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SOIL-FORMING PROCESSES UNDER NATURAL FOREST IN NORTHERN KYOTO

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Chapter 1
Introduction

1.1 Background of the study

Podzolic soils are widely distributed from sub–arctic to tropical regions under humid climatic conditions. They have a noticeable profile feature, that is, differentiation of eluvial and illuvial horizons. Their forming–process has been a controversial pedological problem. Today, podzolic soils are identified based on the existence of podzolic B or spodic horizon rather than that of eluvial or albic horizon. In the soil classification systems of England and Wales (Avery 1980), Canada (Canada Soil Survey Committee 1978), and USDA (Soil Survey Staff 1975), the (Fep+Alp)/clay ratio has been employed in common as a criterion to define the podzolic B (or spodic) horizon. Since pyrophosphate extractable Fe or Al is considered to be organically complexed one (McKeague et al. 1971; Farmer et al. 1983), the most common concept of podzolic B horizons is an accumulation of organo–mineral complexes.

A mechanism of translocation of Al and Fe in the form of organo–mineral complexes[1] has long been postulated (e.g. Stobbe and Wright 1959; De Coninck 1980; Mokma and Buurman 1982) in the studies on podzolization and soil organic matter in podzolic soil profiles has been studied for its ability as complexing agents of metal ions. Bloomfield (1953) and De Long and Schnitzer (1955) observed complexing capacities of organic matter in leaf extracts, and many complexing agents were identified in litter or soil extracts and discussed in relation to podzolization (e.g. Stevenson 1967; Vance et al.1986; Pohlman and McColl 1988). The Classification of Forest Soils in Japan (Forest Soils Division 1976) also employs the organo–mineral theory in the explanation for the development of P_D soils (Dry podzolic soils)[2].

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[1]Organo–mineral complex theory is summarized most comprehensively by De Coninck (1980) as follows: In soils, mobile organic substances are formed during breakdown of plant remains. If at the top of the mineral soil enough polyvalent cations, especially Al and Fe, are available, the mobile organic substances formed are immobilized immediately and no migration occurs. In case insufficient amounts of Al and/or Fe are available to completely immobilize the mobile compounds, these cations are complexed by the mobile compounds and transported downward. Immobilization may occur at some depth through supplementary fixation of cations, through dessication or on arrival at a level with different ionic concentration.

[2]Classification of Forest Soils in Japan (Forest Soils Division 1976) describes that P_D (Dry podzolic soil) is a subgroup of podzolic soils, which is mainly distributed in the subalpine zones, but can be found also in mountainous regions of the temperate zone. This soil is distributed at relatively dry sites such as mountain tops, ridges, upper convex slopes or the edges of plateau. At these sites litter is poorly decomposed, Ao horizon is well developed, and organic acids are released. Consequently, the soils are podzolized.

The organo-mineral complex theory, however, could not fully explain the formation of the Bs horizons, in which amorphous Al and/or Fe compounds are illuviated without concomitant illuviation of organic matter. As alternative explanations for pedogenetic processes of such B horizons, formation of imogolite as a result of migration of Fe and/or Al-Si sols (proto-imogolite)[3] (Farmer et al. 1980; Anderson et al. 1982), or of weathering reactions involving carbonic acid (Ugolini and Dahlgren 1987) was proposed. These controversies about podzol formation appeared to be caused by morphological diversity of podzolic B horizons. Thus, a more detailed examination on the forming process of illuvial B horizons developed under various conditions must be conducted.

1.2 Study objectives

The primary objective of this study is to investigate soils under natural forest in the northern Kyoto region with special reference to their pedogenetic processes in comparison with the existing podzolization theories. A secondary objective is to examine the processes in terms of soil acidification under natural forested ecosystem.

The Ashiu Experimental Forest of Kyoto University is located in the Miyama Township, northern Kyoto, Japan. The area is covered mainly by Brown forest soils (B_D)[4] (85 %), while Dry podzolic soils (P_D)[4] distribute along high mountain ridges (3.5 %) (Shidei et al. 1958). In the USDA soil classification system, most of the soils with well-developed B horizons are classified into Dystrocrepts. Hirai et al. (1988) reported that some degrees of Al eluviation and illuviation were generally observed among the forest soils in the area, whereas Fe also migrated in the podzolic profiles. They concluded that a weak podzolization process was involved in the brown forest soil formation. Shidei et al. (1958) observed that the P_D soils in the Experimental Forest were often located along ridges, stretching from north to south, and exposed to northwesterly winds. They also reported that the P_D soils were distributed under a vegetation consisting of *Cryptomeria japonica* in many cases. Therefore, such factors as topography and vegetation may be important in the podzol formation in the Experimental Forest.

Hirai et al. (1988) reported that, in the illuvial B horizons in this area, the

[3]Anderson et al. (1982) described the podzol formation as follows: During the formation of an Iron Podzol, positively charged inorganic sols carry aluminium, silicon and iron from the A_2 and deposit them in the B_2 horizon; subsequently, with the development of an H layer, colloidal humus migrates through the A_2 and precipitates on the positive colloids at the top of the B_2 horizon to form a Bh horizon, in which remobilized ferric species are trapped by the organic matter.

[4]This classification corresponds to the Classification of Forest Soils in Japan (Forest Soils Division 1976).

Cp/(Fep+Alp) atomic ratio was often lower than that in typical spodic horizons, suggesting the presence of organo-mineral complexes with metal-rich, humus-poor characteristics. It is difficult to explain forming processes of such humus-poor B horizons with the organo-mineral theory, in which a gradual saturation of acidic functional groups of organic matter with metal ions is postulated as a commanding factor of their illuviation in the B horizons. Rather, the B horizons in this area should have been formed as amorphous Al and/or Fe compounds were illuviated without concomitant illuviation of organic matter.

In addition to the above-stated feature in the formation of illuvial B horizons, some local factors may be involved in the pedogenesis in the Experimental Forest. For example, this area has clayey soils derived mainly from paleozoic shale, whereas typical podzolic soils, or Spodosols, are considered to develop on sandy materials (Soil Survey Staff 1975; Forest Soils Division 1976). Because of a high clay content, the soils with Fe translocation in the Experimental Forest fail to be classified into Spodosols in the USDA system (Hirai et al. 1988). The clayey texture may affect the process of Fe mobilization through redox reaction and it is assumed that mechanisms of translocation of Al and Fe are considerably different in this study area from those in ordinary podzolic soils.

Thus, the forest soils in the Ashiu Experimental Forest have two pedogenetic features that must be clarified, i.e. forming processes of the B horizons and an effect of redox reaction in Fe translocation.

Chapter 2
General description of the soils studied

2.1 Study area

This study was carried out in the Ashiu Experimental Forest of Kyoto University. The elevation ranges from 355 m to 959 m and the topography is generally steep. The basement rocks consist of paleozoic shale, sandstone, and chert, and the influence of volcanic ash appears to be little.

The climatic data at the altitude of 637 m are as follows (Shidei et al. 1958): The mean annual temperature is 11.4°C and the annual precipitation is about 2800 mm. Snow covers the area from the middle of December to the end of April and the depth ranges from one or two meters to three meters depending on the elevation and topography. There is no distinct dry season and the soils in the area do not seem to have been exposed to extremely dry conditions.

The vegetation of the experimental forest is dominated by deciduous broad-leaved species and a greater part of the area is still covered by the natural vegetation. The present study was carried out only in the areas at an elevation above 600 m, in which *Fagus crenata* and *Quercus mongolica* are the dominant tree species and *Cryptomeria japonica* is often an accessory species.

2.2 Site description

Ten forest soil profiles were investigated in this study. All the profiles were classified into Inceptisols in the USDA soil classification system (Soil Survey Staff 1990). Based on the Classification of Forest Soils in Japan (Forest Soil Division 1976), Sw-2, N-1b, H-2 and S-3 were classified as typical Brown Forest soils (B_D), whereas N-4b, H-1a, H-1b, Sw-1, Sw-3, and Sw-4 were classified as Podzolic soils (P_D or $P_{W(i)}$). Among the Podzolic soils, N-4b was a weakly podzolized soil with an illuvial horizon but without a conspicuous eluvial or albic horizon, whereas the other profiles had both eluvial and illuvial horizons. Descriptions of these profiles are given in Appendix 1, according to the Soil Survey Handbook (Group of Japanese Pedologists 1984). The horizon designation, however, is given after the Keys to Soil Taxonomy (Soil Survey Staff 1990).

Most of the sampling sites were located along ridges, except for N-1b on a convex slope. The podzolic soils were characterized by a relatively thick coarse litter layer (5 to 10 cm) compared with the brown forest soils. The A and AB horizons of the brown forest soils had mostly a crumb structure, while the E (H-1a, H-1b, Sw-1, and Sw-4) and the AB (N-4b) horizons of the podzolic soils had a normally sub-angular blocky structure. As for the B horizons, the Fe-illuviated Bs horizons of the podzolic soils had a sub-angular blocky structure and were more friable than the Bw horizons of the brown forest soils.

The vegetation type is summarized as follows: Deciduous broad-leaved species such as *Fagus crenata* and *Quercus mongolica* are dominant in N-4b and N-1b. They also dominate in H-1a, H-1b, and H-2 with minor coniferous species, i.e. *Cryptomeria japonica*. In contrast, *Cryptomeria japonica* is the dominant vegetation in S-3, Sw-1, Sw-2, Sw-3, and Sw-4.

2.3 Physico-chemical and mineralogical properties of the soils studied

2.3.1 Analytical methods

Soil samples were air-dried and crushed to pass through a 2 mm sieve, and then examined using the following methods.

1) The pH was measured with a glass electrode pH meter using a soil to solution (H_2O or 1 M KCl) ratio of 1 to 2.5. The pH(NaF) was measured in 1 M NaF solution after stirring for 2 min, using a soil to solution ratio of 1 to 50.

2) Exchangeable cations and CEC:

(a) Exchangeable bases were extracted with 1 M NH_4OAc at pH 7.0 and then Ca and Mg contents were determined by atomic absorption and Na and K contents by flame photometry.

(b) Exchangeable Al and H were extracted with 1 M KCl and exchange acidity was determined by titration with 0.01 M NaOH, and exchangeable Al by aluminon colorimetry. The content of exchangeable H was calculated from the difference between the value of exchange acidity and that of exchangeable Al.

(c) CEC: After replacement of exchangeable bases, washings with deionized water and ethanol and replacement of NH_4^+ with 10% NaCl were successively performed by centrifugation. Content of NH_4-N was determined by the Kjeldahl distillation method.

3) Total carbon and nitrogen was determined by a dry combustion method using a CN corder (Yanagimoto MT-500).

4) Extractable Al, Fe, Si, and carbon:

(a) Feo, Alo, and Sio were extracted with acid ammonium oxalate (0.2 M, pH 3.0) in the dark (McKeague and Day 1966), and then filtered using 0.45 μm millipore filter.

(b) Fed, Ald, and Sid were extracted with a citrate-bicarbonate mixed solution buffered at pH 7.3 with the addition of sodium dithionite (DCB) at 80°C (Mehra and Jackson 1960) and then filtered using a 0.45 μm millipore filter.

(c) Fep, Alp, Sip, and Cp were extracted with 0.1 M pyrophosphate (pH 10) (Schuppli et al. 1983) and then centrifuged at 10,000**g* and filtered using a 0.025 μm millipore filter.

Fe, Al, and Si contents were determined by multi-channel inductively coupled argon plasma atomic emission spectroscopy (ICP-AES: Nippon Jarrell-ash, ICAP-750). Carbon content in the extracts was determined by a wet combustion method with a reflux condenser attached to the flask.

5) Phosphate retention was determined by the method of Blakemore et al. (1987).

6) Zero point of charge (ZPC) and σ_p were determined by the STPT and PAT method

proposed by Sakurai et al. (1988; 1989), and expressed as 'STPT-ZPC', 'PT-ZPC', 'STPT-σ_p', 'PAT-σ_p'. Cut off time in the PAT method was 12 s for 0.01 and 120 s for 0.1 M NaCl as the supporting electrolyte solutions.

7) Particle size distribution was determined by a pipette method.

8) Clay minerals were identified by X-ray diffraction analysis using Cu-Kα radiation.

9) Ten major elemental oxides (SiO_2, Al_2O_3, Fe_2O_3, MnO_2, TiO_2, CaO, MgO, K_2O, Na_2O, and P_2O_5) were analyzed by the method of Ochi and Okashita (1987) using an X-ray fluorescence spectroscopy.

2.3.2 Physico-chemical and mineralogical properties of the soils studied

General physico-chemical and mineralogical characteristics for the selected four profiles (Sw-2, N-1b, N-4b, and Sw-1) are given in Table 2.1. 2.2, and 2.3, and for the other profiles in Appendix 2. They are summarized as follows:

1) The pH of each site, especially in the surface horizon, was very low. Judging from the very low base saturation (less than 5 % in most cases) and a high contribution of Al to effective CEC, all the soils were highly acidified. Exchangeable Al occupied most part of the exchange acidity and was highest at the surface in the brown forest soil profiles, whereas it was highest at E to B horizons in the podzolic profiles. This suggested that an effect of soil acidification reached to deeper horizons in the podzolic profiles.

2) Most of the soils showed a relatively high clay content, often exceeding 40 %. As shown in Fig. 2.1 for Sw-1 and Sw-2 profiles, the dominant clay mineral species in the deeper horizons were 2:1-2:1:1 intergrades. In contrast, expansible 2:1 minerals such as vermiculite and smectite dominated above the horizons with a high content of exchangeable Al (often exceeded 10 cmol(+) kg^{-1}). Gibbsite was detected in the deeper horizons, whereas it disappeared in the surface horizons in which smectite was dominant. Some of the C horizons (N-1b and Sw-1) had a relatively high clay mica content as compared to the well-developed B horizons. These results were consistent with the report by Hirai et al. (1989), in which the alteration sequence of 2:1 type clay minerals with soil acidification was concluded as follows: clay mica - 2:1-2:1:1 intergrades - vermiculite - high charge smectite.

