Depth Distribution and Predictors of Soil Organic Carbon in Podzols of a Forested Watershed in Southwestern Canada

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Abstract: Forest soils of coastal British Columbia, Canada, may store significant amounts of organic matter because of the cool climate and high forest productivity of the area. The objectives of this study were to determine the distribution of soil organic carbon (SOC) in the profile and to identify the most important predictors of SOC in Podzols of a forested watershed in southwestern British Columbia. We sampled 9 soil profiles in undisturbed forest plots by morphological horizon and measured SOC using a dry combustion method. We also determined soil pH, texture, moisture content, total nitrogen, loss on ignition, and pyrophosphate- and oxalate-extractable Fe and Al.

The average soil profile stored 15.9 kg C/m^2 over a depth of 100 cm, which is higher than SOC stocks estimates for inland Canadian forests. The organic layer (LFH) only accounted for one fourth of the C stock. Sixty percent of the profile SOC (including the forest floor) was found in the subsoil of depth greater than 20 cm. Studies of SOC dynamics that only sample the topsoil are therefore inappropriate.

Although the clay concentration was low (~5%), the clay fraction accounted for one third of SOC. This suggests that organo-mineral interactions were an important factor for SOC storage. The major predictors of SOC in the mineral horizons were organically complexed Al and Fe and short-range order inorganic material. Crystalline clays also seemed to play a role in organic matter accumulation, but were not as important as poorly crystalline compounds. In the organic layer, organically complexed Fe forms correlated negatively with SOC, indicating that the amount of Fe available for adsorption to organic matter is limited. Organically complexed Al did not show the same negative association, suggesting the existence of a mechanism for upward translocation of Al into the FH horizon.

Key words: Soil organic carbon, soil organic matter, Podzol, pyrophosphate-extractable Fe and Al, clay, poorly crystalline aluminosilicates.

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Interest in soil organic matter (SOM) dynamics is ever increasing as the recognition of the potential role for soil carbon in climate change is added to more traditional concerns such as soil physical properties and nutrient content (Lal, 2004). Generally, information about soil C stocks is rather scarce (Nalder and Merriam; 1995; Kurz et al., 2002). Soil organic carbon (SOC) stocks have been measured in inland Canadian forests (Bhatti et al., 2002; Bois et al., 2009) and on the coast of Washington and Oregon states (Smithwick et al., 2002; Homann et al., 2005), but to the best of our knowledge, no information is available for the British Columbian coast. Considerable SOC stocks may exist because of mild winters and the lack of pronounced moisture deficit during the summer (Environment Canada, 2004), favoring a high primary productivity.

Information on soil C stocks is especially scarce below the top 10 to 20 cm of the soil profile. It is common in C dynamics studies to restrict sampling to the topmost layer(s) of the soil profile (e.g., Covington, 1981; Bock and Van Rees, 2002; Rey et al., 2008). However, in coastal forests of western Washington and Oregon, Homann et al. (2005) reported that more than one half of the soil C stock was found below the 20-cm depth. This points to the need for field studies, taking into account subsoil as well as topsoil C, especially because controls on C dynamics may be different (Salomé et al., 2010). Although SOC turnover generally decreases with depth, both fast cycling and more persistent SOC forms are present in significant amounts in the lower part of the soil profile (Trumbore, 2000; Diochon and Kellman, 2009).

The prospect of using soils to sequester C requires a thorough understanding of mechanisms for SOC stabilization (Sollins et al., 2007). In the meanwhile, recent advances on the C saturation concept (Six et al., 2002) demonstrate that the intrinsic characteristics of soils determine the stabilization capacity of SOM pools and limit accumulation of SOC.

The association of SOM with minerals has been recognized as one of the main processes leading to the stabilization of organic matter (Mayer, 1994). Clay-sized particles are thought to be particularly important for SOC retention. It has been established that clays may stabilize SOM through mechanical occlusion, sorption of the organic substrate to mineral surfaces, and/or inactivation of microbial extracellular enzymes (Paul, 1984; Oades, 1988; Sollins et al., 1996; Baldock and Skjemstad, 2000).

Short-range order (SRO) and amorphous inorganic phases such as imogolite, allophane, ferrihydrite, and other poorly defined Al and Fe phases have the potential to stabilize large amounts of SOC because of their reactivity and large specific surface area (Eusterhues et al., 2005). The contribution of SRO phases to SOC retention is well established in volcanic soils (Zunino et al., 1982; Torn et al., 1997; Rasmussen et al., 2006). Podzols have received more recent interest (Riise et al., 2000). Kaiser et al. (2002) and Eusterheues et al. (2005) proposed that iron oxides and SRO Al and Fe phases were the most important substrates for the formation of organo-mineral associations in Podzols. Mikutta et al. (2005, 2006) and Kleber et al. (2005) suggested that the most important mechanism for SOM stabilization in acid subsoils is the interaction with poorly crystalline minerals and polymeric metal species. Spielvogel et al. (2008) demonstrated that a specific fraction of the SOC pool is preferentially associated with SRO Al and Fe material and is then potentially stabilized for thousands of years.

Organic matter stabilization by polyvalent cations, especially Fe and Al, has also been extensively studied. In volcanic soils, the formation of organic-metallic complexes is commonly invoked to explain the inhibition of organic matter mineralization (Broadbent et al., 1964; Egli et al., 2008). In acid forest

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soils, the formation of organic-metallic complexes of Al and Fe has also been shown to be involved in the precipitation of dissolved organic matter and its subsequent stabilization (Skjemstad, 1992; Rasmussen et al., 2006; Scheel et al., 2007). The Al-humus complexation may be particularly effective at preventing microbial decomposition through the occurrence of Al toxicity (Tate and Theng, 1980) or inhibition of enzyme activity (Sollins et al., 1996). The Al ions may also enhance the sorption of humic acids on clays through the formation of Al bridges between the clay and organic matter (Varadachari et al., 1991) and result in physical protection of sorbed organics.

Although it is generally accepted that crystalline clays, SRO phases, and polyvalent cations all have a stabilizing effect on SOM, the relative importance of each mechanism seems to be site specific. Several authors have reported a strong correlation between SOC and the clay fraction (Spain, 1990; Arrouays et al., 1995; Alvarez and Lavado, 1998; Homann et al., 1998; Shen, 1999; Dexter et al., 2008). It seems, however, that when present, reactive Al and Fe phases are stronger determinants of SOM retention than crystalline phyllosilicates (Spielvogel et al., 2008).

