horizon. Differences between highly and slightly altered rock fragments are greatest in the A horizons for both humic and fulvic acids.

In the A1 and A2 horizons, the $\Delta^{14}C$ of the bulk organic matter was larger in the fine earth than in the highly altered rock fragments in those horizons (Table 6). In the A1 horizon, the $\Delta^{14}C$ of the bulk organic matter revealed the presence of 'bomb ¹⁴C', with values of +69.9‰ in the fine earth and +23.3‰ in the highly altered rock fragments, corresponding to mean residence times of 130 and 230 years, respectively. In the A2 horizon, the bulk organic matter had negative values of $\Delta^{14}C$ and so had a longer MRT than at the surface: 520 years for the fine earth and 820 years for the rock fragments.

The results of the radiocarbon analyses on the CO₂ evolved from the basal respiration of fine earth and highly altered rock fragments from A1 and A2 horizons (Table 6) showed that the respired organic C had positive $\Delta^{14}C$ values for both fractions and horizons. The fine earth had $\Delta^{14}C$ values of +135.4‰ in the A1 and +38.7‰ in the A2, while the rock fragments from the same horizons had values of +183.9‰ and +117.2‰, respectively. The mean residence time of the mineralized organic matter was less than 60 years in the A1 horizon and 180 years in the A2 horizon.

The $\delta^{13}C$ signatures of humic and fulvic acids extracted from the fractions of the three horizons ranged from -24.4‰ to

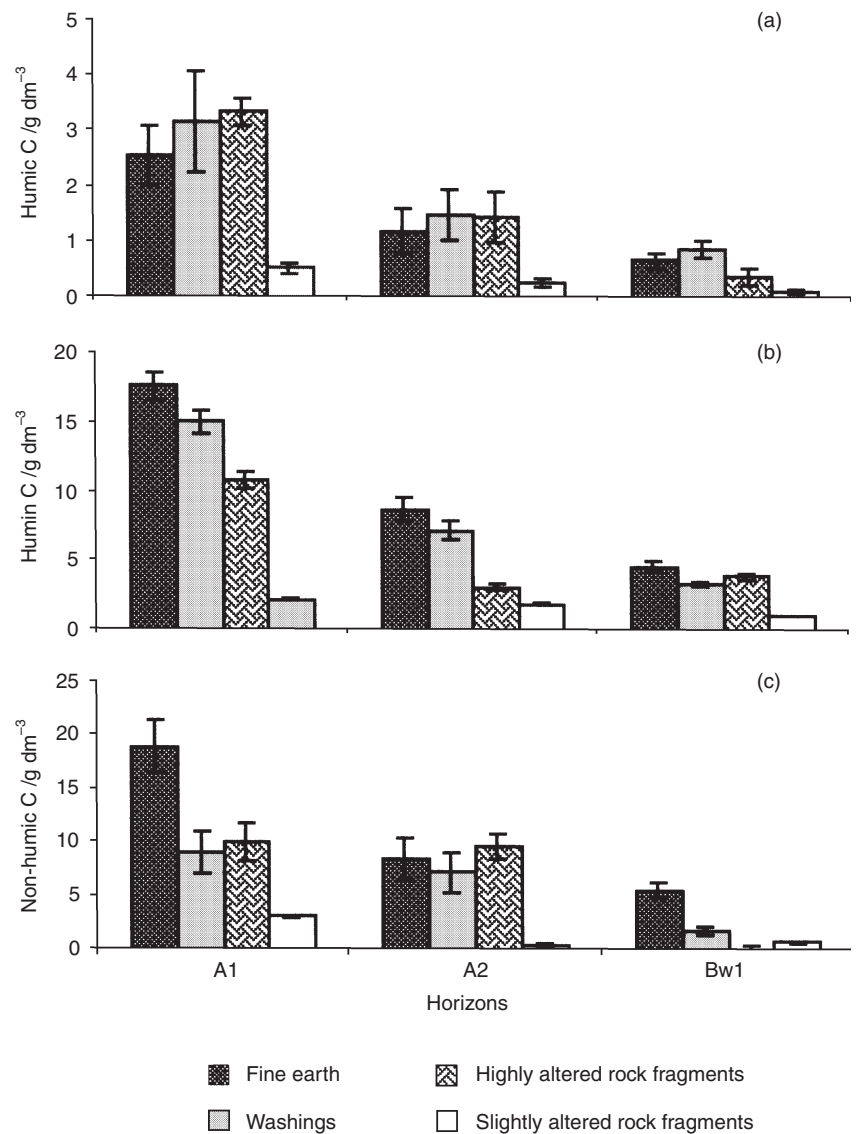


Figure 3 Distribution of the organic C in (a) humic (humic + fulvic acids), (b) humin and (c) non-humic substances in fine earth, washings, and highly and slightly altered rock fragments from the Cavalla profile. Error bars represent the standard errors.