3) Judging from the distribution patterns of Alo and Feo, a degree of eluviation and illuviation of Al appeared to have occurred in most of the profiles, whereas that of Fe was observed only in the podzolic profiles. Alp/Alo or Fep/Feo often exceeded 0.5, so that a large part of the amorphous compounds was considered to be organically complexed. However, the B horizons except for the Bs1 of H-1b represented a significantly lower Cp/(Fep+Alp) atomic ratio than the chemical criterion for the spodic horizon proposed by Mokma and Buurman (1982), that is, 5.8, suggesting a metal-rich, humus-poor characteristics of the illuvial B horizons of the forest soils in this area. Moreover, a general decrease of Alp/Alo and Fep/Feo ratio in the B horizons compared with the surface horizons suggested an increase of amorphous compounds that did not form organo-mineral complexes in the B horizons. The Sio content of nearly zero suggested that amorphous Al-Si compounds scarcely existed. A

clear decrease of Alo in the surface horizons with increased exchangeable Al in some profiles was considered to show a progress of monomerization of amorphous Al in those horizons.

4) Most of the B horizons with Al illuviation (Alo > $0.9*10^{-2}$ kg kg^{-1}) showed bulk density < 1.0, pH(NaF) > 10, and phosphate retention > 85 %. This was typical for the B horizon of the brown forest soil or podzolic soil in the cool temperate forest zone, which is characterized by a relatively high content of amorphous Al compounds in the soil, as discussed by Hirai et al. (1991).

5) Bulk density was generally low, i.e. less than 1.0 throughout the profiles. It was notable that the eluvial E horizon of podzols had a higher bulk density than the underlying B horizons, suggesting some influence of soil physical properties on the pedogenetic process including Fe translocation in the profiles. This will be discussed in detail in Chapter 5.

6) PAT- and STPT-ZPC showed a good agreement in a pH region > 4.0. The PAT-ZPC, however, was often not determined in pH < 3.5, in which permanent charge minerals dominated in the clay fraction, while the STPT-ZPC did exist. A relatively long equilibration time (four days) in the STPT method in contrast to a short equilibration in the PAT method (within three hours) might have caused further dissolution of surface oxides with a relatively low activity. It was considered that such a disappearance of PAT-ZPC was reflected more sensitively on the succession of clay mineral composition, that is, a gradual predominance of permanent charge minerals such as vermiculite and/or smectite in the EB to Bs horizons of the podzols. PAT- and STPT-σ_p showed values close to the sum of exchangeable bases rather than ECEC, suggesting that exchangeable Al was kept retained on the soil particles under the salt concentration of 0.01 to 0.1 M in these analyses.

7) Total chemical composition showed that the E horizons of the podzols became more siliceous as a result of eluviation of Al and Fe. In all of the profiles, a high contribution of Al in the cationic components (more than 60 % in molar basis) was notable, followed by Fe. So that, in a long pedogenetic periods, Al was considered to be particularly important in the acid buffering by the soil solid phase, whereas the basic cations (K, Mg, and Ca) that are low in their contents might have been recycled within the soil and vegetation and their contribution to acid neutralization should have been rather limited.

Table 2.1. Brief description and general physico-chemical properties of the soils from the selected profiles.

Site and horizon	Depth (cm)	Moist color	Structure[a]	Bulk density ($g\ cm^{-3}$)	Particle size distribution Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	Clay mineral species[b]
Sw-2									
A	0-2	7.5YR2/3	2mcr	.	40.8	47.4	8.9	2.9	H.C.Sm > Vt, Ch, Mica, Kao
AB	2-11	7.5YR3/2	1mcr	0.64	42.1	46.0	9.7	2.3	Vt > Ch, Mica, Kao
BA	11-25	7.5YR4/4	2msabk	.	44.8	45.6	7.6	2.0	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
Bw	25-50	7.5YR5/6	2msabk	0.83	40.9	48.8	7.3	2.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
BC	50-73	10YR5/6	2msabk	0.87	46.8	44.2	6.1	2.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
C	73-80	10YR5/6	---	.	32.4	39.0	12.2	16.5	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
N-1b									
A	0-5	7.5YR3/4	2mcr	.	49.1	32.3	14.7	3.9	H.C.Sm, Vt, 2:1-2:1:1 int. > Ch, Mica
BA	5-19	7.5YR4/6	2fcr	0.58	40.6	39.1	17.5	2.8	2:1-2:1:1 int. > H.C.Sm, Vt, Mica, Kao, Gb
Bw	19-55	7.5YR5/6	2fsabk	0.72	52.6	31.8	13.1	2.5	2:1-2:1:1 int. > Mica, Kao, Gb
BC	55-86	7.5YR5/6	2cabk	0.81	54.6	32.8	1.5	1.2	2:1-2:1:1 int. > Mica, Ch, Kao, Gb
C	86-99	10YR6/6	---	.	33.8	35.3	24.1	6.8	2:1-2:1:1 int. > Mica, Ch, Kao, Gb
N-4b									
A	0-6	7.5YR2/1	2fcr	.	42.5	46.7	9.8	1.1	H.C.Sm > Mica, Kao
AB	6-12	7.5YR3/3	2msabk	0.73	43.2	45.8	10.3	0.6	H.C.Sm > Vt, Mica, Kao
BA	12-15	7.5YR3/4	2fabk	.	44.1	44.2	10.9	0.8	Vt > H.C.Sm, Mica, Kao
Bs	15-30	7.5YR4/6	2fsabk	0.55	54.8	36.3	8.0	0.8	2:1-2:1:1 int. > Vt, Mica, Kao, Gb
Bw1	30-40	7.5YR5/8	2msabk	.	48.0	36.6	5.8	9.7	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
Bw2	40-52	7.5YR5/6	2csabk	0.78	46.3	45.5	6.3	1.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
BC	52-83	7.5YR5/8	2cabk	.	52.0	40.9	5.7	1.4	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
C	83-100	7.5YR5/8	2cabk	.	47.2	37.0	9.7	6.2	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
Sw-1									
A	0-2	10R2/1	2mcr	.	31.0	35.4	16.9	16.7	H.C.Sm-Mica > Kao
E	2-10	7.5YR4/2	2msabk	1.01	33.2	36.0	16.8	14.0	H.C.Sm-Mica > Kao
EB	10-23	7.5YR4/4	2msabk	.	40.7	33.0	14.7	11.6	H.C.Sm-Mica, Vt-Mica > Kao
Bs	23-45	7.5YR4/6	2msabk	0.70	49.6	31.2	10.4	8.9	Vt, 2:1-2:1:1 int. > Mica, Kao, Gb
BC	45-60	10YR5/6	1msabk	.	34.2	27.5	12.5	25.9	2:1-2:1:1 int. > Mica, Kao, Gb
C	60-73	10YR5/8	---	.	17.0	16.2	18.5	48.4	2:1-2:1:1 int., Mica > Kao, Gb

[a]Grade: 1, weak; 2, moderate; 3,strong. Size: f, fine; m, medium; c, coarse. Type: cr, crumb; sabk, subangular blocky; abk, angular blocky.
[b]Kao, kaolin minerals; Mica, clay mica; H.C.Sm, high charge smectite; Vt, vermiculite; Ch, chlorite; Gb, gibbsite; 2:1-2:1:1 int., 2:1-2:1:1 intergrade mineral; Mica-H.C.Sm, interstratified mineral of clay mica and high charge smectite; Mica-Vt, interstratified mineral of clay mica and vermiculite.

Table 2.1. (continued)

Site and horizon	Depth (cm)	pH H_2O	pH KCl	pH NaF	Exchangeable cations[c] Na+K+ Mg+Ca -----(cmol(+) kg^{-1})-----	Al	H	STPT method[d] ZPC	σ_p[e] ($cmol\ kg^{-1}$)	PAT method[d] ZPC	σ_p[e] ($cmol\ kg^{-1}$)
Sw-2											
A	0-2	3.82	2.91	7.05	8.08	10.83	2.31	3.18	3.89	< 3.0	n.d.
AB	2-11	4.05	3.17	8.48	1.47	11.71	0.76	3.56	2.32	3.59	0.99
BA	11-25	4.35	3.53	9.68	0.63	8.07	0.13	3.98	0.87	3.89	0.15
Bw	25-50	4.50	3.69	10.35	0.62	6.13	0.10	3.99	1.32	4.24	0.42
BC	50-73	4.73	3.77	10.71	0.47	5.04	0.06	4.08	0.82	4.36	- 0.02
C	73-80	4.68	3.70	9.67	0.28	4.72	0.00	4.06	0.80	4.26	0.08
N-1b											
A	0-5	3.91	3.44	8.13	2.17	8.03	2.08	3.79	2.14	3.57	1.42
BA	5-19	4.22	3.80	9.69	0.76	6.25	0.65	4.03	1.82	4.15	0.00
Bw	19-55	4.54	4.22	11.64	0.29	3.12	0.00	4.59	0.22	4.46	0.07
BC	55-86	4.63	4.16	11.38	0.34	2.92	0.00	4.41	0.41	4.52	- 0.06
C	86-99	4.65	4.03	9.90	0.27	2.95	0.23	4.44	0.14	4.48	- 0.08
N-4b											
A	0-6	3.59	2.88	6.72	3.25	8.73	4.61	< 3.0	n.d.	< 3.0	n.d.
AB	6-12	3.76	2.94	7.48	1.30	14.64	3.69	3.13	3.91	< 3.0	n.d.
BA	12-15	3.84	3.21	8.38	0.72	14.55	3.63	3.41	2.74	3.48	1.15
Bs	15-30	4.05	3.52	8.95	0.56	12.43	0.71	3.74	1.86	3.76	0.70
Bw1	30-40	4.36	3.85	10.16	0.44	6.89	0.61	4.06	1.00	4.16	0.85
Bw2	40-52	4.49	3.97	10.29	0.41	6.68	0.00	4.16	0.69	4.34	- 0.09
BC	52-83	4.49	4.01	10.35	0.37	5.78	0.14	4.16	0.76	4.29	0.31
C	83-100	4.57	4.05	10.81	0.34	4.70	0.13	4.41	0.08	4.25	0.69
Sw-1											
A	0-2	3.43	2.37	6.43	3.43	6.88	4.63	< 3.0	n.d.	< 3.0	n.d.
E	2-10	3.65	2.60	7.38	0.76	13.36	1.87	3.04	1.49	< 3.0	n.d.
EB	10-23	3.97	2.99	8.51	0.85	17.81	1.42	3.58	1.16	< 3.0	n.d.
Bs	23-45	4.20	3.19	8.95	0.49	15.58	0.65	3.78	0.86	< 3.0	n.d.
BC	45-60	4.58	3.58	10.83	0.49	6.33	0.05	4.20	0.38	4.18	0.18
C	60-73	4.71	3.95	11.39	0.35	2.52	0.04	4.38	0.24	4.58	- 0.04

[c]Oven dried basis. [d]n.d. = not determined.

Table 2.2. Sesquioxidic properties of the soils from the selected profiles.

Site and horizon	Depth (cm)	Alo[a]	Feo[a]	Sio[a] ($*10^{-2}\ kg\ kg^{-1}$)	Alp[a]	Fep[a]	Sip[a]	Cp[a] ($*10^{-2}\ kg\ kg^{-1}$)	Ald[a]	Fed[a]	Sid[a] ($*10^{-2}\ kg\ kg^{-1}$)	Fep /Feo	Alp /Alo	Cp[b] /(Fep +Alp)
Sw-2														
A	0-2	0.69	0.95	0.04	0.59	0.91	0.00	4.63	0.96	2.10	0.22	0.96	0.86	10.1
AB	2-11	0.81	1.22	0.04	0.72	1.31	0.00	3.51	1.01	2.98	0.17	1.07	0.89	5.8
BA	11-25	0.81	1.40	0.04	0.66	1.01	0.00	1.80	1.13	3.48	0.12	0.72	0.81	3.5
Bw	25-50	0.92	1.34	0.06	0.60	0.89	0.00	1.61	1.28	3.33	0.13	0.66	0.65	3.5
BC	50-73	0.85	0.36	0.10	0.45	0.27	0.01	0.64	1.04	2.08	0.18	0.75	0.53	2.5
C	73-80	0.45	0.26	0.05	0.23	0.15	0.00	0.32	0.77	2.28	0.12	0.58	0.51	2.4
N-1b														
A	0-5	0.77	1.45	0.04	0.66	1.32	0.10	3.81	0.79	2.60	0.17	0.91	0.86	6.6
BA	5-19	1.01	2.07	0.05	0.81	1.62	0.00	2.61	0.95	3.15	0.09	0.78	0.80	3.7
Bw	19-55	2.06	1.59	0.29	0.93	0.71	0.01	1.90	1.68	2.68	0.20	0.45	0.45	3.4
BC	55-86	1.66	1.40	0.23	0.78	0.51	0.05	1.29	1.35	2.48	0.16	0.36	0.47	2.8
C	86-99	0.60	0.72	0.06	0.39	0.40	0.07	0.54	0.67	2.19	0.07	0.55	0.65	2.1
N-4b														
A	0-6	0.39	0.57	0.02	0.24	0.60	0.13	4.35	0.47	1.32	0.25	1.06	0.61	18.5
AB	6-12	0.51	1.44	0.06	0.37	1.18	0.05	3.77	0.58	2.60	0.14	0.82	0.72	9.0
BA	12-15	0.61	2.16	0.03	0.40	1.44	0.00	2.65	0.70	3.79	0.11	0.67	0.65	5.4
Bs	15-30	1.06	3.48	0.04	0.72	1.42	0.04	3.06	1.21	5.57	0.10	0.41	0.68	4.9
Bw1	30-40	1.01	2.05	0.06	0.59	0.84	0.07	1.10	1.23	4.43	0.10	0.41	0.58	2.5
Bw2	40-52	0.98	1.08	0.10	0.55	0.58	0.16	1.04	1.15	3.41	0.12	0.53	0.56	2.8
BC	52-83	1.01	0.99	0.06	0.59	0.51	0.07	1.01	1.14	3.16	0.10	0.52	0.58	2.7
C	83-100	1.12	1.10	0.15	0.57	0.42	0.02	0.75	1.16	2.80	0.15	0.38	0.51	2.2
Sw-1														
A	0-2	0.27	0.24	0.03	0.23	0.19	0.08	4.02	0.33	0.51	0.22	0.79	0.85	28.1
E	2-10	0.30	0.44	0.03	0.22	0.37	0.06	1.33	0.34	1.63	0.13	0.84	0.73	7.5
EB	10-23	0.49	1.38	0.03	0.38	1.33	0.06	1.37	0.51	3.25	0.08	0.96	0.78	3.0
Bs	23-45	0.82	2.28	0.03	0.56	1.56	0.02	1.69	0.83	4.61	0.08	0.68	0.68	2.9
BC	45-60	0.92	1.44	0.03	0.62	0.70	0.00	1.49	0.96	2.82	0.09	0.49	0.67	3.5
C	60-73	0.83	0.40	0.12	0.49	0.16	0.00	0.59	0.78	1.35	0.14	0.40	0.59	2.3

[a]Oven dried basis. [b]Atomic ratio.