A number of authors have found that SOM stabilization was caused primarily by SRO and noncrystalline inorganic phases (Zunino et al., 1982; Schnitzer and Kodama, 1992; Torn et al., 1997; Kaiser et al., 2002; Mikutta et al., 2006; Rasmussen et al., 2006), although others have emphasized the importance of organic-metallic complexes of Al and Fe (Broadbent et al., 1964; Boudot, 1992; Percival et al., 2000; Scheel et al., 2007; Egli et al., 2008). These apparently contradictory findings suggest that the determinants of SOC retention depend on each soil's mineralogical assemblage, organic matter characteristics, and characteristic pedogenic processes (Allison et al., 1949; Krull et al., 2003).

The objectives of this article are to determine whether subsoils are a major contributor to SOC content in Podzols of coastal British Columbia and to identify the most important predictors of SOC concentration. We measured SOC concentration in all pedogenic horizons and developed a regression equation relating SOC to clay content, SRO inorganic material, and organically complexed metals. Environmental variables such as pH and moisture were also considered, as well as a broad indicator of organic matter composition and maturity (C:N ratio). We ranked predictors according to their relative importance in determining SOC. Finally, the implications of these findings for SOC stabilization and pedogenesis in these soils are discussed.

MATERIALS AND METHODS

Sampling Sites

This study was conducted in Roberts Creek Study Forest (49°27′N, 123°41′W) on the Sunshine Coast of southwestern British Columbia. The study forest is located between the towns of Roberts Creek and Sechelt approximately 40 km northwest of Vancouver (Fig. 1).

The area lies within the Coastal Western Hemlock (CWH) biogeoclimatic zone and experiences a mean annual temperature of 10.2°C and mean annual precipitation of 1,369 mm (Environment Canada, 2004). The area subzone is Drier Maritime variant (CWHdm) (Pojar et al., 1991). The climate is oceanic, and the temperature variation between summer and winter is moderate, ranging from 3.7°C in January to 17.6°C in August. Average precipitation ranges from 1,210 to 1,530 mm annually and falls mostly in the winter in the form of rain. Elevation ranges from 350 to 590 m a.s.l., and the forest is situated on a gentle (~15%) southerly slope.
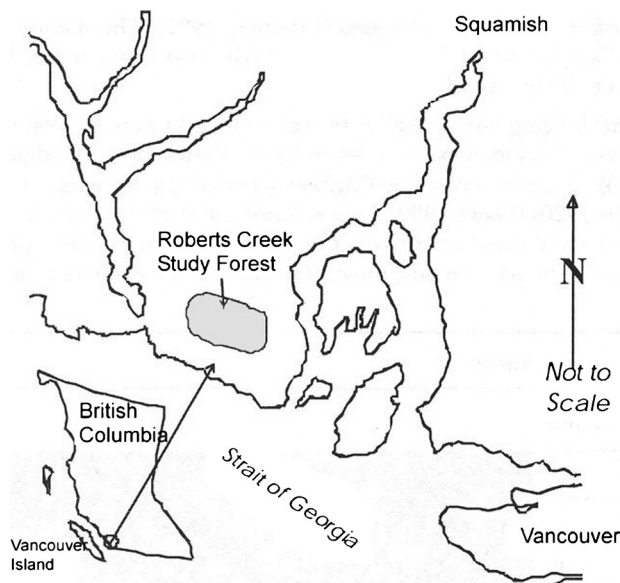

FIG. 1. Location of Roberts Creek Study Forest. Reprinted with permission from the British Columbia Ministry of Forests.

The dominant species is Douglas fir (*Pseudotsuga menziesii*) interspersed with smaller diameter western Hemlock (*Tsuga heterophylla*) and western Redcedar (*Thuja plicata*). Charcoal on standing and fallen snags indicates that the current forest (~140 years old) initiated after wildfires (D'Anjou, 2002). Charcoal is also common in all layers of the profile, indicating that periodic wildfires occurred throughout the period of soil development.

The soil parent material is a basal till deposited on a granodioritic bed rock. This compacted basal till prevents root penetration and restricts water infiltration and the downward extent of pedogenic processes. A perched water table exists in the wet months of the year, as evidenced by mottling and gleying in the BC horizon. The solum ranges from 40 to more than 120 cm in thickness. From top to bottom, the following sequence of horizon is observed: LFH (forest floor), Ae, Bf1, Bf2, BCg, and Cg. The forest floor is thin, ranging from 3 to 8 cm with a mor humus type. The Ae horizon is remarkably thick, commonly reaching 15 cm in thickness.

The soil temperature class was Mesic, and the moisture regime was humid according to Canadian soil climate classification (Lavkulich and Valentine, 1978). The soil type was humo-ferric podzol (Soil Classification Working Group, 1998), Aquentic Haplorthods (Soil Survey Staff, 2006), or Albic Gleyic podzol (IUSS Working Group WRB, 2006) of sandy loam to loamy sand texture.

Sampling and Analyses

Soils were sampled by morphological horizon in nine pits located in undisturbed forested stands of the Roberts Creek Study Forest. Each sample was collected to represent the entire horizon around an approximately 90-cm-diameter soil profile. The forest floor was separated into two parts: (i) living moss and litter and (ii) humic and fibric layer (FH).

We determined organic C and N, organic matter, soil moisture, texture, and pyrophosphate and oxalate-extractable Fe and Al on the less than 2-mm fraction. pH was measured on field moist soils before sieving. Pyrophosphate and oxalate extractions were also conducted on field moist samples because air drying can lead to irreversible changes to the surface properties

and structure of poorly crystalline materials (Hernandez Moreno et al., 1985). Other analyses were conducted on air-dried samples.

Soil pH was determined within 48 h of sample collection. pH measurement was conducted potentiometrically in a 0.01-*M* CaCl$_2$ solution respecting a soil: solution ratio of 1:2 for mineral horizons (Schofield and Taylor, 1955; Van Lierop, 1990) and of 1:4 for organic horizons. Suspensions were allowed to equilibrate for 30 min before measurement.

Total C and N were measured on soil ground to pass through a 0.5-mm sieve by dry combustion using an induction furnace (LECO model CN-2000). All soils were free of carbonates and total C equals organic C. Roots more than 2 mm were not included in mineral soil analyses, possibly leading to underestimation of mineral C stocks. However, Homann et al. (2005) reported that 90% of the mineral SOC was in the less than 2-mm fraction in coastal northwestern forests, so the error is not expected to be large. Forest floor samples were not sieved, and all materials were ground to pass through a 0.5-mm sieve.