Table 5 $\Delta^{14}\text{C}$ of the humic and fulvic acids extracted from the fractions of the Cavalla profile. Data are expressed in ‰ deviation from the $^{14}\text{C}/^{12}\text{C}$ ratio of oxalic acid standard in 1950. The mean residence time (in years) is given in parentheses

Horizon	Humic acids				Fulvic acids			
	Fine earth	Washings	Highly altered rock fragments	Slightly altered rock fragments	Fine earth	Washings	Highly altered rock fragments	Slightly altered rock fragments
A1	-54.1 (640)	+30.0 (210)	+43.4 (170)	-222.8 (2370)	-49.3 (600)	-51.2 (610)	+30.9 (200)	-89.4 (920)
A2	-212.6 (2240)	-45.4 (570)	-49.0 (600)	-333.3 (4070)	-172.5 (1760)	-101.1 (1030)	-69.9 (760)	-151.6 (1530)
Bw1	-292.6 (3380)	-180.7 (1850)	-539.4 (9460)	-633.1 (13920)	-249.6 (2730)	-302.4 (3540)	-352.9 (4430)	-378.3 (4940)

-26.7‰ (Table 7), and the bulk organic matter and respired CO₂ of fine earth and highly altered rock fragments of the A1 and A2 horizons (Table 8) ranged from -24.8‰ to -26.8‰. All these signatures indicate that, as expected at this site, the overall organic components of every soil fraction originate from C3 plants.

Discussion

The data on organic C content show that all the fractions contribute significantly to the total C inventory of the soil. We estimate that the upper 42 cm of the Cavalla profile contains 7.84 g dm⁻³ of organic C, by calculating from the weighted

Table 6 $\Delta^{14}\text{C}$ of the bulk organic matter and the CO_2 produced by the basal respiration of fine earth and highly altered rock fragments from the Cavalla profile. Data are expressed in ‰ deviation from the $^{14}\text{C}/^{12}\text{C}$ ratio of oxalic acid standard in 1950. The mean residence time (in years) is given in parentheses

Horizon	Fine earth		Highly altered rock fragments	
	Bulk organic matter	Respired CO_2	Bulk organic matter	Respired CO_2
A1	+69.0 (130)	+135.4 (5 or 60)	+23.3 (230)	+183.9 (9 or 40)
A2	-37.2 (520)	+38.7 (180)	-73.2 (830)	+117.2 (3 or 70)

Table 7 $\delta^{13}\text{C}$ of the humic and fulvic acids extracted from the fractions of the Cavalla profile. Data are expressed in ‰ deviation from the $^{13}\text{C}/^{12}\text{C}$ ratio of the Pee Dee Belemnite standard (PDB)

Horizon	Humic acids				Fulvic acids			
	Fine earth	Washings	Highly altered rock fragments	Slightly altered rock fragments	Fine earth	Washings	Highly altered rock fragments	Slightly altered rock fragments
A1	-26.3	-26.1	-25.9	-25.9	-26.7	-26.7	-26.6	-26.6
A2	-26.0	-25.7	-25.8	-25.6	-26.4	-26.3	-26.4	-26.3
Bw1	-25.8	-26.2	-24.4	-25.4	-26.0	-26.3	-26.0	-25.7

Horizon	Fine earth		Highly altered rock fragments	
	Bulk organic matter	Respired CO_2	Bulk organic matter	Respired CO_2
A1	-25.9	-24.8	-25.6	-25.7
A2	-25.7	-25.6	-25.6	-26.8

Table 8 $\delta^{13}\text{C}$ of the bulk organic matter and the CO_2 produced by the basal respiration of fine earth and highly altered rock fragments from the Cavalla profile. Data are expressed in ‰ deviation from the $^{13}\text{C}/^{12}\text{C}$ ratio of the Pee Dee Belemnite standard (PDB)

means of the organic C content in all the horizons and their thickness. The fine earth and washings fractions contribute 87.0% and 8.5% of the total C content, respectively. The rock fragments, which range from 9 to 13% of the soil volume, contribute 4.5% of the total C inventory. Of the C contained in the soil skeleton, 81.4% is in sandstone clasts, with 65.7% in the highly altered sandstone fragments.

