

Metal complexation of humus and horizon differentiation in Andisols and Spodosols

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Abstract

From tephra, not only Andisols, but Spodosols can also be formed depending on changes in the soil formation factors. In Andisols, the *in situ* accumulation of humus in the A horizon and that of the active Al and Fe in the A and Bw horizons are the major soil formation processes, whereas in Spodosols, the eluviation and illuviation of organic matter (OM), Al and Fe are predominant. Among the soil characterization data, the pyrophosphate-extractable Al (Al_p), cation exchange capacity (CEC) and organic carbon (OC) content were selected in order to examine the similarities and differences in metal complexation and related properties of these soils. The A horizon soils of the Andisols and the Bh-Bhs and Bs horizon soils of the Spodosols derived from tephra (SPT) and those derived from nontephra deposits (SPN) are similar in their Al_p/OC ratios suggesting that the metal complexation of humus is a property common to these horizons. In contrast, the Al_p/OC ratio of the E horizon soils in the SPT and SPN was significantly lower than those in the Bh-Bhs and Bs horizon soils of the SPT and SPN and the A and Bw horizon soils of the Andisols. Furthermore, the CEC in these E horizon soils did not exceed those in the other horizon soils. These results indicate that the static OM in the E horizons has less total carboxyl groups, including both the complexed and free ones, than that in the other horizons. Recent information on the SPN formation was applicable to the SPT according to their soil characterization data.

Introduction

Metal complexation is one of the factors affecting the stabilization of organic matter (OM) in soil (Wada

and Higashi, 1976; Shoji et al., 1993; Kögel-Knabner et al., 2008). The stabilization of OM contributes to sequestering C in soil. Nutrient release through mineralization of OM for plants and microorganisms in the soil is also affected by metal complexation (Olk 2006; Olk and Gregorich, 2006). Soluble OM enhances translocation of the metallic elements in the soil whereas insoluble OM fixes heavy metals in the soil. Polyvalent cations are effective in precipitating OM (Adachi, 2003). Other important roles of OM in the soil are the sorption of hydrophobic organic chemicals, keeping the soil's physical, chemical and biological properties in good conditions, etc.

In Andisols (AND), abundant humus is accumulated in their A horizons (Fig. 1) and is mostly immobile (Torn et al., 1997; Huang, 2004) at least for the past thousands of years as demonstrated by multi-sequal soil profiles. One of the interpretations for the high stability of humus in AND is the complexation with Al (Wada and Higashi, 1976). The approximate chemical formula of the Al-humus complex in the A horizon of AND was proposed to be $\{C_{36}(COO[Al]_3COO\}_n$ (Nanzyo and Shoji, 1993).

Under humid and appropriately cold soil environments, functions of the dissolved organic materials (DOM) that are biologically produced are strongly expressed and Spodosols (Fig. 1) are formed (van Breemen et al., 2000). Spodosols show a strong horizon differentiation resulting from the translocation of the humus, Al and Fe from the upper horizons and their accumulation in the underlying spodic horizons (Lundström et al., 2000a). Detailed studies were carried out to understand the Spodosol formation processes in Nordic countries (Lundström et al., 2000b). Although it is common that AND form on tephra de-

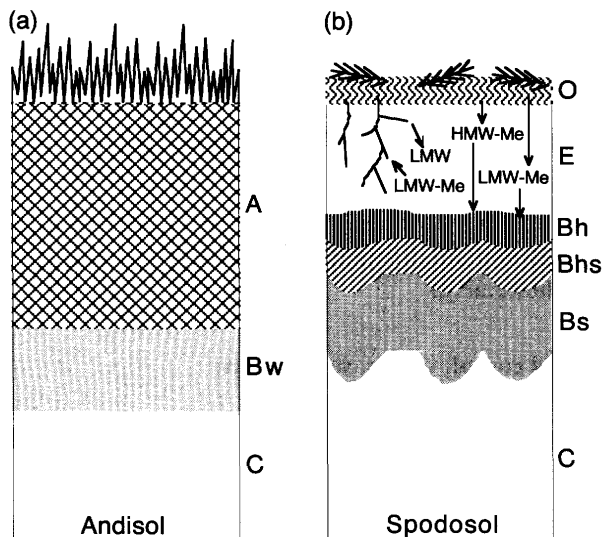


Fig. 1. Schematic diagram showing profiles of Andisol (a) and Spodosol (b). LMW represents low molecular weight organics of less than 1 kD and HMW represents high molecular weight organics of 1 kD or more. Mycorrhizal fungi releases LMW, dissolves metallic ions (Me) and translocates LMW-Me complexes (Lundström *et al.*, 2000b).

posits in a humid climate, Spodosols can also form on tephra during cold and humid climatic conditions. Ito (1994) described the characteristics of tephra-derived Spodosols (SPT) as a high OM content, frequent occurrence of Humods and occurrence of one or more E horizons in a pedon. The E horizon soils of SPT contain scarce allophane and tend to be thinner (about 5 cm) and darker than those of Spodosols derived from nontephra deposits (SPN).