Soil organic matter concentration was determined by loss on ignition in a muffle furnace (Kalra and Maynard, 1991). Samples were oven dried to constant weight then ashed at 375°C for 16 h and cooled in a dessicator. Weights were recorded to the nearest milligram before and after combustion.

Texture was estimated after dispersion in Na hexametaphosphate by a simple method combining wet sieving and sedimentation steps (Kettler et al., 2001). Organic matter concentration in sand, silt, and clay separates was estimated by loss on ignition performed on the different size fractions.

Gravimetric moisture content was determined by oven drying field moist samples at 70°C (FH layer) or at 105°C (mineral horizons) to constant weight (Kalra and Maynard, 1991). All samples were collected during the dry season (August), and no rain occurred during the week preceding sampling. The gravimetric moisture content has no absolute meaning; rather, it allowed a comparison of moisture content across horizons and profiles.

Reactive Al and Fe forms were measured by nonsequential extractions using sodium pyrophosphate (Bascomb, 1968) and ammonium oxalate (McKeague and Day, 1966) followed by analysis on inductively coupled plasma atomic emission spectroscopy. Pyrophosphate solution extracts Al and Fe associated with organic matter (Al$_p$ and Fe$_p$). The oxalate solution extracts Al and Fe from organic complexes and short-range order Fe oxyhydroxides, such as ferrihydrite, and aluminosilicates, such as imogolite and allophane (Dahlgren, 1994). Aluminum and Fe associated with inorganic short-range order material (Al$_{sro}$ and Fe$_{sro}$) were calculated as the difference between oxalate and pyrophosphate extracts.

Estimates of Bulk Density

Bulk density was not measured. The large proportion of coarse fragments and small-scale variability makes accurate field determination of forest soil bulk density problematic (Curtis and Post, 1964). Fortunately, bulk density is strongly correlated to soil organic matter, and SOM concentration can be used to obtain estimates of bulk density (Curtis and Post, 1964; Federer et al., 1993; Prevost, 2004; Périé and Ouimet, 2008; Ruehlmann and Korschens, 2009; Baritz et al., 2010). Huntington (1989) observed that pedotransfer functions obtained in different studies are relatively consistent, which supports the estimation of bulk density from organic matter measurement to calculate estimates of SOC stocks.

To estimate bulk density, we used the empirical regression Eq.(1) developed by Heuscher et al. (2005) using 687 samples from the Orthod soil subgroup. The regression Eq.(1) is based on

SOC concentration and depth of horizon and takes into account the increase in bulk density with increasing soil depth caused by overburden.

$$BD = 1.780 - 0.379 \ SOC^{1/2} + 0.00123 \ depth \quad (1)$$

This equation was developed in mineral soil samples and is not appropriate for the organic layer. For the forest floor, we used a pedotransfer function based on the organic density concept developed by Federer et al. (1993) (2):

$$BD = \frac{BD_{min} \times BD_{org}}{SOM \times BD_{min} + (1 - SOM) \times BD_{org}} \quad (2)$$

where BD: soil bulk density
BD$_{min}$: bulk density of pure organic fraction
BD$_{org}$: bulk density of pure mineral fraction
SOC: soil organic carbon concentration
SOM: soil organic matter concentration

For BD$_{min}$ and BD$_{org}$, we used the values reported by Périé and Ouimet (2008) of BD$_{org}$ = 0.11 and BD$_{min}$ = 1.77. These values are in good agreement with other studies conducted in medium- to coarse-textured acid forest soils (Federer et al., 1993; Prevost, 2004). The estimated bulk density averaged 0.15 g.cm^{-3} in the forest floor. This value is within the range of expected values for LFH horizons in Canada of 0.11 to 0.15 g cm^{-3} (Shaw et al., 2005). The average estimated bulk density in mineral horizons ranged from 1.25 g cm^{-3} in the Bf1 horizon to 1.42 g.cm^{-3} in the BC horizon.

Statistical Analyses

All statistical analyses were carried out using SAS 9.2 (SAS Institute Inc., 2008), and all statistical tests were performed with a significance level of 5% ($\alpha \leq 0.05$). We tested for differences between horizons using one-way analyses of variance and compared group means using Student's *t* test, with no provision for multiple inferences (Webster, 2007).

We investigated the relation between SOC and abiotic variables using a factor analysis followed by multiple regression analysis. The purpose of the factor analysis was to orthogonalize the independent variables and thus avoid the problems linked to

TABLE 1. Factor Pattern for Mineral Horizons

	Fsro	**Fp**	**Fmoist**	**Fclay**	**FpH**	**FCN**
pH[†]	0.18	−0.01	−0.07	−0.03	0.97	−0.11
Moist[‡]	0.17	0.21	0.89	0.34	−0.10	−0.01
Al$_p$[§]	0.31	0.85	0.32	0.15	0.05	0.01
Fe$_p$[§]	0.02	0.94	0.19	0.22	−0.05	0.02
CN[‖]	0.07	0.00	−0.01	0.10	−0.10	0.99
Clay[¶]	−0.03	0.15	0.27	0.94	−0.03	0.12
Al$_{sro}$[#]	0.91	0.02	0.24	−0.06	0.27	0.08
Fe$_{sro}$[#]	0.90	0.28	0.15	0.06	0.17	0.10

[†]pH in 0.01 *M* CaCl$_2$.

[‡]Gravimetric moisture content.

[§]Pyrophosphate-extractable Al and Fe.

[‖]Carbon-to-nitrogen ratio.

[¶]% Clay.

[#]Al and Fe associated with inorganic short-range order material, calculated as oxalate-extractable Al and Fe minus pyrophosphate-extractable Al and Fe.

TABLE 2. Factor Patterns for Organic Horizons

	Fmoist	**FpH**	**FAl$_p$**	**FCN**	**FFe$_p$**
pH[†]	−0.03	0.91	0.26	−0.04	0.33
Moist[‡]	0.99	−0.02	0.11	0.02	0.08
Al$_p$[§]	0.13	0.26	0.92	−0.06	0.27
Fe$_p$[§]	0.11	0.34	0.29	−0.07	0.89
CN[∥]	0.02	−0.03	−0.05	1.00	−0.05

[†]pH in 0.01 M CaCl$_2$.