The presence of humic C in highly altered rock fragments, in concentrations similar to those found in both the fine earth and the washings, indicates that the more altered soil skeleton provides an open system where the organic material undergoes transformation. The small amount of humic C found in the slightly altered rock fragments in all the horizons confirmed the importance of the degree of weathering in making the skeleton an active part of the soil.

In the three horizons examined, most of the organic C was in humin and non-humic forms. Unlike the fine earth, the other fractions had different overall contributions of humin

and non-humic carbon to the total C and varied much with depth. In particular, in the highly altered rock fragments the non-humic C contributed about 41% in the A1, 70% in the A2 and 2% in the Bw1 horizons. Generally, non-humic C is considered to comprise compounds easily transported in solution such as low molecular weight organic acids, amino acids, simple sugars and polysaccharides (Stevenson, 1994). However, their transport can be interrupted by sorption to colloids and by microbial degradation. These processes, which occur preferentially in the upper part of the soil, could explain the observed decrease of non-humic C with increasing depth. Further, in the Bw1 horizon the highly altered rock fragments were less porous but had a relatively large microporosity (Table 4). These facts could also explain the abrupt decrease of the non-humic C in the highly altered skeleton of this horizon, where the humin C is the major component of the organic C in the washings and clasts, reaching 90% in the highly altered fragments.

The presence of 'bomb ^{14}C ' in the humic and fulvic acids (Table 5) extracted from highly altered clasts and the washings of the A1 horizon suggested that these substances were on average degraded and, consequently, resupplied or resynthesized, or both, much more quickly than those of the fine earth in the same horizon. This suggestion is supported by the presence of highly decomposable material in the chemical structure of the humic acids from the washings and from the rock fragments of the A horizons (Agnelli *et al.*, 2000), and by the relatively large ^{14}C content in the CO_2 derived from incubations of the highly altered rock fragments (Table 6).

In the A horizons, $\Delta^{14}\text{C}$ values were similar for humic and fulvic acids extracted from the washings and highly altered rock fragments. In the Bw1 horizon, however, humic and fulvic acids from the washings had signatures closer to those obtained from the humic material isolated from the fine earth than those from such fragments. This could reflect differences in the origin of the washings between surface and deeper horizons. In the biologically more active A horizons, rock fragments are subjected to intense weathering, with consequent weakening of their physical structure. Under these conditions, the cleaning procedure, even though rather gentle, could have removed a large part of the fine material forming the surface of the skeleton. By contrast, less biological activity and less weathered rock fragments in the Bw1 horizon could mean that the washings were mostly material accumulated by illuviation, rather than removed from the weathered surface of the clasts.

Differences between the $\Delta^{14}\text{C}$ values of bulk organic matter and humic substances in the A horizons can be ascribed to the influence of the different kinds of organic C and their distribution in fine earth and rock fragments. In the A1 horizon, the shorter mean residence time of the organic matter from the fine earth than that in the highly altered clasts is probably due to the larger amount of non-humic C (45.1%) in the fine fraction. In fact, while the percentage of humin C of the highly altered clasts (41.6%) was somewhat less than that of the fine earth (48.4%), the percentage of humic C was greater (13.8% against 6.6%) and formed by younger C (Table 5). In the A2 horizon, the smaller $\Delta^{14}\text{C}$ value of the organic matter from the highly altered rock fragments than that in the fine earth could be due to the old mean age of the humin C in the soil skeleton. According to Paul *et al.* (1997), small amounts of very old C can greatly influence the ^{14}C age of the organic matter.