Table 2.3. Total chemical composition of the soils from the selected profiles.

Site and horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	Ignition[a] loss (%)
		($*10^{-2}$ kg kg^{-1})										
Sw-2												
A	0-2	68.19	17.08	8.12	1.32	0.05	0.48	1.03	1.74	0.71	0.08	45.1
AB	2-11	68.95	17.21	8.28	1.32	0.05	0.29	0.99	1.68	0.65	0.04	26.7
BA	11-25	68.34	17.82	8.43	1.32	0.05	0.24	0.97	1.64	0.59	0.01	14.7
Bw	25-50	66.35	19.58	8.88	1.27	0.05	0.24	1.07	1.63	0.61	0.01	13.5
BC	50-73	63.06	23.02	8.23	1.10	0.07	0.18	1.45	1.87	0.53	0.00	10.3
C	73-80	64.50	22.09	7.76	1.07	0.05	0.08	1.34	2.44	0.29	0.00	8.7
N-1b												
A	0-5	65.85	17.33	8.13	1.18	0.03	0.27	1.06	2.08	0.73	0.27	30.2
BA	5-19	67.77	17.78	8.58	1.20	0.03	0.23	1.08	2.05	0.72	0.19	17.1
Bw	19-55	64.24	24.41	8.36	1.08	0.05	0.27	1.42	2.10	0.77	0.13	13.4
BC	55-86	61.90	22.27	8.18	1.06	0.05	0.29	1.52	2.16	0.80	0.10	11.6
C	86-99	69.77	17.66	6.28	1.06	0.03	0.08	1.09	2.21	0.63	0.07	7.1
N-4b												
A	0-6	73.84	14.17	6.12	1.32	0.02	0.34	0.86	1.51	0.76	0.26	49.1
AB	6-12	73.38	13.70	7.17	1.49	0.02	0.20	0.78	1.50	0.66	0.13	23.5
BA	12-15	71.24	13.61	8.91	1.59	0.02	0.17	0.77	1.39	0.59	0.09	15.2
Bs	15-30	63.19	17.34	13.22	1.53	0.02	0.16	0.95	1.45	0.48	0.09	16.6
Bw1	30-40	60.85	21.57	11.18	1.28	0.04	0.19	1.33	1.70	0.54	0.07	11.5
Bw2	40-52	61.52	22.56	9.53	1.20	0.05	0.18	1.51	1.97	0.52	0.06	10.6
BC	52-83	60.51	22.78	9.57	1.18	0.05	0.16	1.50	2.00	0.51	0.06	10.7
C	83-100	58.94	23.86	8.69	1.08	0.04	0.26	1.48	1.91	0.69	0.05	10.9
Sw-1												
A	0-2	73.30	15.85	3.94	1.24	0.02	0.20	0.77	2.93	0.44	0.10	49.1
E	2-10	72.84	16.46	4.28	1.24	0.02	0.05	0.75	3.17	0.28	0.03	13.2
EB	10-23	68.01	18.31	6.69	1.21	0.02	0.03	0.80	3.25	0.23	0.02	11.1
Bs	23-45	62.08	22.07	9.23	1.17	0.02	0.02	0.92	3.41	0.21	0.03	12.9
BC	45-60	61.44	24.84	6.94	1.05	0.02	0.00	0.94	3.47	0.17	0.03	12.4
C	60-73	65.27	23.83	3.61	0.95	0.02	0.00	0.81	3.99	0.12	0.02	8.1

All the data except for ignition loss are given on an ignition basis. [a]Oven dried basis.

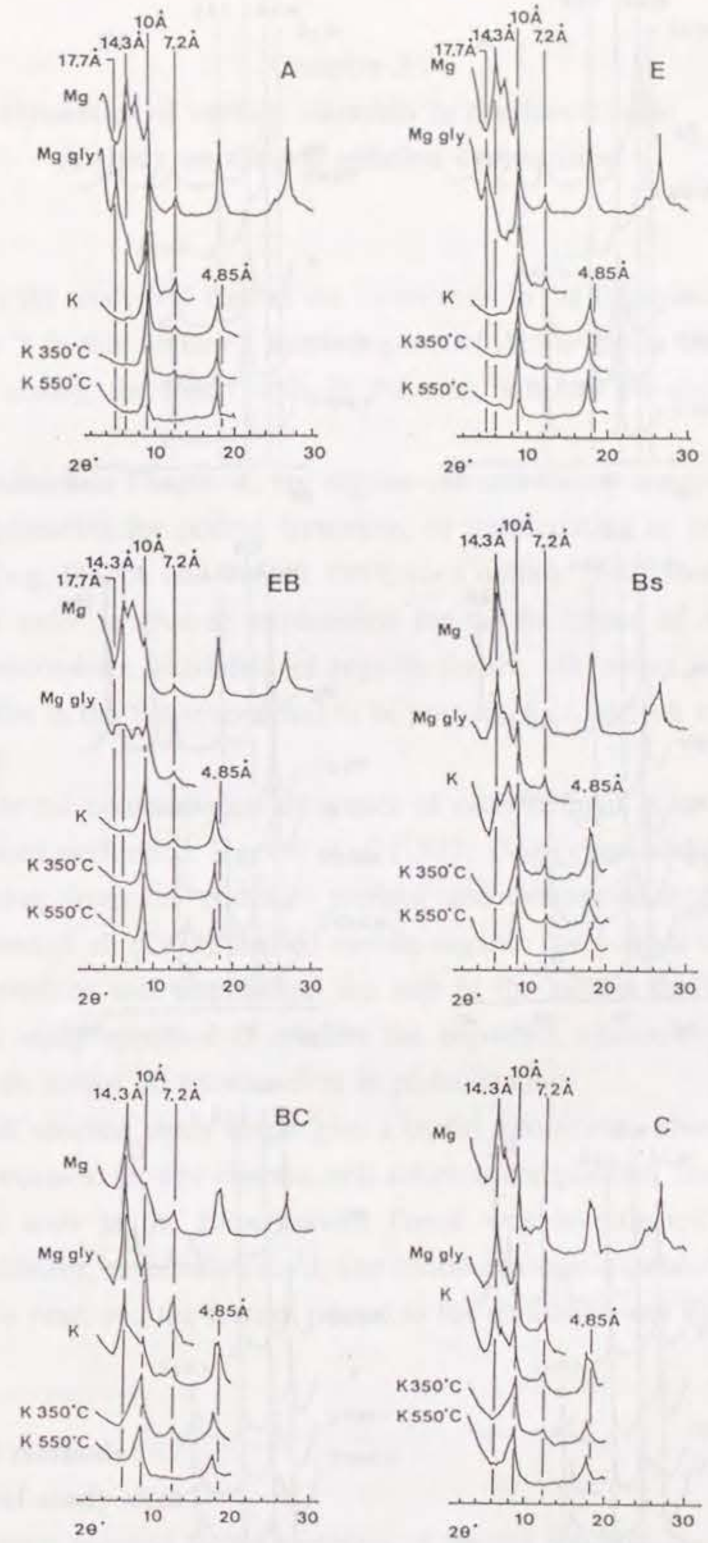


Fig. 2.1.1. X-ray (Cu-Kα) diffractogram from oriented clay specimens of Sw-1 (podzolic soil).

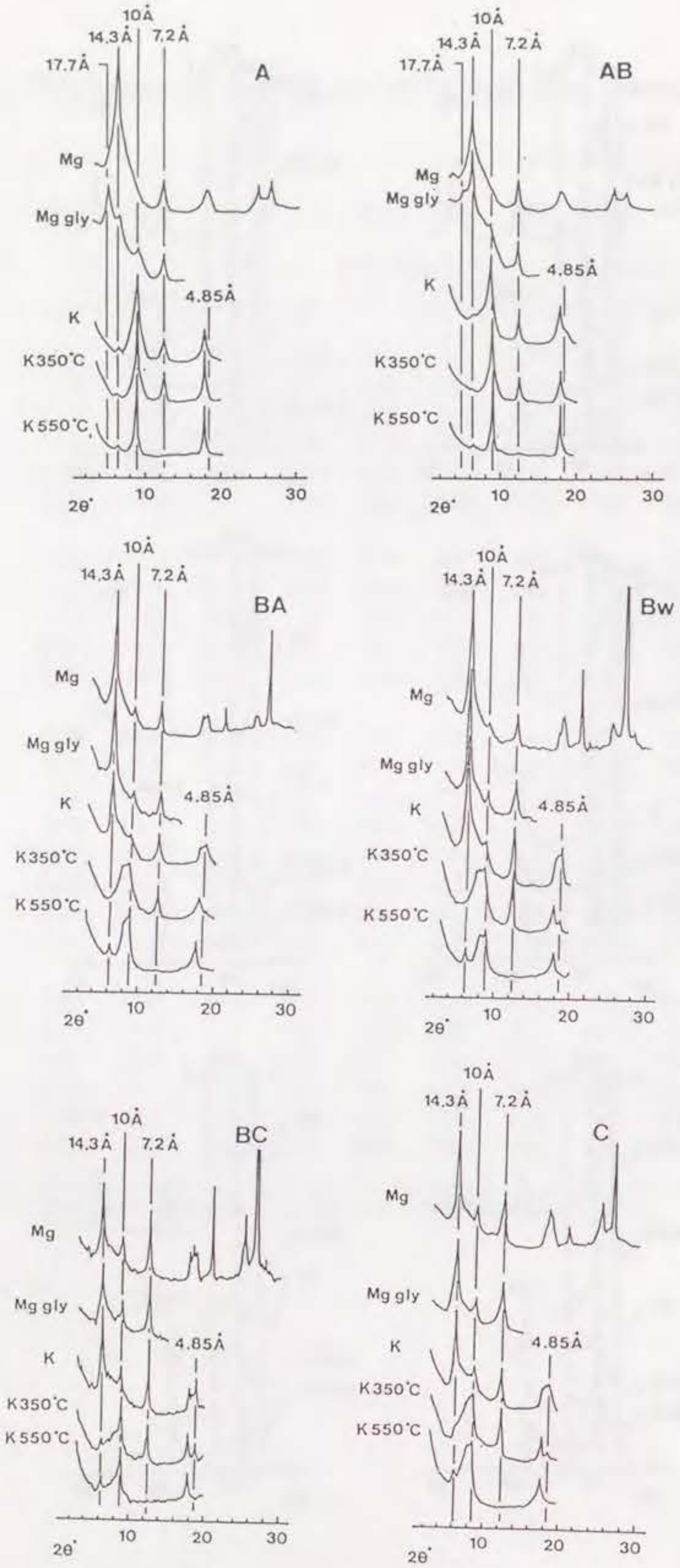


Fig. 2.1.2. X-ray (Cu-Kα) diffractogram from oriented clay specimens of Sw-2 (brown forest soil).

Chapter 3
Dynamics of various elements in the forest soils: A study on the soil solution composition

3.1 General

Judging from the analytical data of the forest soils in the Experimental Forest (Hirai et al. 1988; Chapter 2 in this volume), some degrees of Al eluviation and illuviation were generally observed among the forest soils in the area, whereas Fe also migrated in the podzolic profiles.

As was introduced in Chapter 1, the organo-mineral theory appeared to be the most widely accepted explanation for podzol formation, or translocation of Fe and/or Al in the forest soil profiles (e.g. Stobbe and Wright 1959; De Coninck 1980; Mokma and Buurman 1982). However, in order to give an explanation for the formation of Al-, Fe-illuvial B horizons without concomitant illuviation of organic matter, alternative processes including formation of imogolite in the B horizons had to be postulated (Anderson et al. 1982; Ugolini and Dahlgren 1987).