[‡]Gravimetric moisture content.

[§]Pyrophosphate-extractable Al and Fe.

[∥]Carbon-to-nitrogen ratio.

multicollinearity. Factors were obtained by factor analysis based on the correlation matrix followed by equamax orthogonal rotation. The equamax rotation aims to achieve simple factor structure. The objectives of the factor analysis were to obtain a set of factors that (i) were orthogonal, eliminating interpretation problems linked to variable multicollinearity, and (ii) showed a simple structure where each factor only loads on one or two variables, simplifying interpretation. Dimension reduction was not the objective of the factor analysis.

Table 1 shows the correlation between original variables and orthogonal factors used in regression analysis of mineral horizons. Factors were named according to the variables that loaded on them. A separate set of factors was derived for the organic horizons, for which there was no oxalate and percent clay data (Table 2). As shown in Tables 1 and 2, the factor analysis successfully created orthogonal new variables or factors that correlated highly with only one or, in some instances, two related initial variables.

RESULTS AND DISCUSSION

The Soil Profile

Table 3 shows the average characteristics of soil profiles. Soils were coarse textured and acidic, with pH measured in 0.01 M CaCl$_2$, ranging from 3.6 in surface horizons to 4.8 in the mineral subsoil. The depth distribution of elements was characteristic of podzolic soils. The leached Ae horizon had the lowest concentration of SOC, N, and extractable Fe and Al,

TABLE 4. Carbon and Nitrogen Stocks Estimates (Mean ± SEM) in an Average Profile of 100-cm Depth

Profile Portion	Carbon		Nitrogen	
	Average Stock, kg/m^2	Total Stock, %	Average Stock, kg/m^2	Total Stock, %
Entire profile	15.9 ± 1.3	100	0.66 ± 0.06	100
Organic layer	3.6 ± 0.5	23	0.10 ± 0.01	16
Mineral soil	12.3 ± 1.3	77	0.55 ± 0.07	84
Ae	1.1 ± 0.2	7	0.04 ± 0.01	6
Bf1	2.6 ± 0.7	16	0.10 ± 0.03	15
Bf2	3.7 ± 0.6	24	0.18 ± 0.03	28
BC	4.8 ± 0.6	30	0.23 ± 0.03	35
Top 10 cm of profile	4.3 ± 0.3	27	0.13 ± 0.01	21
Top 20 cm of profile	6.1 ± 0.3	38	0.18 ± 0.01	28

which accumulated into the illuviated Bf horizons and to a lesser extent into the BC horizon.

C and N Distribution in the Profile

Table 4 shows estimates of the SOC and N stocks distribution in an average 100-cm-deep profile. Soil organic C and N contents were calculated using SOC and N concentrations, horizon thickness, and estimated bulk density. In the mineral soil, the estimates were adjusted for coarse fragment content assuming a specific gravity of 2.65 g/cm^3.

Estimated C stocks in Roberts Creek soils ranged from 11.7 to 25.1 kg C/m^2, with an average of 15.9 kg C/m^2 or 159 Mg C/ha. These values are generally higher than those reported for inland Canadian forests. Bhatti et al. (2002) reported an average of 10.9 kg C/m^2 in boreal forest soils of central Canada, whereas Bois et al. (2009) reported an average of 2.8 kg C/m^2 in the forest floor and 8.8 kg C/m^2 in the mineral soil of well-drained spruce-fir forests of central British Columbia. The humid climate and high primary productivity of coastal forests may contribute to the relatively high C accumulation in Roberts Creek soils. Previous studies have also reported relatively high C stocks on the coast of Washington and Oregon states compared with inland forests (Smithwick et al., 2002; Homann et al., 2005).

TABLE 3. Sequence of Horizons and Average Characteristics (Mean ± SEM) (N = 9)

Horizon	Thickness[†]	pH$_{CaCl2}$	Texture	SOM[‡]	SOC[§]	N[§]	Clay[∥]	Moisture[¶]	Al$_p$[#]	Fe$_p$[#]	Al$_{sro}$[††]	Fe$_{sro}$[††]
FH	6 ± 1	3.6 ± 0.1	Organic	72.1 ± 4.0	38.1 ± 2.1	1.06 ± 0.07	n/a	0.87 ± 0.10	2.3 ± 1.3	0.7 ± 0.2	0.6 ± 0.2	0.6 ± 0.1
Ae	6 ± 1	3.6 ± 0.1	Sandy loam	2.5 ± 0.1	1.6 ± 0.2	0.06 ± 0.01	3.6 ± 0.4	0.10 ± 0.02	0.6 ± 0.1	0.5 ± 0.1	0.3 ± 0.0	0.2 ± 0.1
Bf1	13 ± 2	4.5 ± 0.1	Sandy loam	4.0 ± 0.4	2.2 ± 0.3	0.09 ± 0.01	5.5 ± 0.5	0.13 ± 0.01	2.9 ± 0.3	1.6 ± 0.2	5.6 ± 0.8	2.5 ± 0.3
Bf2	30 ± 4	4.8 ± 0.1	Loamy sand	3.5 ± 0.4	1.6 ± 0.2	0.08 ± 0.01	5.2 ± 0.6	0.13 ± 0.01	2.3 ± 0.5	1.2 ± 0.3	6.1 ± 1.2	2.0 ± 0.3
BCg	37 ± 6	4.7 ± 0.1	Loamy sand	2.8 ± 0.3	1.4 ± 0.2	0.07 ± 0.01	4.9 ± 0.7	0.13 ± 0.02	2.3 ± 0.4	1.1 ± 0.4	5.3 ± 0.7	1.9 ± 0.2
Cg	n/a	4.8 ± 0.1	Loamy sand	2.1 ± 0.3	0.9 ± 0.1	0.04 ± 0.01	3.7 ± 0.7	0.09 ± 0.01	1.8 ± 0.3	0.9 ± 0.3	5.3 ± 0.4	2.0 ± 0.1

[†]Thickness of horizons in centimeters.

[‡]Soil organic matter (SOM) concentration, expressed as mass percentage.

[§]Soil organic carbon and nitrogen concentration, expressed as mass percentage.

[∥]Clay concentration (<2μm), expressed as mass percentage.

[¶]Gravimetric moisture content expressed on oven-dried soil basis.

[#]Organically complexed (pyrophosphate-extractable) iron and aluminum concentration (g/kg).

[††]Iron and aluminum associated with short-range order inorganic material, calculated as the difference between oxalate and pyrophosphate extracts (g/kg).