The objectives of the present study were (i) to compare the degree of complexation between the metal and humus in different soil horizons of AND, SPT and SPN, and (ii) to discuss the differences in properties among these soil horizons based on recent researches (Lundström, *et al.*, 2000b; Kögel-Knabner *et al.*, 2008; von Lützwow *et al.*, 2008).

Materials and methods

Several sets of soil characterization data were used to compare the properties of 8 horizon soils that are A and Bw horizon soils of AND, and the E, Bh-Bhs and Bs horizon soils of SPT and SPN. They are from the Andisols TU database (Shoji *et al.*, 1993), a database by the Kurobokudo Cooperative Research Group (Wada, 1986), the tour guide of the Ninth International Soil Classification Workshop (SMSS and Japanese

Committee, 1987), the database on SPT (Ito, 1994), the tour guide of the Fifth International Soil Correlation Meeting (SCS-USDA, 1988a), the narrative pedon description and primary characterization data of Alaska soils (SCS-USDA, 1988b), and three Spodosols from Nordic countries (Karlton *et al.*, 2000).

Based on these data sets, the soil horizon data were classified into 8 groups according to their soil order, parent materials and horizon designation as shown in Table 1. They are the A and Bw horizon soils of AND, and the E, Bh-Bhs and Bs horizons soils of SPT and SPN. These data include buried horizons but the uppermost A horizons were excluded from the A horizon soils of AND in order to reduce the effect of fresh OM. The Bh and Bhs horizons were combined in one group as Bh-Bhs. The uppermost Bs horizon soil was used from the 3 Nordic pedons as each Bs horizon had several subdivisions (Karlton *et al.*, 2000). In order to examine the metal complexation of OM, the OC content, pyrophosphate-extractable Al (Al_p) and Fe (Fe_p) were obtained from these data sets. The OC content in the fine earth fraction of the air-dried soils was determined by the dichromate method (Ping *et al.*, 1989) or the dry combustion method (Shoji *et al.*, 1993). Al complexed with humus is best evaluated as Al_p (Dahlgren, 1994). In addition to Al_p , Fe_p was also used to evaluate the Fe complexed with humus in the SPT and SPN although oxalate-extractable Fe is mostly ferrihydrite in the AND (Child, 1991). Logarithmic class intervals were used for the histogram construction to cover the widespread data. In order to examine the relationships between the OC and cation exchange capacity (CEC), the soil horizon data were grouped into 15 classes according to the index cation used to determine the CEC, soil orders, parent materials and horizon designation as shown in Table 2.

Results and Discussion

1. Frequency distribution of OC content

Accumulation of abundant OC ranging between 10 and 200 g C kg⁻¹ is an outstanding characteristic of the A horizons in AND. A similar amount of OC (40 - 230 g C kg⁻¹) is also accumulated in the Bh-Bhs horizons of SPT as shown in Fig. 2. A large amount of OC is also accumulated in the Bh-Bhs horizons of SPN although it is less than that in SPT. Thus, all of these horizons show high OC contents in spite of the fact that their genetic processes are not the same.

Table 1. Collected soil horizon data to examine metal complexation.

Soil order	Locations of pedons	Horizon designation ^{*1}	Number of pedons	Number of horizons	References
Andisols	Alaska,	A ^{*2}	33	85	Shoji et al. (1993)
	Northeastern Japan	Bw	33	61	
Spodosols (formed on tephra)	Alaska,	E	37	48	Ito (1994), Shoji et al. (1993), Shoji and Yamada (1991)
	Northeastern	Bh, Bhs	30	52	
	Japan	Bs	36	64	
Spodosols (formed on nontephra)	New England,	E	8	9	Shoji and Yamada (1991), SCS-USDA (1988a,b), Karlton et al. (2000)
	Nordic	Bh, Bhs	5	8	
	countries	Bs	10	17	

*1: Buried horizons were included.

*2: Uppermost A horizons were excluded to reduce the effect of fresh plant residues.

Table 2. Soil horizon data collected for examining relationships between OC and CEC.