To investigate the contemporary dynamics of each element in the soil profiles, soil solution study has been performed. Ugolini et al. (1977; 1988) examined the composition of a natural soil solution from the podzolic profiles and demonstrated the progression of podzolization. Dawson et al. (1978) studied mobile organic compounds in the soil solution from the podzolic profiles and emphasized the role of the mobile fulvic acid fraction in podzolization. Their study appeared to confirm the important relationship between soluble organic matter and Fe and/or Al translocation in podzolization.

Thus, the soil solution study might give a useful information about the dynamics of the soil-forming processes. In this chapter, soil solution composition from both the brown forest and podzolic soils in the Experimental Forest was investigated to determine the movement of each element, especially Fe, Al, and dissolved organic carbon (DOC), in the soil profiles throughout a year, and the factors related to the eluviation and illuviation of Fe and Al were discussed.

3.2 Materials and methods

3.2.1 Description of study sites

Six profiles were selected for the sampling of the soil solution. N-1b and Sw-2 were brown forest soils. N-4b was a weakly podzolized soil with an illuvial horizon but without a conspicuous eluvial or albic horizon. H-1a, Sw-1, and Sw-3 were podzolic soils with both eluvial and illuvial horizons. Detailed site descriptions and physico-chemical properties of the soils are given in Chapter 2 and Appendix 1 and 2.

Judging from the distribution patterns of the free oxides, the eluvial characteristics of the E horizons of the H-1a, Sw-1, and Sw-3 profiles and the illuvial characteristics of the

Bs horizons of the N-4b, H-1a, Sw-1, and Sw-3 profiles were clearly noted. Even in the brown forest soils (Sw-2 and N-1b), a degree of eluviation and illuviation of Fe and/or Al appeared to be present.

3.2.2 Study Methods

Sampling method: At the six sites described above, porous cups (Daiki Rika Kogyo, Soil Water Extractor, 1.1 cm of inside diameter and 6 cm high) were buried into the soil at four depths that corresponded to the horizons, as shown in Table 3.1, in five replications. These porous cups were connected to 500 mL Erlenmeyer flasks on the ground, which were evacuated using a hand-operated vacuum pump and kept under depressed pressure conditions (approximately 70 kPa) for about one day. As a result, the soil solutions were taken from the above-mentioned 4 depths 8 times for the N-4b, N-1b, H-1a profiles in 1988 and 5 times for Sw-1, Sw-2, Sw-3 profiles in 1989.

Analytical methods: The samples collected were preserved at 4°C, after measurement of the pH. They were filtered through 0.45 μm millipore filters before the analyses. Analyses were conducted using the following methods.

1) pH was measured soon after sampling with a glass electrode.

2) Cations and anions: Contents of Na and K were determined by flame photometry and of Mg and Ca by ICP-AES. The contents of Cl, NO_3 and SO_4 were measured by high performance liquid chromatography (HPLC) (Shimadzu LC-6A).

3) The contents of Fe, Al, and Si were determined by ICP-AES.

4) The amount of DOC was determined as follows: 4 mg of 0.5 mol(+) L^{-1} $K_2Cr_2O_7$ / conc. sulfuric acid solution was added to 2 mL of the sample solution and then well shaken. After cooling down to the room temperature, the absorbance of the solution was measured at a 645 nm wavelength with a spectrophotometer (Shimadzu spectrophotometer UV-120-01) (Tatsukawa 1966).

3.3 Nature of the soil solutions collected with the porous cup method

The soil solutions were collected within one to four days after respective rainfall events. The quantity of the collected samples ranged from 20 to 50 mL in most cases. Based on the tensiometer readings taken in the field, since the soil moisture tension at each sampling site ranged from about 3 to 10 kPa, the matric suction of the soil solution collected with this method was considered to range from 3 to 70 kPa (suction exerted by the vacuum pump) under the undisturbed soil conditions. The amount of water retained within the above suction range was estimated at about 10 to 15 mL / 100 mL of bulk soil based on the pF - moisture curves (see Chapter 5). Therefore, it was assumed that 50 mL of the soil solution may be collected from about 500 mL of bulk soil around the porous cup, which is equivalent to a sphere 10 cm in diameter. Therefore, it was considered that the soil solution collected by this method was likely to represent the low suction capillary water rather than freely draining gravitational water collected by the tension-free lysimeter method (e.g. Joffe 1938; Arimitsu

1982). Thus, the composition of the soil solution may better reflect the nature of the soil particle-water interaction.

3.4 Soil solution composition

Soil solution composition in the Experimental Forest is shown in Fig. 3.1 for describing seasonal variation of each element in the selected two horizons of each site. Mean annual concentration of each element was calculated as the average for four sampling dates in July (rainy season), August (summer), October (autumn), and November (after leaf-fall), and given in Table 3.1. They are summarized as follows:

1) The seasonal variations of the Na, K, Mg, and Cl concentrations were conspicuous with peak concentrations after October.

2) The concentration of NO_3 in the Sw-1, Sw-2, and Sw-3 profiles was much higher than that in the N-1b, and H-1a profiles. In N-4b, the concentration of NO_3 sharply increased after summer with a limited fall of pH. In Sw-1, Sw-2, and Sw-3, the temporal pattern in the A and B horizons was opposite to that of the pH, that is, the pH of the soil solution fell as the NO_3 concentration rose. Therefore, NO_3 was considered to be, at least to some extent, responsible for the decrease of the pH through nitrification.

3) The Ca and SO_4 concentrations did not show a clear seasonal variation.

4) The Si concentration did not show any clear seasonal variations. In the B horizons, Si concentration was relatively stable throughout the sampling period and the Si concentration in the soil solution from the Sw-1, Sw-2, and Sw-3 profiles was higher than that from N-4b, N-1b, and H-1a profiles. Therefore, the weathering process and/or the destruction of clay minerals in the former profiles was considered to be more active as compared to the latter.

5) The concentration of Fe and Al did not show any clear seasonal variations and were generally high under the condition of pH lower than 5 (Fig. 3.2; 3.3). The Fe concentration in the soil solution from the podzolic soils (N-4b, H-1a, Sw-1, and Sw-3 profiles) was clearly high in the surface horizons and sharply decreased in the Bs horizons, indicating the presence of eluviation from the A horizons and illuviation in the B horizons (Fig. 3.3). The temporal pattern in the A horizons seemed to be in phase with that of the concentration of DOC.

The Al concentration in the soil solution from the N-4b, H-1a, Sw-1, Sw-2, and Sw-3 profiles was high in the A horizons and varied with the pH of the soil solution on the sampling dates. The Al concentration also generally decreased in the Bs or Bw horizons, though it sometimes remained high even in the B horizons when the pH of the soil solution was below 5 (Fig. 3.3). Therefore, it is considered that Al must also migrate from the A horizons to the B horizons and it seemed to penetrate into deeper horizons than Fe, when the soil solution pH remained below 5 in the B horizons.

6) The DOC concentration in the soil solution generally decreased in autumn. In the A horizons, except for N-1b, more than 1 mM L^{-1} of DOC was detected. The concentration

of DOC decreased with depth in the N-4b and H-1a profiles, while that in the Sw-1, Sw-2, and Sw-3 profiles often remained high even below the upper B horizons.

7) The pH in the A horizons, except for N-1b, was very low, mostly below 5 and often below 4.5. Its fluctuations with the sampling dates showed the same pattern at each site, suggesting that the pH of the soil solution was controlled by a factor common to all the sites, e.g. precipitation. In general, it sharply increased below the upper B horizons.

In conclusion, the composition of the soil solution showed that the environmental conditions of the Sw-1, Sw-2, and Sw-3 profiles were quite similar and apparently different from those of the N-4b, N-1b, and H-1a profiles in the following two aspects: 1) the concentration of NO_3 in the Sw-1, Sw-2, and Sw-3 profiles remained high throughout the sampling period, and was probably responsible for the decrease of soil solution pH, unlike NO_3 in the N-4b, N-1b, and H-1a profiles. 2) Si concentration in the soil solution from the B horizons of the Sw-1, Sw-2, and Sw-3 profiles was higher than that of the N-4b, N-1b, and H-1a profiles.

These differences were considered to be related to the appearance of a litter layer at each sampling site, that is, a coarse, scarcely degraded litter of *Cryptomeria japonica* accumulated on the ground in the Sw-1, Sw-2, and Sw-3 profiles, unlike in the N-4b, N-1b, and H-1a profiles.

Based on the distribution patterns of Fe and Al in the soil solution, it was considered that the N-4b, H-1a, Sw-1, and Sw-3 profiles were currently undergoing an active process of podzolization.

3.5 Ion balance and the nature of DOC in the soil solution

In most cases, the sum of the cations exceeded the sum of the anions. It was considered that a greater part of the sum of positive charges in the soil solution consisted of the cations measured in this study, namely, Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Al^{3+}, and H^+. Therefore, the deficit of the sum of anions relative to the sum of cations was assumed to be equal to the amount of anions not measured as such in this study.

As for the inorganic anions, a small amount of HCO_3^- (pKa=6.35) may be present at a pH below 5 in the surface horizons, for which the deficit was relatively large. Judging from the high value of the DOC concentration in the soil solution with a pH below 5, it was assumed that a fairly large quantity of organic acids was present in the soil solution. Thus, especially in the soil solution from the A horizons of the podzolic soils, it was assumed that a large part of the anion deficit could be ascribed to the negative charges originating from the dissociation of acidic functional groups of DOC.

3.6 Translocation of Fe and Al in the soil profiles

Judging from the results, the low pH of the soil solution below 5 is considered to depend on the H^+ supply originating from DOC dissociation and/or nitrification. Since the Fe

and Al solubility in the soil solution remarkably increased at a pH below 5 in the surface horizons, it was considered that such a low pH was responsible for Fe and/or Al eluviation (Fig. 3.2). For Al, the decrease of its concentration in the B horizons always accompanied a pH rise, suggesting that progress of hydrolytic reaction as a result of acid neutralization might control Al illuviation in the subhoizons (Fig. 3.3). This issue is discussed in detail in Chapter 4 and 7. On the other hand, some factors other than solution pH were considered to be involved in the active Fe eluviation in the area, because a small quantity of Fe was present in the soil solution from the AB horizon of Sw-2 or the Bs horizon of N-4b in spite of the low solution pH in that horizon. This issue is discussed in Chapter 5.

3.7 Forming processes of the surface and B horizons in relation to dynamics of dissolved organic matter in the profiles

Surface horizons: In view of the low value of (Feo+Alo) in the E horizons of H-1a (0.43 %), Sw-1 (0.74 %), and Sw-3 (0.52 %), the eluviation of Fe and Al must have been active in these horizons. The low pH and high concentrations of Fe and Al in the soil solution from the E horizons showed evidence of an on-going eluviation of Fe and Al. Moreover, it was unlikely that DOC originating from the litter layer would be immobilized in such eluvial E horizons as they are poor in Fe and Al amorphous components. Thus, a large part of DOC may migrate into the B horizons along with Fe and Al, though the mode of interaction in the soil solution remains to be elucidated.

On the contrary, in the N-4b, N-1b, and Sw-2 profiles, a small quantity of Fe and Al has been eluviated and a large amount of (Feo+Alo) still remains in the A horizons (1.95, 3.08, and 2.03 %, respectively). Consequently, a part of supplied DOC has been immobilized in the surface horizons leading to gradual formation of humus-rich A horizons of the brown forest soils. However, the present analysis of the soil solution has shown that Fe and Al in the AB horizon of N-4b and Al in the AB horizon of Sw-2 are being actively eluviated. Therefore, it is possible that the AB horizon of N-4b and even that of Sw-2 would eventually develop into clear eluvial horizons.

Illuvial B horizons: In the illuvial Bs horizons of the podzolic soils, a large amount of DOC comparable to that found in the A horizons was often detected in the soil solution (Fig. 3.1 and Table 3.1). For example, in the soil solution from the Bs horizon of Sw-1 the DOC was as much as 78 % of the amount in the E horizon. A similar figure of 61 % was recorded for Sw-3, while it was 22 % for N-4b and 16 % for H-1a. Therefore, the amount of DOC that was immobilized in the Bs horizons of Sw-1 and Sw-3 was smaller than that in N-4b and H-1a.

This difference in the behavior of DOC could be partly ascribed to the quantity of amorphous components in the soil solid phase, that is, the capacity to immobilize DOC by sorption on amorphous components must be higher in the B horizons of N-4b (Feo+Alo = 4.54 %) and H-1a (4.28 %) than in those of Sw-1 (3.10 %) and Sw-3 (2.11 %). This assumption would also account for the fact that a large amount of DOC ran through the B horizon of Sw-2 (2.26 %).

Dynamics of DOC in the soil profiles: It was quite unique that DOC in the soil solution often did not simultaneously accumulated with Fe and/or Al in the B horizons especially in the Sw-1, Sw-2, and Sw-3 profiles. This fact was inconsistent with the organo-mineral theory, in which a co-precipitation of Fe and/or Al with DOC was postulated. The dynamics of DOC in the soil profiles appeared to be better explained in reference to the distribution of the amorphous compounds in the soil solid phase. The nature and dynamics of dissolved organic matter will be further discussed in Chapter 6.

3.8 Conclusion

The soil solution composition has clearly shown that podzolization is an on-going soil-forming process.

In the eluvial E horizon of the podzolic soils, Fe and Al occurred in a large amount in the soil solution, which has a low pH and high contents of DOC and NO_3. Whereas in the B horizons the amount of Fe and Al was smaller and the pH of the soil solution was high. These observations indicate that the examined profiles are undergoing an active process of podzolization.

It is considered that an acidification by H^+ originating from DOC dissociation and/or nitrification is indispensable for podzolization. The pH of the soil solution may be the factor which determines intensity of eluviation of Fe and/or Al from the A horizons. The soil solution pH per se could also be a factor contributing to the differentiation of podzolic soils from brown forest soils.