Despite its high SOC concentration (38%; Table 3), the organic layer only accounted for about one fourth of the C stock in Roberts Creek soils. Most SOC was found in the mineral soil (12.3 kg C/m^2 on average). The first podzolic horizon Bf1 had the highest C concentration of the mineral soil and stored twice as much C as the A horizon, but its contribution to the total SOC stock was eclipsed by the contribution of the deeper horizons Bf2 and BC. Although the SOC concentration in these horizons was lower, their thickness resulted in a C store of more than one half of the total SOC present in the profile.

The N stocks generally followed a depth distribution pattern similar to C stocks (Table 4). The main difference was that the forest floor stored relatively less N (only 16% of total N stocks), whereas deeper mineral horizons (Bf2 and BC) stored relatively more N (two thirds of total N stock).

It has previously been proposed that temperate to boreal forests store most of their SOC in the forest floor and/or the topmost mineral horizon (Jenny, 1950). When considering the humid temperate forest subset, Jobbágy and Jackson (2000) reported that 54% of SOC on average is stored in the upper 20 cm of the profile. The comparatively small proportion of SOC accounted for by the forest floor and top mineral horizons in Roberts Creek may be an indication of effective translocation of organic matter to the mineral subsoil through roots and illuviation (Sanborn and Lavkulich, 1989; Buurman and Jongmans, 2005). Mixing by soil animals was not an important process, as evidenced by the low organic carbon concentration in the A horizon and the mor humus type.

Studies of SOC commonly focus on the upper 10 to 20 cm of the soil profile (e.g., Covington, 1981; Olsson et al., 1996; Tremblay et al., 2006; Kranabetter, 2009). In our soils, such studies would have much reduced interest and significance because they would account for less than one half of our SOC stocks and less than one third of N stocks.

Because bulk density was estimated from depth and SOM concentration rather than being directly measured, the C and N stocks reported here are subject to some errors. De Vos et al. (2005) reviewed the predictive quality of 12 models for bulk density estimation and found that all models produced underestimates of field bulk density. Underestimation error was up to 9% to 36% (Boucneau et al., 1998; De Vos et al., 2005). It is, thus, likely that the estimates of C and N presented here are conservative estimates.

SOM and Size Fractions

Size fractionation is useful for separating SOM pools with different biogeochemical characteristics, functions, and dynamics (Anderson et al., 1981; Kögel-Knabner et al., 2008; Xu et al., 2009). Table 5 shows the distribution of SOM in sand, silt, and clay size fractions of the mineral soil.

Organic matter associated disproportionally with the clay fraction. The clay fraction only represented 5% of the soil but
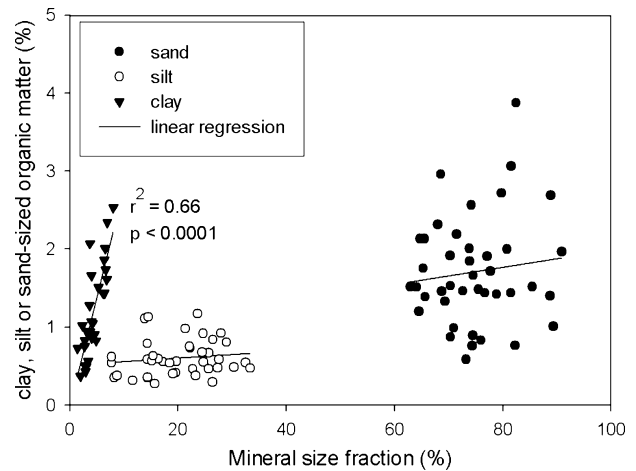
FIG. 2. Correlation of organic matter size fractions with corresponding mineral size fractions. The r^2 and *P* value represent the linear regression between clay-sized organic matter and percent clay. Regressions for sand- and silt-sized organic matter are not significant.

accounted for one third of the organic matter pool. This may be caused by the fact that a major pathway for SOC to enter the mineral soil in Podzols is via dissolved organic matter precipitating on reactive mineral surfaces (Kaiser et al., 2002; Rumpel et al., 2004; Kalbitz and Kaiser, 2008).

We found a strong correlation between clay-sized SOM and percent soil clay, whereas sand- and silt-sized organic fractions showed only a weak correlation with soil clay and no correlation with sand- and silt-sized fractions (Fig. 2). This indicates that interactions between mineral and organic fractions were largely restricted to clay-sized material (Zinn et al., 2007). Clay-sized SOM is likely to be stabilized by sorption to clay phases, whereas particulate organic matter accumulation mechanisms seem largely independent of the mineral phase (Kaiser et al., 2002).

The last column of Table 5 gives the ratio of clay-sized SOM to clay (SOM_{clay}:clay). The ratio was relatively constant, averaging 21.6 g SOM/100 g clay. This may suggest that a given amount of clay stabilizes a generally fixed amount of clay-sized organic matter, and that the clay fraction is saturated with organic matter (Six et al., 2002). A consequence of this hypothesis is that additional inputs of organic matter would only accumulate in labile soil C pools with a relatively fast turnover rate (Gulde et al., 2008).

An exception to the constant SOM_{clay}:clay ratio may occur in Bf1, where this ratio is slightly higher (albeit not significantly so) than in other horizons. The Bf1 horizon is rich in free Fe and Al and SRO material (Grand and Lavkulich, 2008), with a greater capacity for SOM stabilization (Torn et al.,

TABLE 5. Soil Texture and Association of SOM With Different Size Fractions (Mean ± SEM)

	Sand	Silt	Clay	SOM Fraction Associated With Sand	SOM Fraction Associated With Silt	SOM Fraction Associated With Clay	Clay-Sized SOM:Clay Ratio
	--g/100 g mineral soil--			---------------------------g/100 g OM---------------------------			g/100 g clay
Ae	69 ± 2	27 ± 2	3 ± 0	57 ± 3	17 ± 1	26 ± 3	20 ± 1
Bf1	75 ± 2	20 ± 2	5 ± 1	54 ± 2	16 ± 1	30 ± 2	24 ± 3
Bf2	76 ± 3	20 ± 3	5 ± 1	48 ± 5	17 ± 1	35 ± 6	21 ± 2
BC	78 ± 3	17 ± 2	5 ± 1	51 ± 4	17 ± 2	32 ± 4	22 ± 3
Overall	75 ± 1	20 ± 1	5 ± 0	51 ± 2	17 ± 1	31 ± 2	22 ± 1