Index cation	Soil order	Locations of pedons	Horizon ^{*1} designation	Number of pedons	Number of horizons	References
NH ₄ ⁺	Andisols	Kanto to Hokkaido	A ^{*2}	13	34	SMSS-USDA and Jpn Committee (1987)
			Bw	12	25	
	Andisols	Kyushu to Hokkaido	A ^{*2}	25	77	Wada, 1986
			Bw	18	33	
	Spodosols (formed on tephra)	Alaska, Northeastern Japan	E	21	33	Ito (1994), Shoji et al. (1993), Shoji and Yamada (1991)
			Bh, Bhs	19	32	
			Bs	23	51	
	Spodosols (formed on nontephra)	New England, Nordic countries	E	8	8	Shoji and Yamada (1991), SCS-USDA (1988a,b), Karlton et al. (2000)
Bh, Bhs			7	9		
Bs			7	16		
Ca ²⁺	Andisols	Alaska, Northeastern Japan	A ^{*2}	33	85	Shoji et al. (1993)
			Bw	33	61	
	Spodosols (formed on tephra)	Alaska, Northeastern Japan	E	8	14	Shoji et al. (1993)
			Bh, Bhs	3	8	
			Bs	9	14	

*1: Buried horizons were included.

*2: Uppermost A horizons were excluded to reduce the effect of fresh plant residues.

OM in the A horizons of AND accumulates *in situ* whereas OM in the Bh-Bhs horizons of SPN translocate from the overlying horizons. OM in the Bh-Bhs horizons of SPT may partly be a combination of OM translocated from overlying horizons and that previously accumulated in the buried soil because SPT has sometimes two or more E horizons.

The OC contents in the Bs horizons of SPT and SPN are lower than those in the Bh-Bhs horizons

(Fig. 2) and the OC content in the Bh-Bhs and Bs horizons of SPN tends to be lower than that of SPT. The OC content in the Bw horizons of AND tend to be even lower than those in the Bs horizons of both SPT and SPN. Thus, translocation of OM from the A to Bw horizons, if any, is less than the OM illuviation in the Bs horizons of SPT and SPG.

The biggest difference in the OC content was found in the E horizons between SPT and SPN. The OC

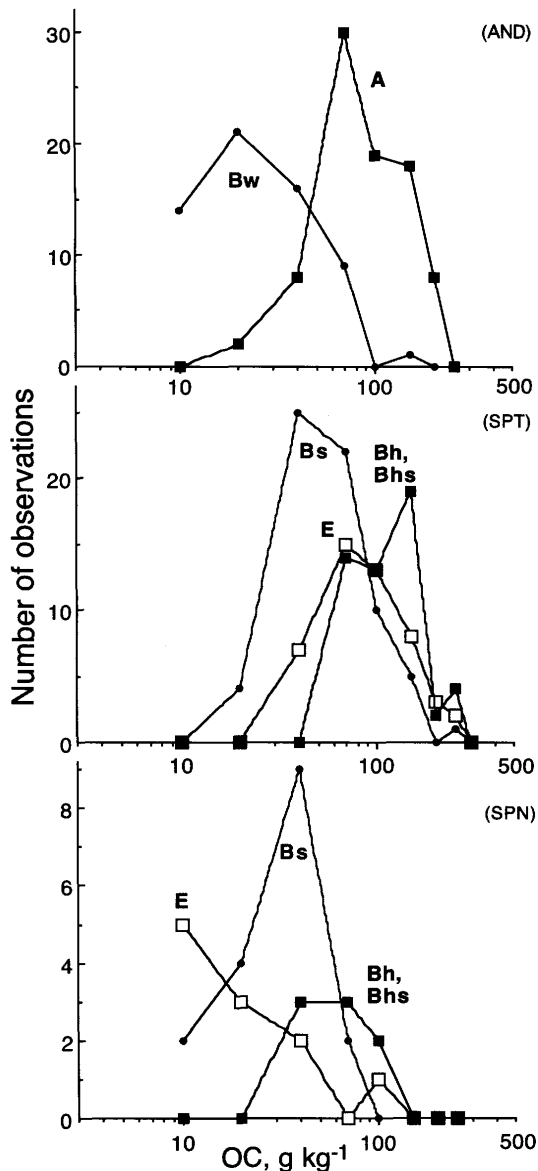


Fig. 2. Frequency distribution of organic C (OC) content in the A and Bw horizon of Andisols (AND), E, Bh-Bhs and Bs horizon of Spodosols derived tephra (SPT) and those derived from nontephra (SPN). For example, a plot at 20 g kg^{-1} shows the number of observations for $10 < \text{OC} \leq 20 \text{ g kg}^{-1}$.

content in the E horizons of SPT is much higher than that of SPN as Ito (1994) stated. The OC content in the E horizon of SPT is similar to that in the Bh-Bhs horizons of SPT and also to that in the A horizons of AND. The total dissolved OC content of the 3 SPN pedons in Nordic countries (van Hees, et al., 2000) ranged between 4 and 9 mmol L^{-1} . As the content of the readily mobile OC is calculated to be 0.018 and 0.078 g kg^{-1} , postulating a water content is 500 g kg^{-1} , the OC in the E horizons is mostly static.