The CO_2 derived from incubations of fine earth and highly altered rock fragments (Table 6) had larger $\Delta^{14}\text{C}$ values than the bulk organic matter or the humic and fulvic acids isolated from the same horizons (Table 5). This suggests that the bulk organic matter consists of at least two pools, one cycling faster (with MRT of a few years to several decades) and one slower (with MRT of hundreds of years, as in humic substances isolated from the same horizons), and that the first one, which dominates the respiration flux, does not represent the

majority of the organic C in the soil. For both fine earth and highly altered rock fragments, the decrease in $\Delta^{14}\text{C}$ of bulk organic matter and respired CO_2 from the A1 to A2 horizons can be attributed to a diminishing of the relative contribution of the faster cycling pool to the organic C in the soil.

In the highly altered rock fragments, the metabolized pools may be considerably younger, as testified by the large $\Delta^{14}\text{C}$ and the corresponding short mean residence times estimated for the A1 and A2 horizons (Table 6). The difference in behaviour of the two soil fractions could again be related to the quality of organic matter present in the fine earth and the highly altered skeleton. In fact, only selected organic materials such as dissolved organic matter, microroots, root exudates, and microbial biomass products can enter into the pores of the rock fragments. These substances, readily utilizable by the microorganisms, can be assumed to make up a component of the non-humic C. In the A1 horizon, the relative amount of non-humic C pool was larger in the fine earth than in the highly altered rock fragments. In the A2 horizon the non-humic C is similar in amount in both fine earth and such fragments (Figure 3), but in the latter it represented about 70% of the total organic C. Hence, while the fine earth provides a reservoir containing organic material of every degree of complexity, the rock fragments are less heterogeneous (Agnelli *et al.*, 2000).

The radiocarbon data indicate that the organic matter inside the rock fragments has a dual nature:

- 1 young organic matter rich in radiocarbon, which penetrates the rock fragments during weathering; and
- 2 old organic matter containing little radiocarbon, inherited from the parent material or accumulated slowly over very long times, or both.

As demonstrated by the radiocarbon measurements, while the old C prevailed in the subsurface horizons, the organic C of recent origin was mostly in the superficial horizons, where the rock fragments are most altered (Ugolini *et al.*, 1996) and are most porous (Table 4). In fact, porosity permits simple organic compounds to enter the rock fragments in solution and so foster an active microflora. This in turn favours the progressive alteration of the rock fragments.

The humic and fulvic acids of the soil fractions appeared to be enriched in ^{13}C with increasing age and depth of the profile. This fact, reported also by Scharpenseel & Neue (1984) and Bol *et al.* (1999), has been interpreted as being caused by isotopic fractionation by decomposer organisms (Boutton, 1996), supporting the findings that biological activity occurs inside the rock fragments (Agnelli *et al.*, 2001). The mobility of the fulvic acids was probably responsible for the similar $\delta^{13}\text{C}$ values in all the fractions and horizons. The humic acids had $\delta^{13}\text{C}$ signatures that were more variable and generally more enriched than those of the fulvic acids. The bulk organic matter showed no notable change in the $\delta^{13}\text{C}$ values for both fine earth and highly altered rock fragments of the A1 and A2 horizons. We think that the reason is the poor discrimination