TABLE 6. C Ratios

Horizon	C:SOM, %	C:N	C:Al$_p$	C:Fe$_p$	C:(Al+Fe)$_p$	Al:(Al+Fe)$_p$, %
FH	53.0 ± 1.2 b	36.2 ± 1.1 a	359.9 ± 63.8 a	948.6 ± 208.6 a	253.9 ± 44.7 a	72.0 ± 3.0 a
Ae	60.3 ± 4.4 a	29.3 ± 2.4 b	33.7 ± 4.1 b	46.5 ± 12.0 b	18.8 ± 2.9 b	55.4 ± 2.5 c
Bf1	55.2 ± 3.2 b	27.4 ± 2.1 b	7.7 ± 0.6 c	15.0 ± 2.0 c	5.0 ± 0.4 c	65.2 ± 2.4 b
Bf2	45.3 ± 3.7 c	22.2 ± 2.1 c	7.3 ± 0.5 c	17.8 ± 2.4 c	5.1 ± 0.5 c	69.1 ± 2.5 ab
BC	46.3 ± 2.2 c	22.5 ± 1.6 c	6.0 ± 0.4 c	18.7 ± 3.8 c	4.7 ± 0.4 c	71.5 ± 2.3 a

Means are given ± SEM and are not significantly different between horizons at the 0.05-level if followed by the same letter.

1997; Basile-Doelsch et al., 2007). The maximum amount of organic matter that may be stabilized in Bf1 could thus increase (Six et al., 2002).

These results are based on loss on ignition. As a result, clay-sized SOM fraction may be overestimated because of dehydration of clays, but the error cannot explain the overwhelming association of SOM with clay. Despite the very coarse texture of Roberts Creek soils, organo-mineral interactions in the clay fraction seem to have a major influence on SOC accumulation.

C:N and C:SOM Ratios

The C:N and C:SOM ratios are indicators of the composition of SOM. The C:N ratio was generally wide (Table 6), reflecting the low nitrogen content of coniferous litter (McGroddy et al., 2004) and relatively slow transformation of organic matter. The C:N ratio was highest in the FH layer, with an average of 36, and decreased with depth to reach a value of 22 in lower horizons. This indicates that the organic matter at depth showed a higher degree of transformation (Norris et al., 2011).

Soil organic matter contained 49% of organic C on average (Table 6), yielding a conversion factor between values of SOC and SOM of 2.080. The C concentration of organic matter varied significantly with depth, ranging from approximately 60% in Ae to approximately 45% in deep mineral horizons. This precludes the use of any single Van Bemmelen-type factor to convert between SOM and SOC.

Organic matter of the Ae horizon had a significantly higher C concentration than adjacent horizons (Table 6). This indicates that organic matter dynamics in the Ae horizon is different from lower horizons and supports the proposition of Rumpel et al. (2004), who suggested that Podzols act as "chromatographic systems." In a chromatographic system, the A-horizon preserves

long-chain alkyl structures with a hydrophobic tendency. Small, highly oxidized, polar organic compounds are preferentially removed by leaching and are retained in illuvial horizons by adsorption onto Al and Fe soil minerals (Eusterhues et al., 2003). Accordingly, the illuviated horizons of Roberts Creek Podzols showed a lower C:SOM ratio than the Ae horizon.

Pyrophosphate-Extractable Fe and Al

Pyrophosphate-extractable Al and Fe showed a strong correlation with SOC in the mineral soil (Fig. 3), indicating that Fe$_p$ and Al$_p$ are strongly associated with SOM and that poorly crystalline hydroxide phases are unlikely to have contributed significantly to the pyrophosphate extracts (Kaiser and Zech, 1996). In view of the literature, the strength of the correlation observed between Al$_p$ or Fe$_p$ and organic C also suggests that stabilization and accumulation of organic matter are promoted by organically bound Fe and Al (Zanelli et al., 2006; Egli et al., 2008).

As expected in the organic layer, the relationship between C and pyrophosphate-extractable metals was weak. Contrary to what was observed in the mineral horizons, the correlation was negative (Fig. 4), indicating that in the FH layer, the amount of metals available to form complexes with humus was limiting; samples high in organics and with a low mineral content resulted in the formation of fewest organo-mineral complexes.

The negative correlation between pyrophosphate-extractable metals and SOC in the organic soil was more pronounced for Fe$_p$. Although the slopes of the regression lines were similar for both metals ($P = 0.80$ in Wilk's λ multivariate test), the regression line associated with Al$_p$ was not statistically significant because of the presence of high Al$_p$ outliers (Fig. 4). This suggests that there may be a mechanism for upward translocation of some Al into the FH horizon.
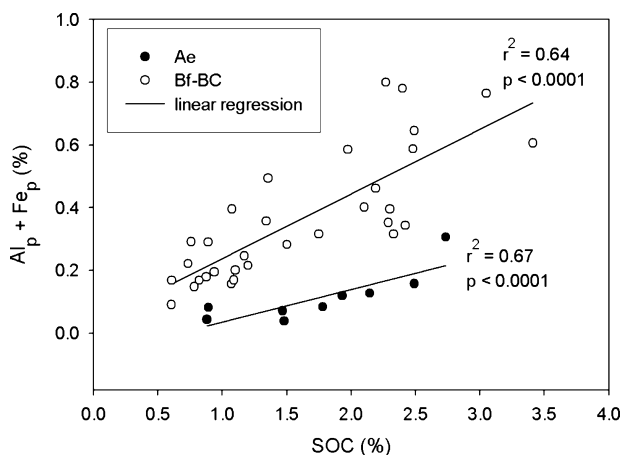

FIG. 3. Relation between soil organic carbon (SOC) and (Al + Fe)$_p$ in the mineral soil. Similar relations are observed for Al$_p$ and Fe$_p$.
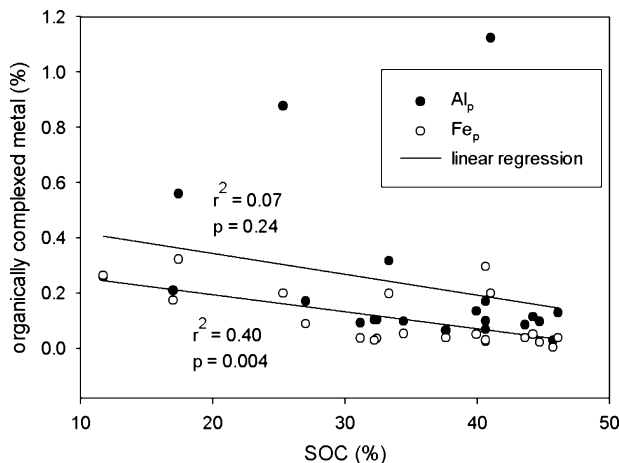

FIG. 4. Relation between soil organic carbon (SOC) and Al$_p$ and Fe$_p$ in the FH layer.