2. Relationship between OC and Al_p

The Al_p content shows Al complexed with humus although the content is changeable with pH (Wada and Okamura, 1980; Takahashi et al., 2006). A linear relationship between the OC and Al_p was recognized for the A horizon soils of AND (Fig. 3) as previously reported by Wada and Higashi (1976) and Shoji et al. (1993). However, the same plots for the SPT (Fig. 4) and SPN (Fig. 5) were more scattered than those for AND in spite of the fact that the O horizons were excluded from these plots. Among the plots for E, the Bh-Bhs and Bs of SPT and SPN, the plots for the Bs horizon soils are relatively linear distributed. In contrast, the plots for the E and Bh-Bhs horizon soils showed broad scattering and those for the E horizon soils of both SPT and SPN were in the low Al_p area (Figs. 4 and 5, Ping et al., 1989; Shoji and Yamada, 1991). The plots for the Bh-Bhs horizon soils were distributed in the wide range between those for the Bs and E horizon soils. It was suggested from Figs. 4 and 5 that there is an upper limit in the Al_p/OC ratio.

In order to compare the degree of Al complexation in OM among the 8 groups of soils (E, Bh-Bhs and Bs horizons of SPT and SPG and A and Bw horizons of AND), the frequency distribution of the atomic Al_p/OC ratio (FD- Al_p/OC) of these soil horizons are shown in Fig. 6. A multiple comparison was done at the $p=0.05$ level according to Scheffé's F test after the logarithmic transformation. The Turkey-Kramer test was not used because the variance was not the same and the normality was abandoned in the FD- Al_p/OC

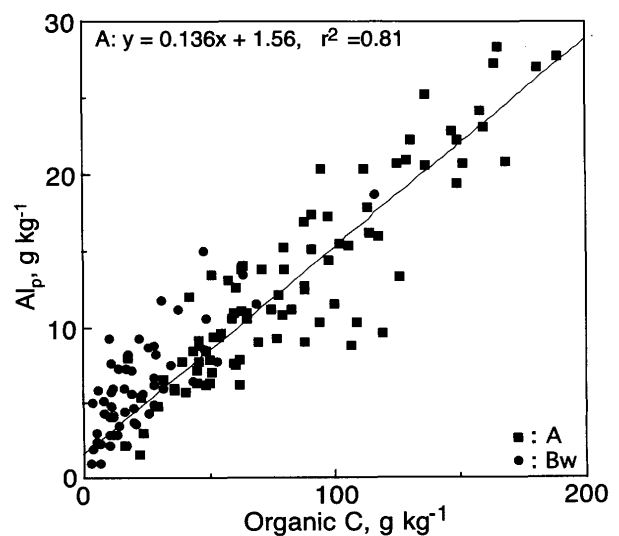


Fig. 3. Relationship between organic C content and pyrophosphate-extractable Al (Al_p) of Andisols.

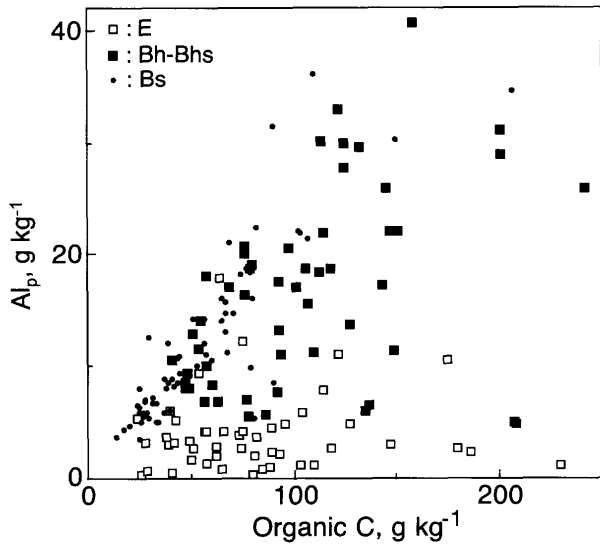


Fig. 4. Relationship between organic C content and pyrophosphate-extractable Al (Al_p) of Spodosols derived from tephra.