On the other hand, along with an increase of the soil solution pH in the illuvial Bs horizons, the Fe and/or Al concentration clearly decreased with or without a concomitant decrease of the amount of DOC. This phenomenon indicates that the co-precipitation of Fe and/or Al with DOC does not necessarily occur and that the solubility of Fe and/or Al in the soil solution may be mainly controlled by the pH rather than the quantity of DOC.

Table 3.1. Mean annual values[a] of pH and concentrations of each element in the soil solution.

Site and horizon	Depth (cm)	pH	Fe ($*10^{-2}$ mmol L^{-1})	Al ($*10^{-2}$ mmol L^{-1})	DOC (mmol L^{-1})
N-4b (podzolic soil)					
AB	10	4.36	0.79	4.40	2.1
Bs	20	4.66	0.13	2.23	0.5
Bw2	40	5.21	0.04	0.62	0.2
BC	60	5.69	0.02	0.38	0.3
N-1b (brown forest soil)					
A	10	5.27	0.04	0.63	0.2
Bw	20	5.29	0.02	0.35	0.2
Bw	40	5.51	0.02	0.27	0.2
BC	60	5.79	0.03	0.28	0.2
H-1a (podzolic soil)					
E	10	4.36	1.20	5.35	2.4
BE	20	4.84	0.41	2.46	0.8
Bs2	40	5.08	0.20	2.10	0.4
BC	60	5.36	0.07	1.35	0.2
Sw-1 (podzolic soil)					
E	5	4.08	0.34	2.90	1.8
EB	15	4.36	0.22	1.72	1.7
Bs	40	4.75	0.13	1.20	1.4
BC	60	5.12	0.07	0.75	1.1
Sw-2 (brown forest soil)					
AB	5	4.58	0.07	3.13	1.3
BA	20	4.69	0.04	2.66	1.1
Bw	40	5.59	0.03	0.43	1.4
BC	60	6.05	0.03	0.42	1.9
Sw-3 (podzolic soil)					
E	10	4.11	0.57	3.73	2.4
EB	15	4.44	0.57	2.96	2.1
Bs	40	4.74	0.10	2.27	1.5
Bs	60	5.09	0.08	1.33	1.6

[a]Averages in July 8, Aug. 27, Oct. 5, and Nov. 3, 1988 for N-4b, N-1b, and H-1a, and in July 15, Aug. 17, Oct. 25, and Nov. 29, 1989 for Sw-1, Sw-2, and Sw-3.

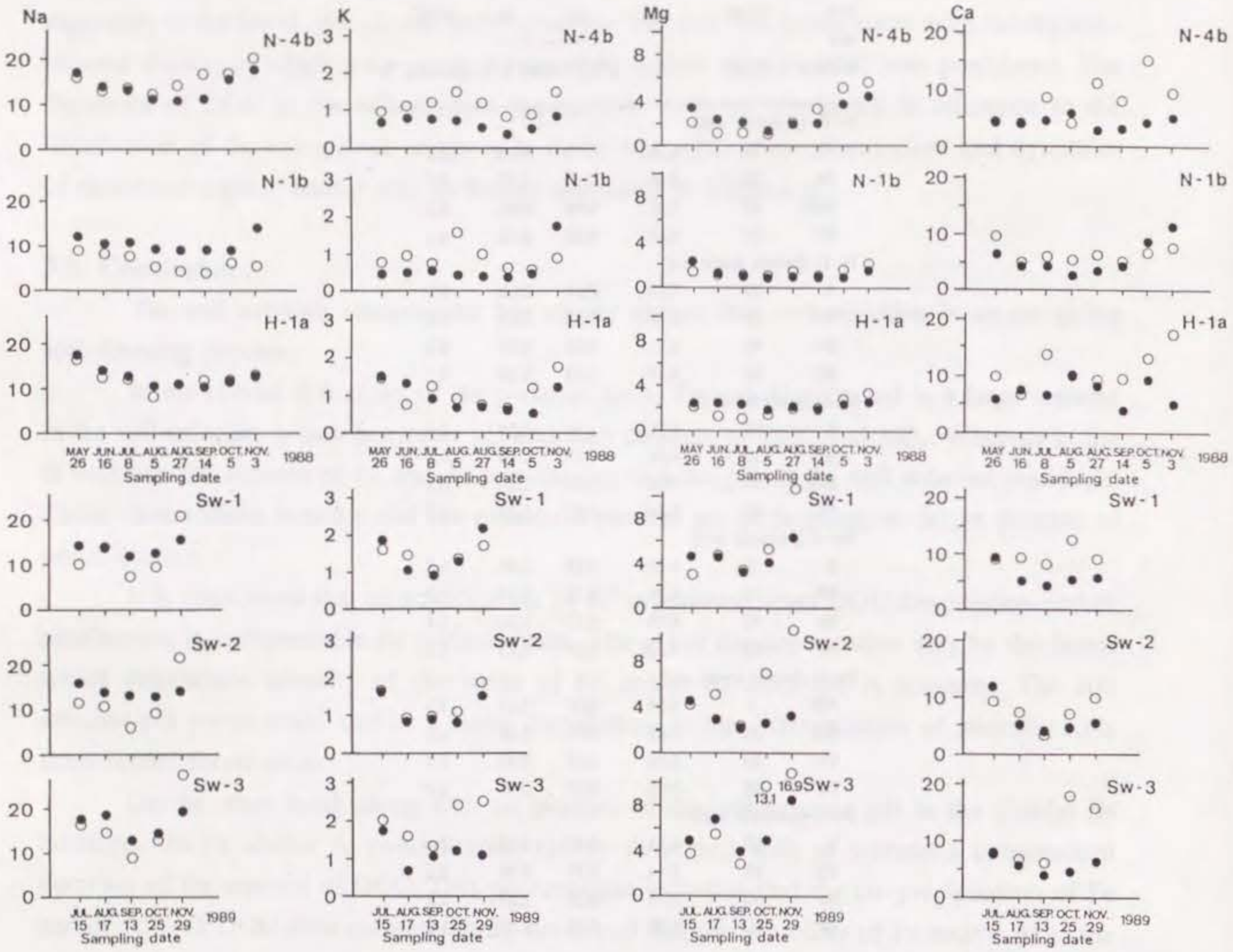


Fig. 3.1. Seasonal variations of each component in the soil solution from the surface (○) and the B (●) horizons: the surface horizons correspond to the A horizon of N–1b, the AB horizons of N–4b and Sw–2, and the E horizons of H–1a, Sw–1, and Sw–3, whereas the B horizons correspond to the Bw horizons of N–1b and Sw–2 the Bs horizon of N–4b, H–1a, Sw–1, and Sw–3.

Na, K, Mg, Ca: *10^{-2} mmol(+) L^{-1}; Cl, NO_3, SO_4: *10^{-2} mmol(−) L^{-1}; Fe, Al, Si: *10^{-2} mmol L^{-1}; DOC: mmol L^{-1}

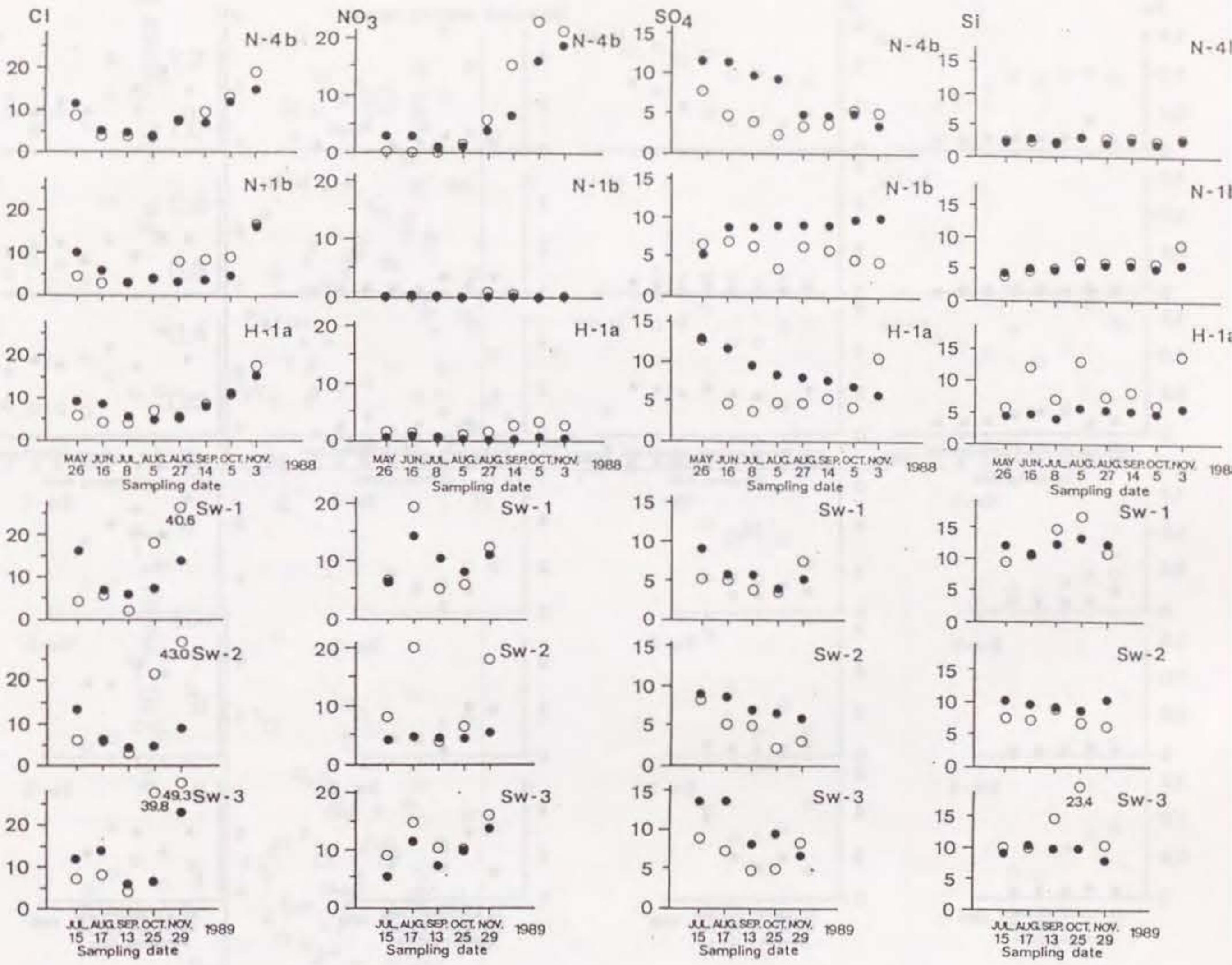


Fig. 3.1. (continued)

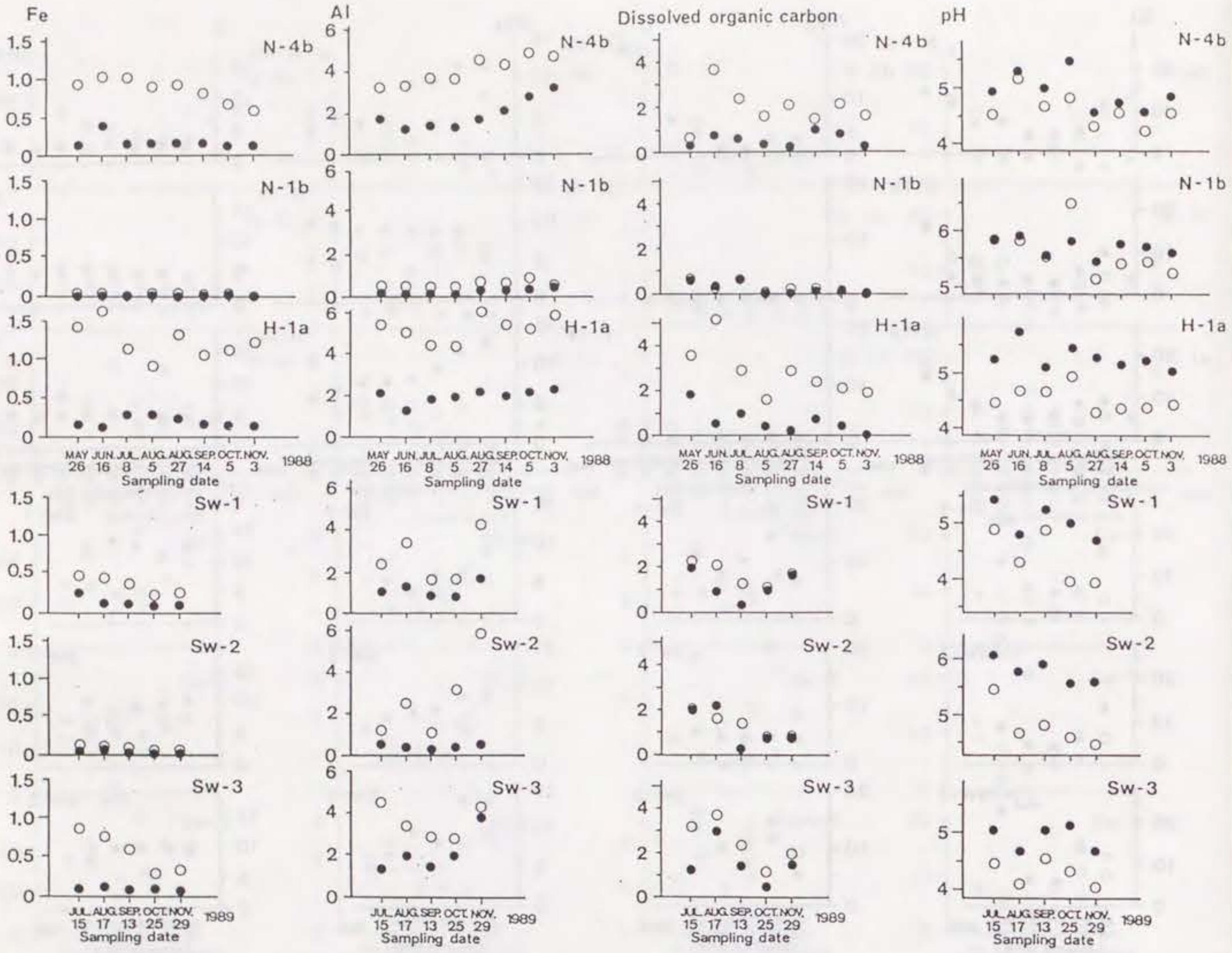


Fig. 3.1. (continued)