TABLE 7. Regression Results Summary for Mineral Horizons Showing Significant Independent Variables and the Associated Coefficients

Dependent Variable	% SOC
Independent Variables	**Fsro, Fp, Fmoist, Fclay, FpH, FCN**
Model R^2 and Significance	**$R^2 = 0.76$, $P < 0.0001$**
Significant Factors ($\alpha = 0.05$)	**Coefficient**
Intercept	1.77
Fp	0.62
Fmoist	0.35
Fsro	0.32
Fclay	0.20
FpH	−0.19
FCN	0.10

Further support for upward translocation of Al into FH was found by examining the proportion of Al in $(Al + Fe)_p$ (Table 6). In the mineral horizons, the contribution of Al_p to $(Al + Fe)_p$ increased with depth. This is caused by the increase in pH with depth. Jansen et al. (2003) showed that at pH 3.5, dissolved "free" Al dominates, whereas at pH 4.5, Al-SOM complexes were more common. Complexation of Fe and SOM is independent of pH (Nierop et al., 2002; Jansen et al., 2003), and as a result, at low pH, SOM-Fe complexes should be more abundant than at high pH.

Despite the low pH (3.6), the proportion of Al_p averaged 72% in the forest floor, a value significantly higher than the top mineral horizons. This suggests the existence of a mechanism for Al enrichment of the FH horizon. Lundström et al. (2000) and Smits and Hofflands (2009) suggested that ectomycorrhizal fungi may play a role in upward transport of Al into organic horizons of Podzols. Whether a similar mechanism is at work in Roberts Creek soils deserves further investigation.

Table 6 shows that both $C:Al_p$ and $C:Fe_p$ tended to narrow with depth. This trend was more pronounced than the narrowing of C:N ratio, suggesting that metal enrichment is an active process. The C:metal ratios have been used to estimate the degree of Al and Fe saturation of humus (Matus et al., 2006). The $C:Al_p$ and $C:Fe_p$ ratios were high in the FH layer, suggesting that organic matter complexation sites were not saturated with metals. These ratios decreased to intermediate values in the Ae horizon. In the Bf-BC horizons, the $C:Al_p$ and $C:Fe_p$ ratios were comparatively low. The $C:Al_p$ ratio was consistently less than 10, suggesting that organic matter is very insoluble (Skjemstad, 1992). It is likely that in these horizons, the formation of Al-SOM complexes played a role in the precipitation of dissolved organic matter and accumulation of stable SOM (Scheel et al., 2007). The $C:(Al + Fe)_p$ ratio was low (around 5) and relatively constant in illuvial horizons (Table 6), suggesting that humus-metal complexation may have reached a maximum in the subsoil and that most organic complexation sites are occupied.

Predictors of SOC

We investigated the relationship between SOC and other soil variables using multiple regression analysis. Soil variables included pH, C:N ratio, percent clay, moisture, Al and Fe associated with SRO inorganic material, and organically complexed Al and Fe. To avoid problems arising from multicollinearity in soil variables, we performed a factor analysis before multiple regression analysis (Kadono et al., 2009). The regression analysis was based on the orthogonal factors.

The factor analysis was based on the correlation matrix so factors are standardized, meaning that the regression coefficients can be directly interpreted for sign and magnitude. The simple factor structure displayed in Tables 1 and 2 allows us to confidently extend results obtained for factors to corresponding initial variables. In the following discussion, the term *variable* refers to the initial variables, whereas *factor* refers to the new set of variables constructed during factor analysis.

Mineral Horizons Results

Regression results and factors significant at the $\alpha = 0.05$ level in a *t* test based on type III sum of squares are shown in Table 7. All factors entered in the model were significant at the $\alpha = 0.05$ level, suggesting that all of the associated variables have an effect on SOC.

The Fp was the most important predictor of SOC (Table 7). The Fp represents a linear combination of Al_p and Fe_p, with minor contributions from other variables (Table 1). This indicates that organically complexed Al and Fe were major determinants of SOC. The coefficient was positive, suggesting that Al_p and Fe_p have a stabilizing influence on SOC, in agreement with the literature (Skjemstad, 1992; Rasmussen et al., 2006; Scheel et al., 2007). The coefficient of Fsro was also positive (Table 7) and similarly suggests that Fe and Al associated with inorganic SRO material contributed to SOC accumulation (Eusterhues et al., 2005; Kleber et al., 2005; Mikutta et al., 2005). The Fclay was also a significant predictor of SOC, even in the presence of Fp and Fsro. This suggests that crystalline clays played a role in organic matter accumulation.

Other factors that correlated significantly with SOC include Fmoist, FCN, and FpH (Table 7). Excess moisture can impede microbial activity and decrease SOM decomposition. However, Roberts Creek soils are coarse and well drained, and aeration is not believed to be a limiting factor of SOM decomposition in the solum. The positive correlation between SOC and moisture is better explained by the water retention capacity of SOM.

The main function of FpH and FCN in the model was to differentiate between horizons. These factors were not significant when regression analysis was applied to any individual horizon. The coefficient associated with FpH was negative, and the one associated with FCN was positive, indicating that horizons high in organic matter had a low pH and a high C:N ratio.

Organic Layer Results

The FFe_p and FCN were the only significant factors at the $\alpha = 0.05$ level (Table 8), indicating that moisture, pH, and Al_p were not important predictors of SOC in the organic layer. The FFe_p was the most significant factor in the regression, but contrary to what was observed in the mineral horizons, the

TABLE 8. Regression Results Summary for the Organic Layer Showing Significant Independent Variables and the Associated Coefficients

Dependent Variable	% SOC
Independent Variables	**FFe_p, FAl_p, Fmoist, FpH, FCN**
Model R^2 and Significance	**$R^2 = 0.42$, $P = 0.006$**
Significant Factors ($\alpha = 0.05$)	**Coefficient**
Intercept	34.39
FFe_p	−5.40
FCN	3.39

coefficient was negative. As previously mentioned, this indicates that in the organic layer, the amount of Fe available for adsorption by SOM was limited. This can be thought of as a dilution effect, where larger amounts of SOM cause a dilution of the Fe_p pool. The Al_p did not show the same negative correlation with SOC as Fe_p, possibly because of the mechanism for upward translocation of Al into the FH layer previously discussed.