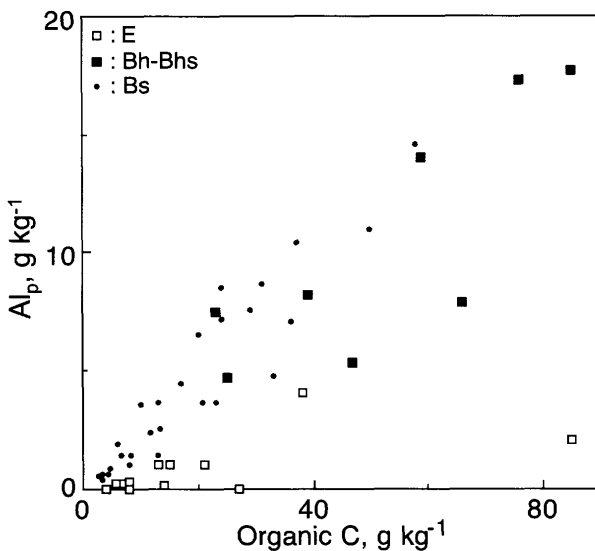


Fig. 5. Relationship between organic C content and pyrophosphate-extractable Al (Al_p) of Spodosols derived from nontephra.

of the Bh-Bhs horizon soils even after the logarithmic transformation. FD- Al_p/OC of the Bw horizon soils (AND) was not significantly different from those for the Bs of SPT and the Bh-Bhs and Bs of SPN. The A horizon soils of AND are not significantly different from those for the Bh-Bhs and Bs horizon soils of both SPT and SPN, although the Al_p/OC values for the Bh-Bhs and Bs horizon soils tends to be higher than those for the A horizon soil of AND. In contrast, the Al_p/OC values for the E horizons of both SPT and SPN are significantly lower than those for the other

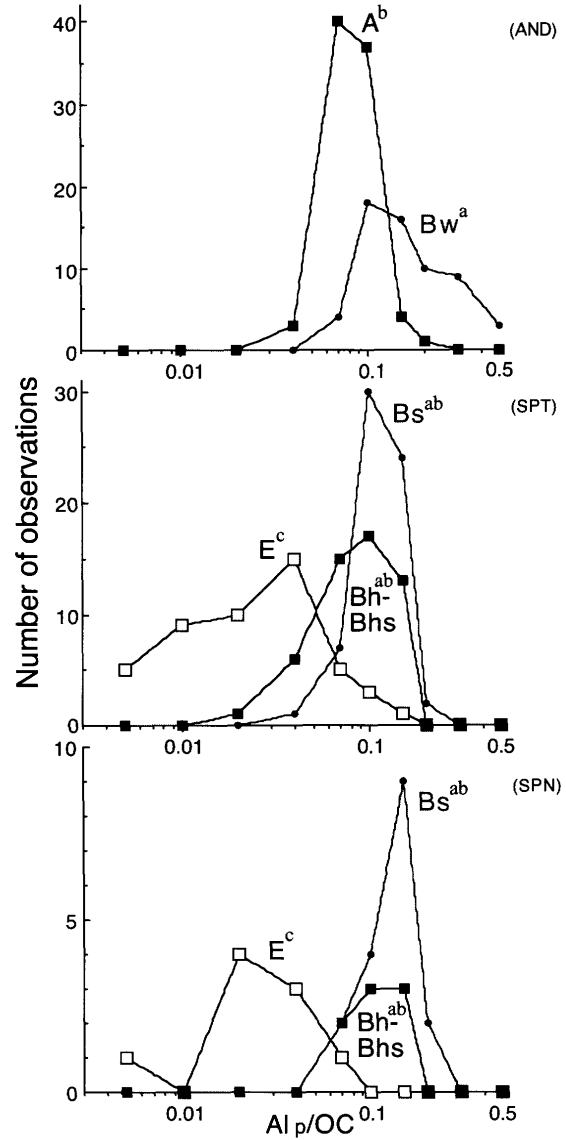


Fig. 6. Frequency distribution of atomic Al_p/OC ratio in the A and Bw horizon of Andisols (AND), E, Bh-Bhs and Bs horizon of Spodosols derived tephra (SPT) and those derived from nontephra (SPN). For example, a plot at 0.02 shows the number of observations for $0.01 < OC \leq 0.02$. Mean values for the soil horizons followed by the same letter are not significantly different at $p=0.05$ level according to Scheffé's F test after logarithmic transformation.

soil horizons. Thus, humus in the E horizon soils of both SPT and SPN has a lower degree of Al complexation than that in the other soil horizons. The degree of Al complexation in the E horizons appears similar (Fig. 6) between SPT and SPN although the OC content in SPT is higher than that in SPN (Fig. 2).

Almost similar relationships are obtained using $(Al+Fe)_p/OC$ instead of Al_p/OC as indicated in Fig. 7.