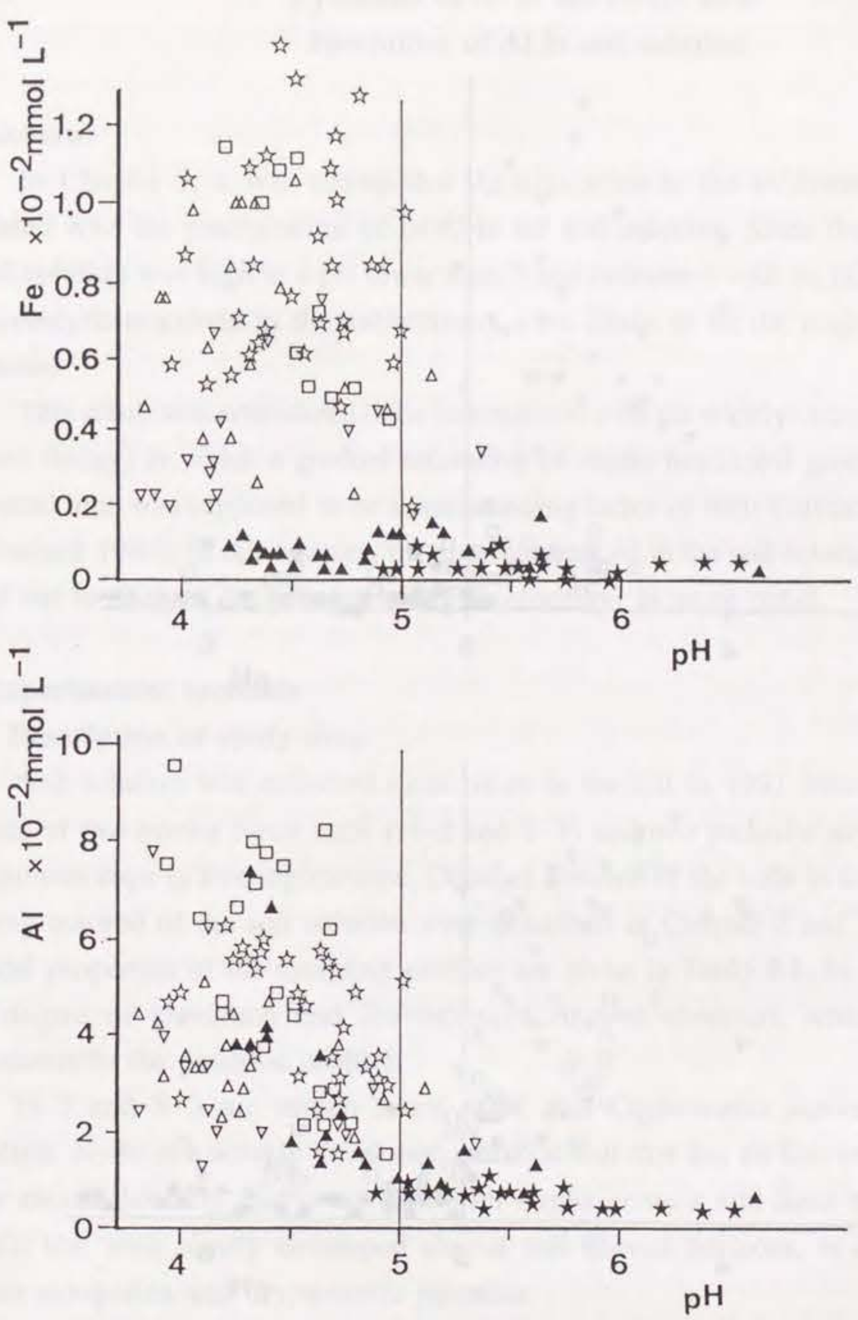


Fig. 3.2. Relationship between pH and Fe or Al concentration in the soil solution from each surface horizon.

☆, N-4b; ★, N-1b; □, H-1a; ▽, Sw-1; ▲, Sw-2; △, Sw-3.

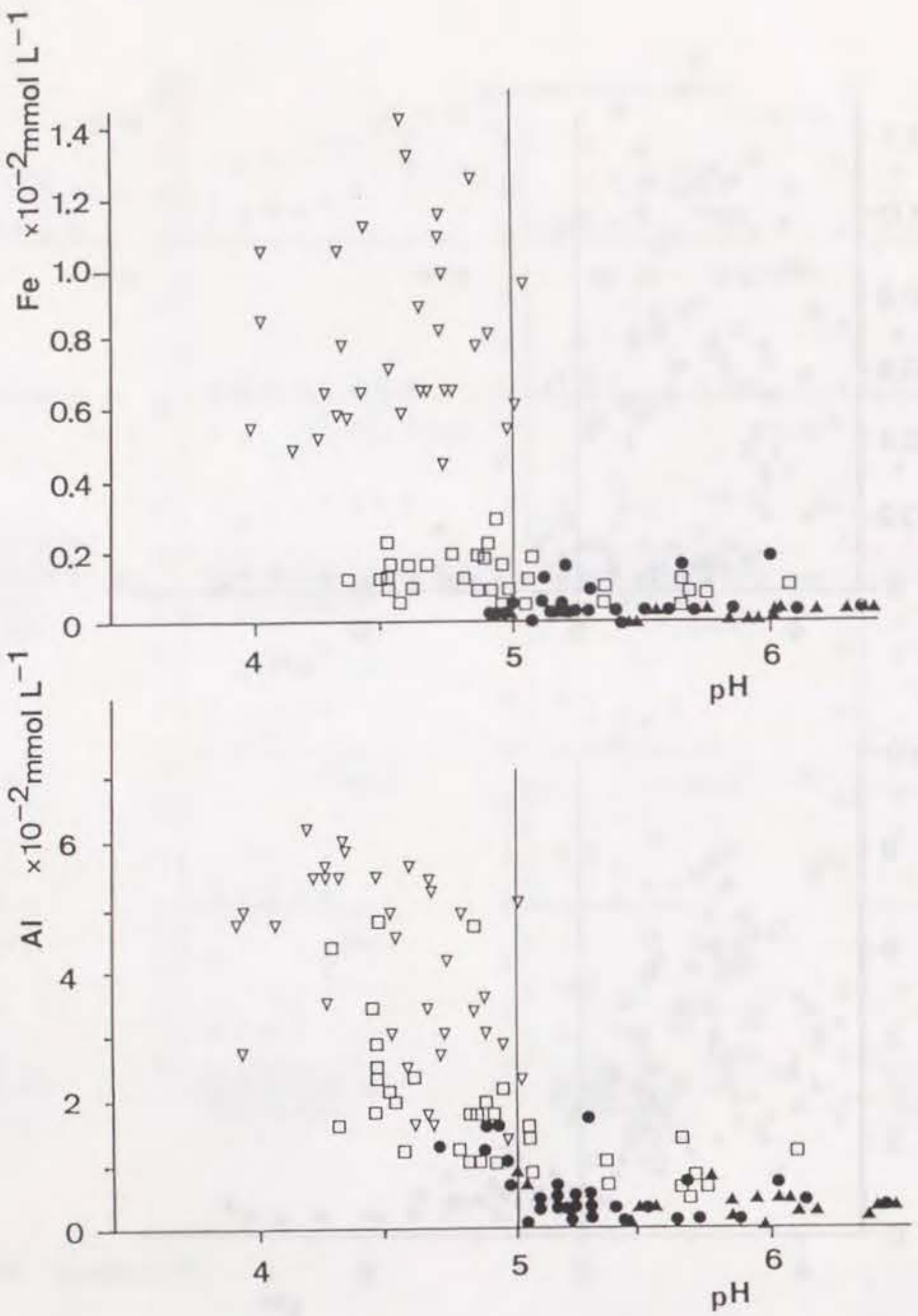


Fig. 3.3. Relationship between pH and Fe or Al concentration in the soil solution from the N–4b profile.

▽, AB hor.; □, Bs hor.; ●, Bw2 hor.; ▲, BC hor.

Chapter 4
Dynamics of Al in the forest soils: Speciation of Al in soil solution

4.1 General

In Chapter 3, it was shown that Al illuviation in the subhorizons was not always associated with the precipitation of DOC in the soil solution. Since the Al concentration in the soil solution was high at a pH lower than 5 and decreased with an increase of the solution pH, hydrolytic reactions in the subhorizons were likely to be the major mechanisms of Al illuviation.

This result was considered to be inconsistent with the widely–accepted organo–mineral complex theory, in which a gradual saturation of acidic functional groups of organic matter with metal ions was supposed to be a commanding factor of their illuviation in the B horizons (De Coninck 1980). In this chapter, the speciation of Al in the soil solution of forest soils was carried out to analyze the process of Al translocation in more detail.

4.2 Experimental methods

4.2.1 Description of study sites

Soil solution was collected three times in the fall of 1991 from three representative horizons of two brown forest soils (H–2 and S–3) and two podzolic soils (N–4b and H–1b) using porous cups in five replications. Detailed features of the soils in this study area and the sampling method of the soil solution were described in Chapter 2 and 3. Selected physico–chemical properties of the sampling profiles are given in Table 4.1. In most of the profiles, some degree of eluviation and illuviation of Al was observed, whereas that of Fe was conspicuous to the podzolic profiles.

H–2 and S–3 are brown forest soils, and *Cryptomeria japonica* is the dominant vegetation. N–4b is a weakly developed podzolic soil that has an illuvial Bs horizon without a clear eluvial horizon, and is covered with *Fagus crenata* and *Sasa* sp. H–1b, which is a podzolic soil with clearly developed eluvial and illuvial horizons, is covered mainly with *Quercus mongolica* and *Cryptomeria japonica*.

4.2.2 Analytical methods

Soil solution composition: The pH of the sample solution was measured within one day after sampling. Thereafter, the samples were filtered with a 0.45 μm membrane filter, and then used for the measurement of each ionic species. The contents of sodium (Na), potassium (K), ammonium (NH_4), magnesium (Mg), calcium (Ca), chloride (Cl), nitrate (NO_3), and sulfate (SO_4) were determined by HPLC, and the contents of iron (Fe), silicon (Si), and total aluminum (Al) were determined by ICP–AES. The amount of DOC was determined by the method of Tatsukawa (1966).

Al speciation: Based on the rate of reaction with 8–hydroxyquinoline (oxine) and reactivity to a strongly acidic cation-exchange resin, dissolved Al could be speciated into three fractions (Bloom and Erich 1989). The speciation scheme was as follows:

1) The total amount of Al dissolved in the 0.45 μm filtrate was measured by ICP-AES.

2) The total amount of monomeric Al was determined spectrophotometrically by a rapid reaction with oxine in a buffer solution at pH 8.3 (Barnes 1975; modified by LaZerte 1984). The difference between the total amount of Al dissolved and the total amount of monomeric species was assigned to strongly complexed Al, in which polymeric and/or colloidal Al would also be included.

3) The amount of Al that was not adsorbed by a partially neutralized (to pH 4.2) acidic cation-exchange resin (Duolite IR-120B) in a column was determined by the oxine method and assigned to organic monomeric species. The resin treatment was run according to the scheme developed by Hodges (1987).

4) The difference between the total amount of monomeric Al and the amount of organic monomeric Al, or the fraction retained by the cation exchange resin, was assigned to inorganic monomeric Al species. In addition, the following methods were also adopted to compare the results with the Al speciation data described above.

5) The total amount of Al in the 0.025 μm filtrate was determined by ICP-AES. The difference between the amount of Al in the 0.45 μm filtrate and that in the 0.025 μm filtrate was considered to correspond to organic and/or inorganic colloidal Al.

6) The amount of monomeric Al species was determined by a rapid reaction with oxine in a pH 5.0 buffer solution (James et al. 1983).

4.3 General characteristics of the soil solution composition

The soil solution composition is presented in Table 4.2. The amount of DOC in the soil solution appeared to be lower in autumn than in the period from spring to summer (unpublished data), but no significant difference was observed. Fe in the podzolic soils and Al in all the soils appeared to migrate through the profiles, as reported in Chapter 3. There was a significantly negative correlation between the total Al concentration and the solution pH ($R = -0.69^{***}$, $n = 86$).

Negative correlations were observed between the solution pH and NO_3 or DOC concentration ($R = -0.33^{**}$ for NO_3 and $R = -0.45^{***}$ for DOC, $n = 86$), suggesting that nitrification and/or dissociation of organic acids contributed to the decrease of the solution pH. It was considered that a high level of nitrification may occur (NO_3 content was often higher than 0.1 mmol(−) L^{-1}), which was reported to be an important internal proton load in some forested ecosystems (Van Miegroet and Cole 1984). The measured anion deficit (0.1 to 0.3 mmol(−) L^{-1}) may be attributed to the dissociation of dissolved organic acids, or of H_2CO_3 especially in the B horizons (Ugolini and Sletten 1991).