The coefficient associated with FCN was positive, meaning that samples high in SOM had a wide C:N ratio. Wide C:N ratios are generally associated with low degrees of decomposition, and as mineralization progresses, C:N ratios typically narrow as C is lost to the atmosphere. This suggests that FH samples with high SOC tended to have large amounts of fresh undecomposed organic matter.

The relatively low importance of pH and moisture as a determinant of SOC accumulation between profiles may be the result of the narrow range of environmental conditions covered in this study, where all soils are well drained, highly leached, and acidic.

Implications for SOC Retention and Pedogenesis

Determinants of SOC Retention

Roberts Creek soils have a coarse texture and few aggregates. Stabilization caused by physical protection by aggregates is likely to be limited. As a result, sorption of SOC to mineral surfaces and metals is likely to play an important role in SOM retention and stabilization (Baldock and Skjemstad, 2000; Eusterhues et al., 2005).

Organically complexed metals, SRO inorganic phases, and clay content were all identified as significant predictors of SOC by regression analysis, suggesting that these three matrix components contribute to SOC retention. Taken together, they explained 58% of the total variance in SOC concentration. Both Forg and Fsro were much stronger predictors of SOC than Fclay. This agrees well with the weight of published evidence, which shows the prevailing role of reactive Al and Fe phases for controlling SOC storage (Torn et al., 1997; Kleber et al., 2005; Mikutta et al., 2005; Kothawala et al., 2009). It can be concluded that poorly crystalline phases and polyvalent metals are largely responsible for mineral-mediated SOC retention in Roberts Creek. Crystalline clay minerals may be significant for SOC retention in the Ae horizon, where the amount of reactive Al and Fe phases is limited (Eusterhues et al., 2003).

The coefficient associated with Fsro was roughly one half of the coefficient associated with Fp, indicating that organically complexed Al and Fe were stronger predictors of SOC than SRO inorganic material. However, our data do not allow for an assessment of the relative role of organic-metallic interactions and SRO phases for SOC storage. We only measured total SOC, which is not necessarily a good indicator of organic matter stability. Kadono et al. (2009) partitioned soil C into a potentially mineralizable and recalcitrant pool and showed that oxalate-extractable metals correlated only with recalcitrant soil C. Therefore, SRO inorganic material could be a major determinant of SOC recalcitrance and stability while showing a moderate correlation to total SOC. When regression analyses are conducted on individual horizons, the coefficient associated with Fp decreased with depth, whereas the coefficient associated with Fsro increased, suggesting that the significance of inorganic SRO material for SOC stabilization increases with depth.

C Saturation and Podzolization

Because Al and Fe pools are highly dynamic in Podzols, the concept of soil's protective capacity or of C saturation (Six

et al., 2002; Gulde et al., 2008) may need to be revisited. The C saturation concept implies that the mineral phase has a maximum sorptive or protective capacity (Baldock and Skjemstad, 2000). Once that capacity is reached, additional dissolved organic carbon will not be retained. Because large amounts of Al and Fe are continually translocated from the upper part of the profile to the illuvial horizons, pedogenically active Podzols may not have a fixed C sorptive capacity (Kalbitz and Kaiser, 2008). Instead, the potential for organo-mineral associations may fluctuate with time, depending on weathering rates and the strength of the eluviation/illuviation processes.

In Roberts Creek, there are indications that the eluviation/illuviation balance indeed fluctuates following changes in environmental conditions. Grand (2011) found that the SOM concentration, organically-complexed metals, and SRO inorganic materials concentrations were all significantly higher in Bf horizons of harvested plots than in undisturbed plots. Possible causes included an increase in effective precipitation and the effect of large additions of fresh organic matter to the litter layer as logging slash. Longer term changes in environmental conditions, such as climate change, have the potential to permanently alter the illuviation steady state condition and to affect the potential for SOM protection by interaction with Al and Fe phases.

CONCLUSIONS

C Amount and Distribution

This article estimated the amount and distribution of SOC in a coastal forest of British Columbia. The average soil profile stored approximately 15.9 kg C/m^2, which is generally higher than SOC stocks estimated for inland Canadian forests. The humid climate and high primary productivity of coastal forests may contribute to the relatively high SOC accumulation.

The organic layer (LFH) only accounted for about one fourth of the C stock. The upper 10 cm of the profile stored less than one third of SOC, whereas the upper 20 cm stored about 40%. The relatively small proportion of SOC accounted for by the forest floor and top mineral horizons may be an indication of effective translocation of organic matter to the mineral subsoil through roots and illuviation. Field studies restricted to the upper part of the soil profile would have much reduced interest and significance because they would overlook a major portion of SOC stocks.

Despite the coarse texture, organic matter associated overwhelmingly with the clay fraction. The clay fraction represented less than 5% of the fine earth fraction but contained 32% of SOM and is likely to have a disproportionate influence on SOM accumulation.

Predictors of SOC

This study identified the most important predictors of SOC in soils of Roberts Creek using a factor analysis followed by multiple regression analysis. This approach was successful as the orthogonalization step eliminated the problem of model instability because of variable multicollinearity. It produced easily interpretable regression equations that respected correlations present between SOC and the original untransformed variables.

Processes determining SOC concentration were very different in the organic layer and mineral horizons. In the organic layer, Fe_p correlated negatively with SOC, indicating that the amount of Fe available for adsorption by SOM was limited. The Al_p did not show the same negative association, probably because of a mechanism for upward translocation of Al into the FH horizon and possibly involving ectomyccorhizal fungi.

Given the importance of Al in soil processes, including organic matter retention, studies establishing the exact role of fungi in Al translocation would be of great interest.

In the mineral horizons, clay content, organically complexed Al and Fe, and SRO inorganic material were significant predictors of SOC, pointing to a mineral control of SOM retention. The most important determinants of SOC were reactive Al and Fe forms. Because Al and Fe are dynamic components being continually translocated to the illuvial horizons, the potential for OM stabilization may not be a fixed soil property but should fluctuate as a result of short-term disturbance or long-term global change. The consequences for SOM retention should be investigated.

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