The frequency distribution of the $(Al+Fe)_p/OC$ values of the E horizon soils is also lower than those for the Bh-Bhs horizon and Bs horizon soils for both SPT and SPN. Although the reasons for the reduced mobility of DOM may be microbial degradation of organic ligands, sorption of DOM in the Bh-Bhs and Bs horizons, etc., the resultant metal/OC ratio increases in the order $E < Bh-Bhs < Bs$ horizon, and metal complexation may contribute to the stabilization of OM in the Bh-Bhs and Bs horizon soils.

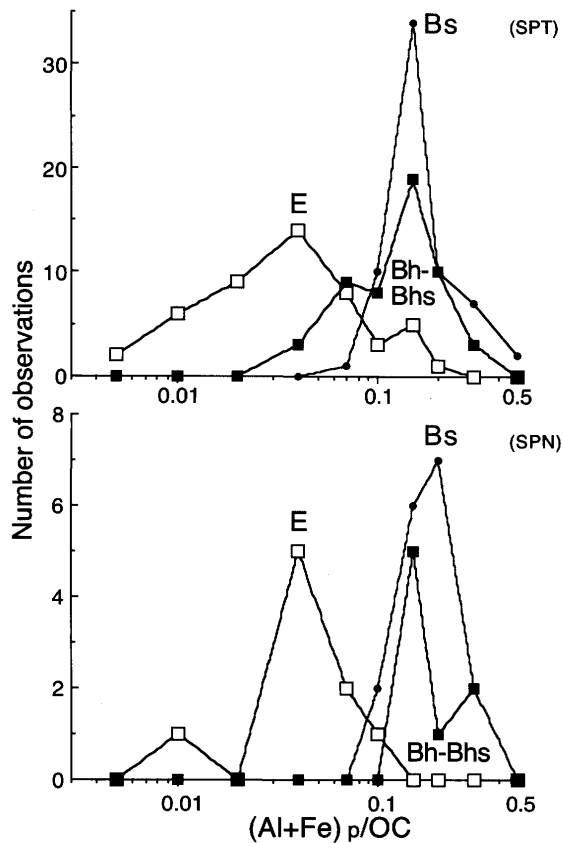


Fig. 7. Frequency distribution of atomic $(Al+Fe)_p/OC$ ratio in the A and Bw horizon of Andisols (AND), E, Bh-Bhs and Bs horizon of Spodosols derived tephra (SPT) and those derived from nontephra (SPN). For example, a plot at 0.02 shows the number of observations for $0.01 < OC \leq 0.02$.

3. Content and chemical state of carboxyl groups evaluated from Al_p and CEC

Possible reasons for the low Al_p/OC and $(Al+Fe)_p/OC$ values of the E horizons are (i) washing effect by DOM to remove Al and Fe from this horizon soils, and/or (ii) low content of carboxyl groups to complex with Al or Fe. If the former is dominant, free carboxyl groups in the E horizons might be abundant. Smectite

in the E horizon has little interlayering of the hydroxy Al polymer even under the low pH conditions (Shoji and Yamada, 1991). If the latter is more significant, the content of free carboxyl group would be low. As an index of the free carboxyl group content, the CEC of the different horizons was examined as a function of the OC.

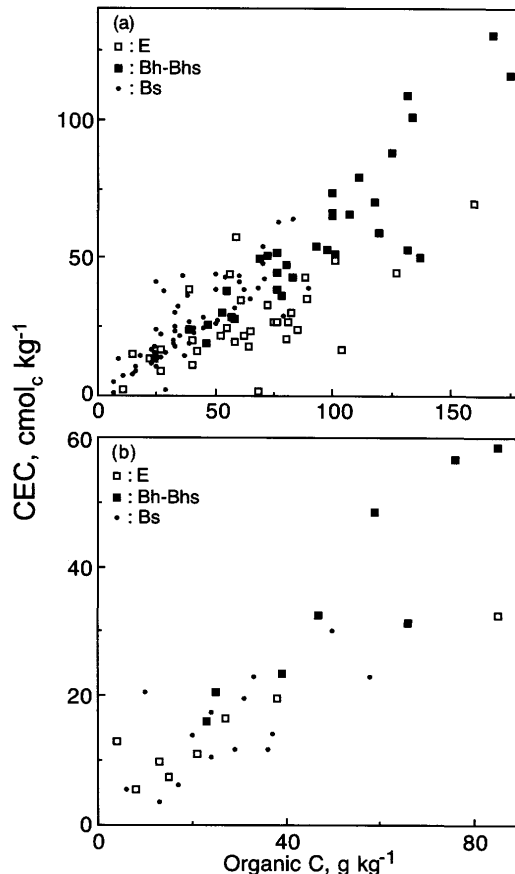


Fig. 8. Relationship between organic C content and cation exchange capacity (CEC) of Spodosols derived from tephra (a) and nontephra (b) by NH_4^+ acetate method.