In general, the solution pH in the surface horizons was lower than that in the

subhorizons. As the soil solution percolates into the deeper horizons, H^+ may be consumed through an acid-neutralizing reaction including further monomerization and/or dissolution of Al in the soil solid phase, resulting in the increase of the pH of the soil solution. As amorphous compounds of Al, which were considered to be particularly reactive to H^+, were abundant in the horizons where the solution pH increased (Table 4.1), this fraction was considered to be mainly responsible for the proton sorption. This issue will be further discussed in Chapter 7. Moreover, the decrease of the NO_3 concentration in the soil solution from the deeper horizons suggests that nitrogen assimilation and/or denitrification were additional proton-consuming processes.

4.4 Al species in soil solution

The results of Al speciation are presented in Table 4.3. As inorganic monomeric Al was dominant in the soil solution (more than 60 % in all the profiles), it was considered to play a major role in the process of Al translocation in the profiles.

4.4.1 Inorganic Al

The concentration of inorganic monomeric Al, which was closely related to the solution pH (Fig. 4.1), was high in the surface horizon and decreased in the subhorizon along with the increase of the pH. Fig. 4.2 shows the ion activities of the soil solutions along with thermodynamic data of Al hydroxides. Ion activity of Al^{3+} was calculated according to the method of Lindsay (1979). The contribution of F^-, which was typically low in natural waters (median concentration is 10^{-5} mol L^{-1} (Stumm and Morgan 1970)), was not included in this calculation. Therefore, if the molar concentration of F^- exceeded that of Al^{3+}, the Al^{3+} activity could be significantly lower than the calculated values (Driscoll et al. 1985). Based on Fig. 4.2, the soil solutions from the surface horizons were undersaturated with amorphous $Al(OH)_3$, whereas they were gradually saturated in the B horizons.

Al-Si species such as imogolite, which was often observed in the B horizons of the podzolic soils (Farmer et al. 1980; Farmer and Fraser 1982), was not included in the above discussion due to the lack of reliable thermodynamic data. The low content of Sio in this study (Table 4.1), however, indicated that such hydrolyzed Al may not be present as amorphous aluminosilicates or imogolite but as amorphous Al hydroxides in the soils. As Shoji et al. (1982) reported that allophane and imogolite were present in soils with $pH(H_2O) > 4.9$, the soils in this study area appeared to be too acidic (pH 4.2 to 4.7 in the B horizons) for the formation of these compounds.

Fig. 4.3 indicates the relationship between Al or Si in the 0.45 μm filtrate and that in the 0.025 μm filtrate. The Si content in the 0.025 μm filtrate was almost equal to that in the 0.45 μm filtrate, whereas the content of Al in the 0.025 μm filtrate was generally lower than that in the 0.45 μm filtrate. Since the contents of Fe and DOC in both filtrates showed the same pattern as that of Si, it is likely that a fairly large quantity of colloidal Al that did not combine with Si, Fe, or organic matter must have been present in the soil solution. Fig. 4.4

shows the relationship between the pH and the content of colloidal Al in the soil solution. In general, the content of colloidal Al was often high in the pH range of 4.4 to 5.2, in which inorganic monomeric Al was gradually saturated with amorphous Al (Fig. 4.2), and decreased at above pH 5 presumably due to precipitation. Thus, it was considered that inorganic monomeric Al in the soil solution gradually formed colloidal polymeric Al hydroxides as the solution pH rose, resulting in the precipitation of amorphous Al in that horizon.

The content of monomeric Al, which was determined by the oxine method at pH 5, was virtually equivalent to that of inorganic monomeric Al, as expressed by the following equation:

$$Al\mathit{ox5} = 0.897 * Al\mathit{inorg} - 0.00028 \quad (R = 0.98^{***}, n = 86) \quad \text{(Eq. 4.1)}$$

where Al*ox5* is the amount of monomeric Al determined by the oxine method in a pH 5.0 buffer solution (mmol L^{-1}) and Al*inorg* is the amount of monomeric inorganic Al (mmol L^{-1}). These results appeared to be consistent with those reported by Bloom and Erich (1989).

4.4.2 Organic Al

Organic monomeric species accounted for only a small part of the total amount of dissolved Al, except in the H-1b profile, in which almost one third of total Al consisted of organic species. The concentration of organic monomeric Al was correlated with the DOC concentration (Fig. 4.5), and was expressed by the following regression equation:

$$Al\mathit{org} = 0.000737 + 0.00324 * DOC \quad (R = 0.84^{***}, n = 86) \quad \text{(Eq. 4.2)}$$

where Al*org* is the amount of organic monomeric Al (mmol L^{-1}) and DOC is the concentration of dissolved organic carbon (mmol L^{-1}). According to the above equation, the molar ratio of DOC / organic Al was about 300. This value is very high compared with the reported values below 100 for Spodosols in the Hubbard Brook Experimental Forest, New Hampshire (Driscoll et al. 1985); and in Cascade Range, Washington (Dahlgren and Ugolini 1989), in which organically complexed Al predominated in the soil solution. In general, the ratio did not decrease in the B horizons compared to the surface horizons, suggesting that Al saturation of the organo-mineral complexes scarcely occurred as solution percolated into the deeper horizons (Table 4.3).

The characteristics of DOC and the humic substances in this study area were discussed in Chapter 6 in detail. The content of the dissociated acidic functional groups of dissolved organic matter was estimated to be about 2.2 mmol(-)/g organic matter based on the anion deficit relative to the sum of the cations in the soil solution from the eluvial horizon of six podzolic profiles. These findings indicate that only about one fifth of the dissociated acidic functional groups is bound to the Al^{3+} ion in the soil solution from the surface horizons.

For the fulvic acids in this study area, which had been considered to be especially strong complexing agents, the contents of the carboxyl and phenolic hydroxyl groups ranged from 4.2 to 6.0 and from 0.6 to 1.3 mmol/g organic matter, respectively. These values were lower than the reported typical values for soil fulvic acids in cool and temperate zones, i.e. 6.1 to 8.5 and 2.8 to 5.7 mmol/g, respectively (Stevenson 1982), suggesting that the chelating

capacity of the fulvic acids in this area is comparatively low. Moreover, the ^{1}H-NMR spectra showed that the fulvic acids in the soil solution appeared to be a mixture of simple phenolic acids, carboxylic acids, and/or polysaccharides, and scarcely contained a soil fulvic acid-like fraction consisting of phenolic components highly substituted by acidic functional groups. On the other hand, in the above-cited cases for Spodosols, a certain amount of a soil fulvic acid-like fraction was detected in the soil solution (Dawson et al. 1978). Thus, the higher ratio of DOC / organic Al in this study could be partly attributed to the lack of a strong chelating agent in the organic matter dissolved in the soil solution. Furthermore, as the surface horizons in this study area, even the E horizon of the podzolic profiles, were relatively rich in amorphous Al and Fe compounds (e.g. Alo+1/2Feo = 0.26 % (H-1b)) compared to the horizons in the Spodosols (less than 0.1 %), it is possible that a portion of DOC with a strong complexing agent was eliminated from the soil solution when the solution percolated through the surface horizons.

The organically-complexed Al content could be slightly higher than the above estimates, because the compounds were also contained in the strongly complexed Al fraction.

4.5 Al translocation in the forest soil profiles

Acid dissolution in the surface horizons and polymerization through hydrolytic reactions in the subsoils are considered to be essential for Al translocation in the soil profiles in this region. The significant contribution of NO_3 to the decrease of the solution pH and increase of Al solubility as well as the low complexing capacity of DOC in this area appears to be unique compared with the studies on dissolved Al species in Spodosols reported by Driscoll et al. (1985) and Dahlgren and Ugolini (1989). According to the USDA system, the soils in this study area exhibit a mesic soil temperature regime, while the Spodosols have a cryic or frigid regime (Soil Survey Staff 1990). Assuming that the lack of a soil fulvic acid-like fraction with a high chelating capacity in dissolved organic matter caused by the increase of the degradation of organic matter and the presence of a large amount of NO_3 (nitrification) are due to a higher microbial activity, the high level of acidity and Al translocation in this study area may be characterized as processes of 'warmer temperature type' compared with the pedogenesis in the Spodosols.

Since Hirai et al. (1991) reported that the enrichment of amorphous Al in the subsoils due to a weak podzolization was generally observed in cool temperate forest soils, the translocation of Al in the processes described above may be involved in the pedogenetic processes of these soils. Further investigations on the dynamics of DOC and nitrogen in various forested ecosystems are necessary to analyze the processes of acidification and Al translocation in forest soils.

4.6 Conclusion

Speciation of Al in the soil solution from brown forest soils and podzolic soils in the northern Kyoto region was carried out.

In the soil solution, more than 60 % of dissolved Al consisted of inorganic monomeric species, whereas only a minor portion consisted of organically-complexed or polymeric Al. The concentration of the organic species was correlated with that of dissolved organic carbon, whereas the concentration of inorganic monomeric Al was controlled by the pH of the soil solution. Based on the ion activities of the soil solutions along with thermodynamic data of the soil minerals, the soil solutions were gradually saturated with amorphous $Al(OH)_3$ in the illuvial B horizons. A certain amount of Al was detected in a colloidal fraction without Si component especially in the soil solutions with high Al saturation, suggesting that polymeric Al hydroxides may be the major products of the hydrolytic reactions.

These results suggest that Al translocation in the soil profile in this region occurs mainly in the form of inorganic Al species. The large amount of NO_3 as well as organic acids may be responsible for the decrease of the pH of the soil solution in the surface horizons. Al is considered to be eluviated from the surfaces due to soil acidification, and precipitate as a result of a hydrolytic reaction associated with the increase of the soil solution pH in the subhorizons.

Table 4.1. Selected physico-chemical properties of sampled soils.

Site and horizon	Depth (cm)	pH H₂O	pH KCl	pH NaF	Exchangeable[a] Al (cmol(+) kg⁻¹)	total[a] carbon	Cp[a]	Alo[a]	Alp[a]	Feo[a]	Fep[a]	Sio[a]
						(*10⁻² kg kg⁻¹)						
H-1b (podzolic soil)												
A	0-9	3.69	2.94	6.47	6.5	28.1	6.36	0.37	0.36	0.44	0.39	0.02
E	9-19	3.67	2.87	7.24	7.9	2.9	0.87	0.19	0.16	0.14	0.12	0.03
Bs1	19-22	3.88	3.24	8.56	16.7	5.4	3.51	0.67	0.54	2.20	1.26	0.02
Bs2	22-36	4.18	3.65	9.62	8.9	4.2	2.71	0.88	0.66	1.60	0.89	0.05
BC	36-49	4.30	3.77	10.16	7.5	3.3	2.12	0.72	0.66	0.79	0.70	0.03
N-4b (podzolic soil)												
A	0-6	3.59	2.88	6.72	8.7	21.3	4.35	0.39	0.24	0.57	0.60	0.02
AB	6-12	3.76	2.94	7.48	14.6	10.2	3.77	0.51	0.37	1.44	1.18	0.06
BA	12-15	3.84	3.21	8.38	14.6	5.8	2.65	0.61	0.40	2.16	1.44	0.03
Bs	15-30	4.05	3.52	8.95	12.4	5.3	3.06	1.06	0.72	3.48	1.42	0.04
Bw1	30-40	4.36	3.85	10.16	6.9	2.1	1.10	1.01	0.59	2.05	0.84	0.06
Bw2	40-52	4.49	3.97	10.29	6.7	1.5	1.04	0.98	0.55	1.08	0.58	0.10
BC	52-83	4.49	4.01	10.35	5.8	1.5	1.01	1.01	0.59	0.99	0.51	0.06
C	83-100	4.57	4.05	10.81	4.7	1.3	0.75	1.12	0.57	1.10	0.42	0.15
H-2 (brown forest soil)												
A	0-6	3.78	3.25	7.89	12.2	11.5	3.37	0.79	0.57	1.66	1.12	0.02
AB	6-14	4.00	3.47	8.69	12.1	7.5	3.11	0.83	0.68	1.82	1.37	0.04
BA	14-28	4.25	3.72	9.44	9.2	4.9	1.99	0.90	0.79	1.95	1.83	0.03
Bw	28-48	4.50	3.90	9.90	6.4	1.8	1.03	0.77	0.71	1.15	1.00	0.06
BC	48-57	4.65	3.95	9.92	5.3	1.3	0.67	0.66	0.57	0.67	0.64	0.07
S-3 (brown forest soil)												
A	0-8	3.50	2.92	6.91	13.4	22.6	6.45	0.69	0.61	1.18	1.07	0.02
AB1	8-21	4.31	3.55	9.43	10.8	8.8	4.04	1.14	1.16	2.06	2.20	0.02
AB2	21-34	4.56	3.89	10.78	6.4	6.1	3.14	1.51	1.38	2.08	1.56	0.08
BA	34-48	4.67	4.01	11.12	4.5	4.6	2.39	1.68	1.38	1.68	1.25	0.14
Bw	48-70	4.65	3.95	10.66	4.5	1.7	1.06	1.14	0.72	1.01	0.49	0.11
BC	70-95	4.66	3.96	10.42	4.3	1.1	0.60	0.98	0.59	0.88	0.54	0.15

[a]Oven-dried basis.

Table 4.2. Composition of sampled soil solution in autumn, 1991.