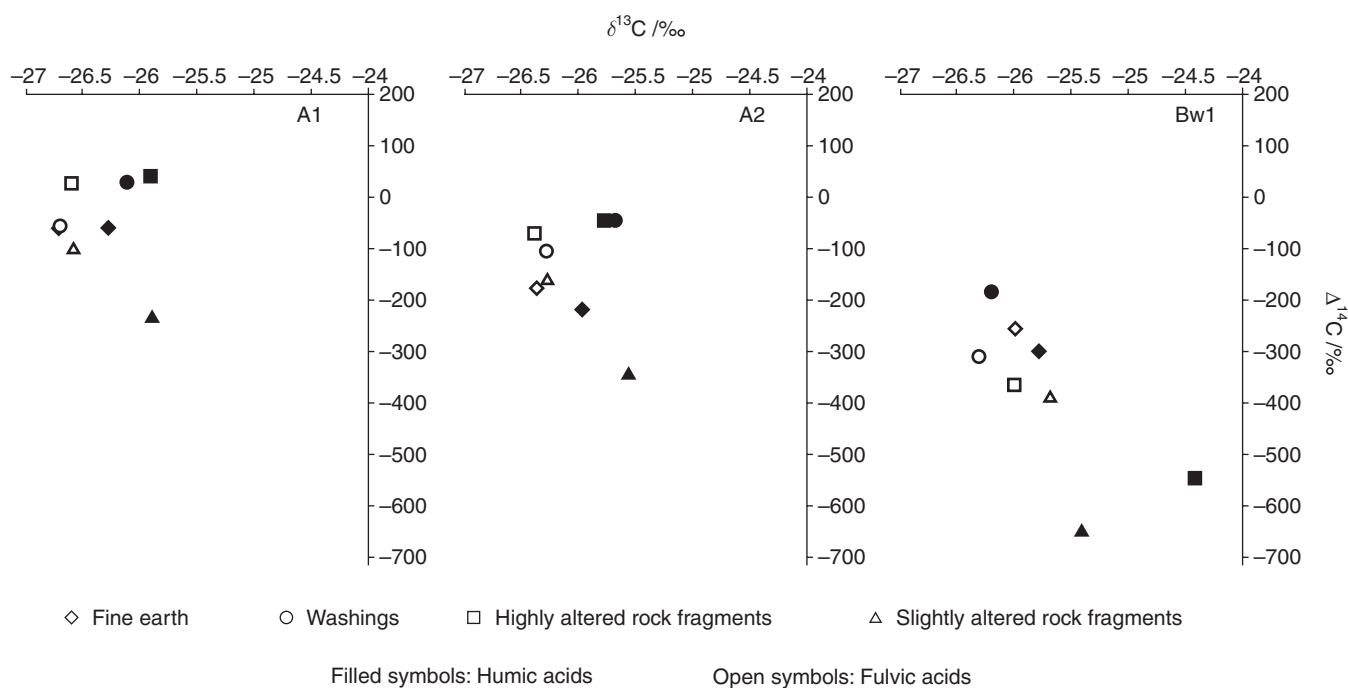


Figure 4 $\delta^{13}\text{C}$ versus $\Delta^{14}\text{C}$ of the humic and fulvic acids extracted from fine earth, washings, and highly and slightly altered rock fragments.

by the technique in the presence of such heterogeneous organic material. By contrast, the CO_2 produced during the basal respiration experiments showed a greater ^{13}C enrichment in the A1 than in the A2 horizon for both fine earth and highly altered rock fragments. As indicated by the $\Delta^{14}\text{C}$ data (Table 6), in the A1 horizon the CO_2 derived from the degradation of short-lived material; hence, the ^{13}C enrichment of the CO_2 was probably due to a differential decomposition of the organic matter by the microorganisms. Evidently, the microflora indirectly enriched the CO_2 , preferentially avoiding slowly decomposing substances containing little ^{13}C , such as lignin (Benner *et al.*, 1987).

When $\delta^{13}\text{C}$ was plotted against the $\Delta^{14}\text{C}$ data (Figure 4), the humic and fulvic acids from all the fractions of the A1 and A2 horizons were clustered together; in the Bw1, the humic acids of the rock fragments were separated from the others. We interpret this trend as depending on the nature of the organic material in the rock fragments, which was recent in the A1 and A2 horizons and very old in the Bw1. Figure 4 also shows that the highly and slightly altered rock fragments are distinguished from each other by the ^{14}C content in their humic acids in the A horizons, and by both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in the Bw1 horizon. This can be explained by the fact that the infilling and the homogenization of organic materials can occur freely in the highly altered rock fragments, as demonstrated by the ^{14}C data, whereas they cannot do so in the poorly accessible slightly altered rock fragments. In the Bw1, the $\delta^{13}\text{C}$ of the humic acids extracted from the highly altered skeleton was considerably more enriched than that

of the humic acids from the slightly altered rock fragments. This occurred despite the humic acids of the highly altered rock fragments being younger than those of the slightly altered ones. This suggests that the degree of weathering affected the presence and activity of the microorganisms inside the skeleton more in the subsoil than in the upper horizons.

Conclusions

The characteristics of rock fragments, at least of the highly altered ones, are similar to those generally assumed to be typical of soil aggregates. In fact, the skeleton contained considerable amounts of organic C, comprising both humic and non-humic substances. Further, a large fraction of that organic C was labile, with mean residence times of years to centuries, rather than just inherited from the sedimentary parent material.