The CEC values basically showed a linear relationship with the OC content for both SPT and SPN (Figs. 8a and b). The Bh-Bhs horizon soils were plotted nearly along the line for the Bs horizon soils. These relationships indicate that the OM of these soils has almost a similar degree of free carboxyl groups. In contrast, the CEC values for the E horizon soils of SPT were plotted in an area lower than those for the Bh-Bhs and Bs horizon soils. Thus, the total content of the carboxyl group, including both the complexed (Figs. 6 and 7) and free ones, in the E horizon soils of SPT is smaller than those for the Bh-Bhs and Bs horizon soils.

A similar result was obtained for SPN as shown in Fig. 8b. In the case of SPN, the E horizon soils were plotted nearly along the line for the Bh-Bhs and Bs horizon soils. A possible reason may be the higher contribution of smectic clays to the CEC of the SPN-E horizon soils than that of the SPT-E horizon soils as estimated from the data reported by Shoji and Yamada (1991). They reported that the SPN-E horizons have a mean clay content of 5.0 % (2.6-8.35, n=7), a mean OC content of 29 g kg⁻¹ (4-85 g kg⁻¹, n=7) and a mean CEC value of 15.7 cmol_c kg⁻¹ (7.5 – 32.6, n=7) while the SPT-E horizon has clay 7.4 (3.9-11.5, n=7), OC 70 (42-82, n=7) and CEC 23.7 (16-30.3, n=7). Although the OC content of the SPN-E horizons is less than half the SPT-E horizons, the CEC of the SPN-E horizons is more than half the SPT-E horizons. The relatively high CEC of the SPN-E horizons is due to their clay content of more than half the SPT-E horizons. Thus, in the E horizon soils, the content of the total carboxyl groups, including the free and Al-complexed ones, is not higher than those for the Bh-Bhs and Bs horizon soils of the SPN.

Although not statistically significant, the Al_p/OC atomic ratio tended to be higher in the Bh-Bhs and Bs horizons of both the SPT and SPN than in the A horizon soils of AND (Fig. 6). The CEC values for the Bh-Bhs and Bs horizon soils of SPT and SPN (Fig. 8a and b) are also higher than those for the A horizon soils of AND (Fig. 9). The approximate ratios of CEC to OC of the Bh-Bhs and Bs horizon soils (Fig. 8a and b) are higher than those for the A horizon soils of AND (Fig. 9). Hence, the total content of the carboxyl group in the Bh-Bhs and Bs horizon soils is greater than those for the A horizon soils of AND. A genetic reason for the high carboxyl group content is that the OM in the Bh-Bhs and Bs horizons were previously soluble or derived from the soluble OM with a high carboxyl group content. Both the chemical and biological processes, such as partial decomposition and/or sorption of DOM, are involved in the process of metal-humus complex formation in the Bh-Bhs and Bs horizons (Lundström et al., 2000). As the CEC (Fig. 9) and Al_p/OC values (Fig. 6) of the Bw horizon soils are higher than those of the A horizon soils, the OM in the Bw horizon may be partly translocated, although the OC content in the Bw horizon is far less than those in the A horizon soils (Fig. 2).