In the A horizons, the humic and fulvic acids extracted from the highly altered rock fragments were richer in ^{14}C and had shorter mean residence times than those of the same fractions isolated from the fine earth. The radiocarbon signatures of the CO_2 produced during the basal respiration further demonstrated the heterogeneity, complexity and overall dynamic nature of the organic matter present in the highly altered clasts.

The weak ^{14}C signatures of humic substances from the slightly altered rock fragments confirmed the importance of the degree of weathering in establishing and improving the interactions between rock fragments and surrounding soil.

The progressive enrichment in ^{13}C from components with high- ^{14}C (more recent) to low- ^{14}C (older) indicated that biological activity occurred in both the fine and the coarse fractions, and that the microflora was able to utilize energy sources contained in all the soil compartments.

Our results demonstrate that sandstone rock fragments are chemically and biologically active in the soil, where they form a continuum with the fine earth. It is also apparent that the organic C in the rock fragments of sedimentary rocks should not be ignored in soil analysis and in the calculation of global soil C budget.

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Appendix

Table A1 Description of the Cavalla soil profile

Elevation: 1100 m a.s.l. Exposure: N-NE. Slope: <5%. Parent material: 'Arenaria del Falterona' (Oligocene sandstone)
 Vegetation: plantation of *Abies alba* Mill. about 75 years old
 Understorey: *Hieracium murorum*, *Prenantes purpurea*, *Luzula nivea*, *Sanicula europaea*, *Senecio fuchsii*, *Rubus idaeus*, *Fragaria vesca*, *Geranium robertianum*, *Cardamine* sp., *Galium* sp., seedlings of *Abies alba*
 Soil: Humic Cambisol (FAO–ISRIC–ISSS, 1998)

Horizon	Depth /cm	Munsell colour		Texture ^a	Structure ^b	Consistency ^c	Plasticity ^d	Roots ^e	Boundary ^f	Other observations ^g
		(moist and crushed)								
Oe	1–0								cw	Partially decomposed fir needles
A1	0–11	10YR3/2		cl	2–3 f–m cr	mfr, wss	wps	3f, 2m	cw	
A2	11–23	10YR3/3		gsil	3–2 m–f sbk	mfr; wss	wps	2f	cw	
Bw1	23–42	10YR5/4		gsil	2–3 m–f abk–sbk	mfr–mfi, wss	wps	1f	ci	
Bw2	42–71	10YR5/5		gsil–gl	2–3 f sbk	mfi, wss	wps	1f	ci	xp
BCb1	71–109	10YR5/4		vstl	2 c–m abk	mfi, wss	wps	1f	ci	xp; some clasts are saprolitic
BCb2	109–149+	10YR4/4		stl–sl	2 c–m abk	mfi, wss	wps	1m		xp; some clasts are saprolitic

^av, very; g, gravelly; st, stony; c, clay; si, silt; s, sandy; l, loam.

^b2, moderate; 3, strong; f, fine; m, medium; c, coarse; abk, angular blocky; sbk, subangular blocky; cr, crumb.

^cm, moist; w, wet; fr, friable; fi, firm; ss, slightly sticky.

^dw, wet; ps, slightly plastic.

^e1, few; 2, plentiful; 3, abundant; f, fine; m, medium.

^fc, clear; w, wavy; i, irregular.

^gxp, fragic properties.

Table A2 Bulk density (in g cm⁻³) of fine earth, washings and rock fragments, according to lithology and degree of alteration, from the Cavalla profile. Values in parentheses are standard errors

Horizon	Fine earth and washings	Rock fragments					
		Sandstone			Siltstone		
		Highly altered	Moderately altered	Slightly altered	Highly altered	Moderately altered	Slightly altered
A1	0.67 (0.09)	1.53 (1.18)	2.07 (0.07)	2.18 (0.14)	1.86 (0.17)	2.08 (0.13)	2.15 (0.07)
A2	0.66 (0.16)	1.51 (0.16)	1.89 (0.03)	2.11 (0.10)	1.76 (0.07)	1.89 (0.13)	1.91 (0.03)
Bw	0.86 (0.09)	1.79 (0.24)	1.86 (0.11)	2.18 (0.01)	1.69 (0.11)	1.87 (0.10)	2.15 (0.14)