Regarding the CEC, the other difference in the A

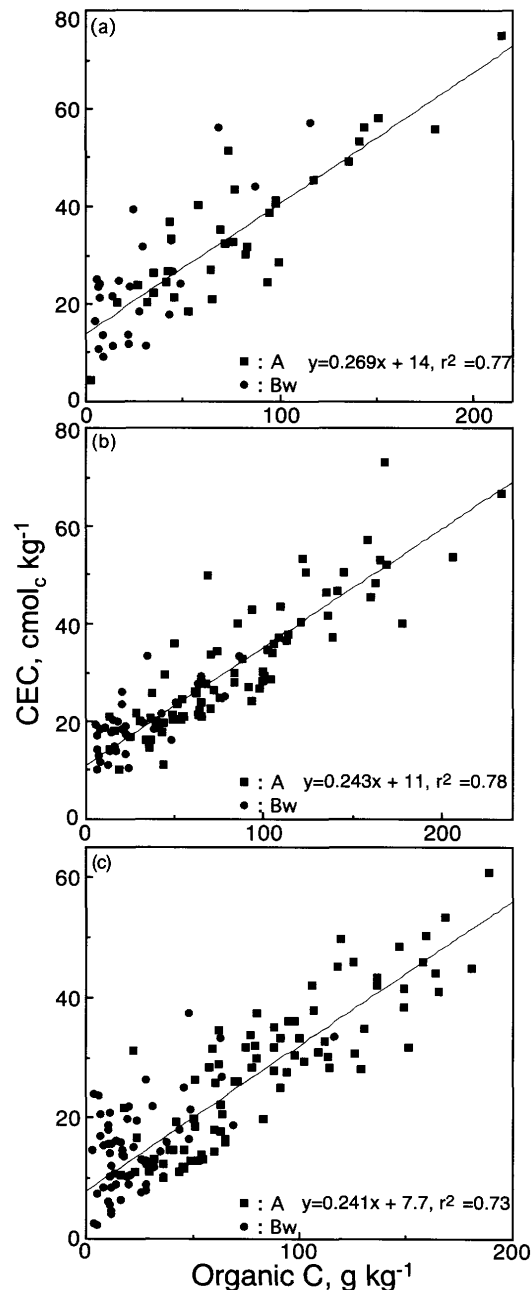


Fig. 9. Relationship between organic C content and cation exchange capacity (CEC) of Andisols determined by NH₄⁺ acetate method in USA (a), by NH₄⁺ acetate method in Japan (b) and by Ca²⁺ acetate method (c).

and Bw horizons of AND from the Bh-Bhs and Bs horizon soils of SPT and SPN is the y axis intercept of about 7.7 - 14 cmol_c kg⁻¹ (Fig. 9), while the y intercept is very low for the Bh-Bhs horizon soils (Fig. 8). The y intercept of A and Bw of AND is possibly due to the negative charge of clay minerals and other components.

There are different methods to determine the CEC of soils. In the above discussion, the CEC was de-

terminated in the USA using NH_4^+ as an index cation at pH 7. These CEC values are close to those determined for AND by Japanese soil scientists basically using the same method (Fig. 9b). The CEC values determined using $0.05 \text{ mol L}^{-1} \text{ Ca}^{2+}$ (Wada and Harada, 1969) is also close to those determined by NH_4^+ acetate (Fig. 9). The same relationships shown in Fig. 8, Fig. 9a and b were also obtained using CEC by $0.05 \text{ mol L}^{-1} \text{ Ca}^{2+}$. The CEC values by Ca^{2+} for the Bh-Bhs horizon soils of SPT is higher than those for the A horizon soils of AND (Figs. 9c and 10). The CEC values for the E horizon soils (Fig. 10) tend to be lower than those for the Bh-Bhs and Bs horizon soils of SPT (Fig. 10, Ping *et al.*, 1989) and the A horizon soils of AND (Fig. 9c).

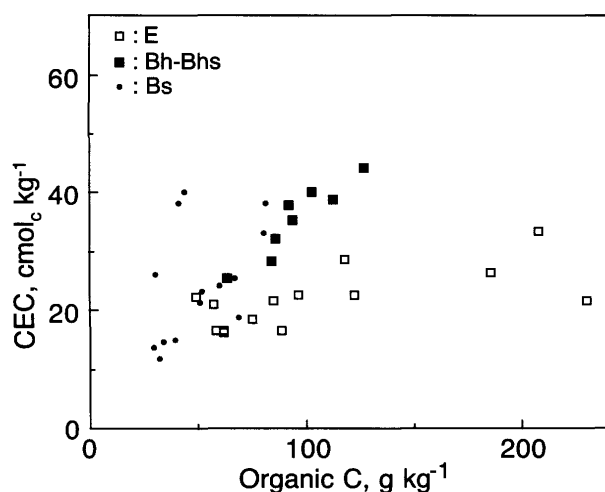


Fig. 10. Relationship between organic C content and cation exchange capacity (CEC) of tephra-derived Spodosols determined by Ca^{2+} acetate method.

The previous discussion about the fact that the Bh-Bhs and Bs horizon soils of SPT and SPN have more carboxyl groups than OM in the E horizon soils is compatible with the ^{13}C -NMR results (Kögel-Knabner *et al.*, 2008). Kögel-Knabner *et al.* (2008) summarized that the content of the alkyl group decreases and carboxyl group increases in the order: EA < Bh < Bs horizon. The reason for the low Al_p , Fe_p and CEC values of the E horizon soils is the low carboxyl group content in the OM.

According to von Lützow *et al.* (2008), the ^{14}C ages of the E horizon soils are close to those for the Bs horizon soils and older than those for the Bh horizon soils. Metal-complexation in the E horizon soils is less than in the A, Bw horizon soils of AND and the

Bh-Bhs and Bs horizon soils of SPT and SPN, and the content of the free carboxyl group is not very high. von Lützow *et al.* (2008) suggested hydrophobicity as a stabilization mechanism of OM in the E horizon although it was not adequately quantified by contact angle measurements. However, a slight Al complexation as well as a low pH may still be effective for stabilizing the OM in the E horizon resulting in its low solubility and low accessibility by microorganisms because the properties of the static OM in the E horizon is somewhat different from that in the Bh-Bhs horizon.

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