Site and horizon	pH	DOC	Fe	Al	Si	Na	K	NH_4	Mg	Ca	Cl	NO_3	SO_4	Anion deficit*
		(mmol L^{-1})	(*10^{-2} mmol L^{-1})			(*10^{-2} mml(+) L^{-1})					(*10^{-2} mmol(−) L^{-1})			
H-1b (podzolic soil)														
E	3.90	2.4	0.40	5.86	10.28	19.92	1.67	0.12	16.90	13.02	38.94	28.87	2.95	11.84
Bs1	4.56	2.1	0.60	3.15	7.03	25.39	2.12	0.26	7.93	9.52	22.22	8.98	7.64	19.78
BC	4.66	1.1	0.08	2.78	4.98	22.45	1.67	0.11	7.52	7.45	17.49	10.19	7.68	14.53
N-4b (podzolic soil)														
AB	4.48	0.7	0.15	3.01	2.30	16.10	1.28	1.01	7.80	5.91	19.57	6.99	2.31	15.87
Bs	4.74	0.2	0.13	2.25	3.16	17.60	1.56	0.29	8.19	6.27	16.21	8.36	3.00	15.17
Bw2	5.07	0.3	0.01	0.81	3.12	19.90	1.28	0.31	5.52	4.83	13.39	1.77	5.78	14.20
H-2 (brown forest soil)														
AB	4.46	0.3	0.06	4.50	4.14	28.52	3.84	0.27	15.79	20.30	36.61	19.18	6.86	23.16
Bw	4.81	0.2	0.01	2.94	4.21	20.10	1.52	0.07	11.81	22.46	23.71	17.45	2.83	22.36
BC	5.08	0.0	0.01	0.69	3.93	16.52	0.99	0.00	7.29	13.52	13.55	4.88	5.41	17.40
S-3 (brown forest soil)														
AB1	4.52	0.9	0.04	6.11	6.53	21.97	1.99	0.24	16.69	28.96	30.28	31.65	6.37	22.98
BA	4.83	0.5	0.02	3.08	4.65	29.68	2.25	0.14	14.44	32.17	16.91	34.30	13.81	24.42
Bw	5.18	0.8	0.02	1.24	5.78	28.58	3.18	0.31	14.80	35.80	23.98	22.94	13.12	27.05

*Anion deficit is calculated as the difference between the sum of cations (H^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, and Al^{3+}) and sum of anions (Cl^-, NO_3^-, and SO_4^{2-}).

Table 4.3. Speciation of Al in the soil solution.

Site and horizon	pH	DOC	inorganic monomeric Al	organic monomeric Al	strongly complexed Al	monomeric Al (pH 5)	colloidal Al	DOC/ organic Al*
		(mmol L^{-1})	(*10^{-2} mmol L^{-1})			(*10^{-2} mmol L^{-1})		
H-1b (podzolic soil)								
E	3.90	2.4	4.05	1.10	0.71	4.22	0.00	215
Bs1	4.56	2.1	2.03	0.77	0.35	2.00	0.31	268
BC	4.66	1.1	2.05	0.46	0.27	1.91	0.66	235
N-4b (podzolic soil)								
AB	4.48	0.7	2.28	0.50	0.22	2.01	0.47	136
Bs	4.74	0.2	1.85	0.17	0.23	1.52	0.48	118
Bw2	5.07	0.3	0.72	0.05	0.04	0.54	0.27	600
H-2 (brown forest soil)								
AB	4.46	0.3	4.10	0.25	0.15	3.13	0.28	120
Bw	4.81	0.2	2.64	0.06	0.24	2.16	0.43	283
BC	5.08	0.0	0.50	0.02	0.17	0.35	0.30	0
S-3 (brown forest soil)								
AB1	4.52	0.9	5.15	0.45	0.51	5.14	0.44	193
BA	4.83	0.5	2.51	0.10	0.47	2.30	0.55	500
Bw	5.18	0.8	0.78	0.13	0.33	0.70	0.22	646

*Atomic ratio.

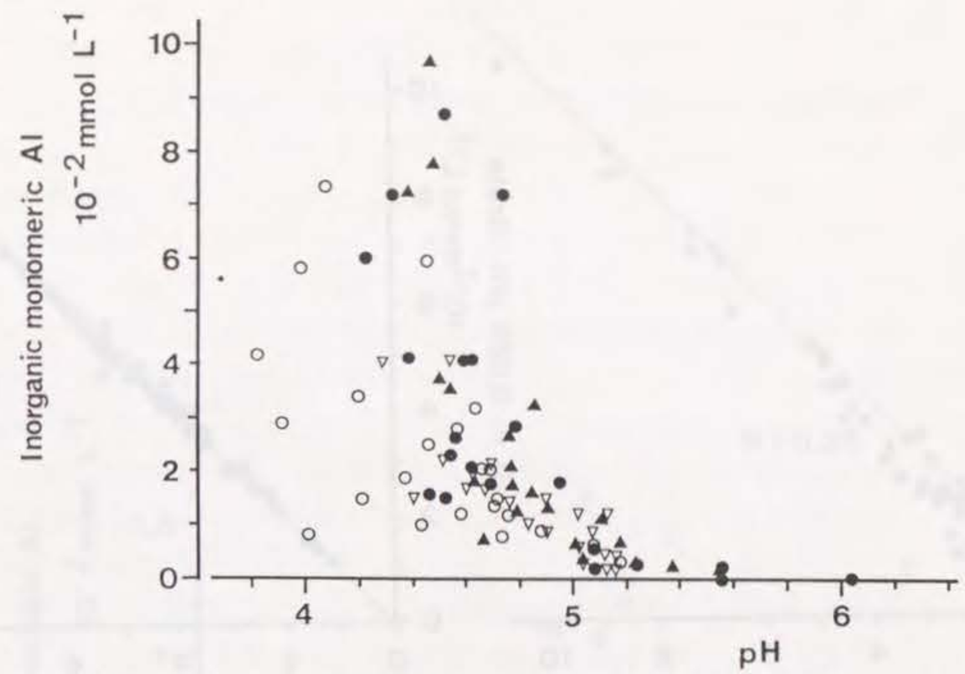


Fig. 4.1. Relationship between pH and inorganic monomeric Al concentration in the soil solution.

○ H-1b; ▽ N-4b; ● H-2; ▲ S-3

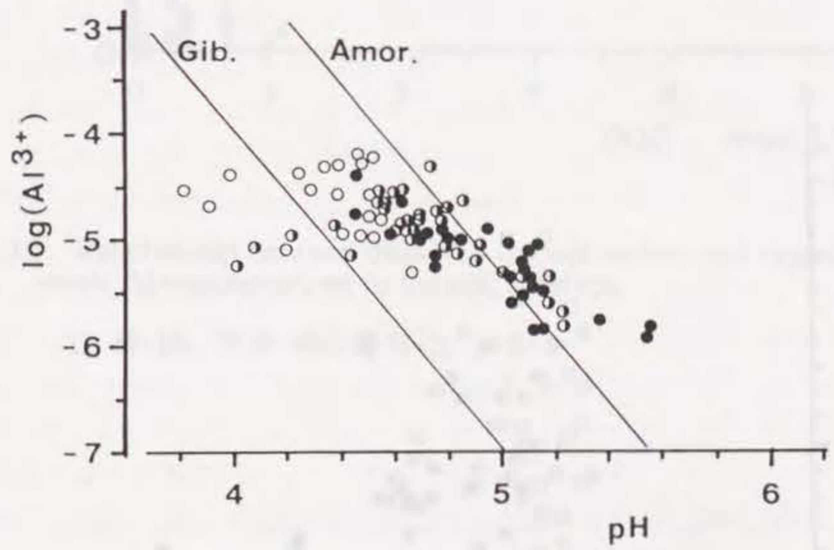


Fig. 4.2. Ion activities of soil solutions from each horizon superimposed on a solubility diagram of gibbsite and amorphous $Al(OH)_3$. (Al^{3+}) represents the ion activity of inorganic monomeric Al. Thermodynamic data were cited from Lindsay (1979).

○ H-1b E, N-4b AB, H-2 AB, and S-3 AB1 horizons
◑ H-1b Bs1, N-4b Bs, H-2 Bw, and S-3 BA horizons
● H-1b BC, N-4b Bw2, H-2 BC, S-3 Bw horizons

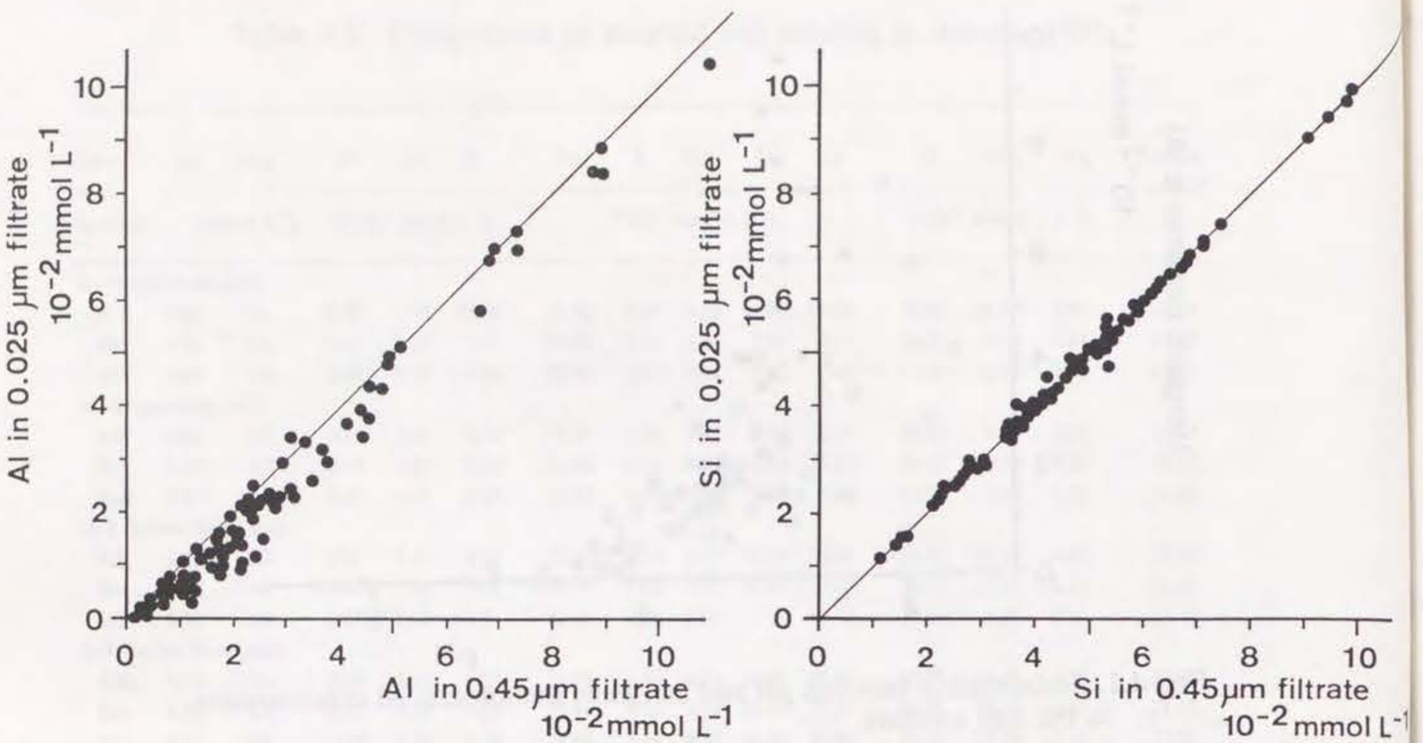


Fig. 4.3. Scattergrams between Al or Si in 0.45 μm filtrate and that in 0.025 μm filtrate.

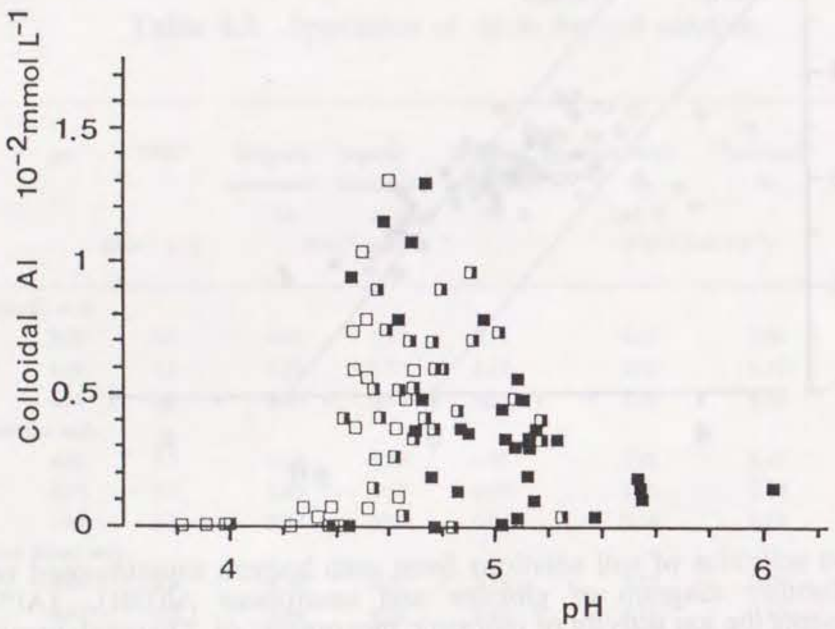


Fig. 4.4. Relationship between pH and colloidal Al in the soil solution.

□ H–1b E, N–4b AB, H–2 AB, and S–3 AB1 horizons
◨ H–1b Bs1, N–4b Bs, H–2 Bw, and S–3 BA horizons
■ H–1b BC, N–4b Bw2, H–2 BC, S–3 Bw horizons

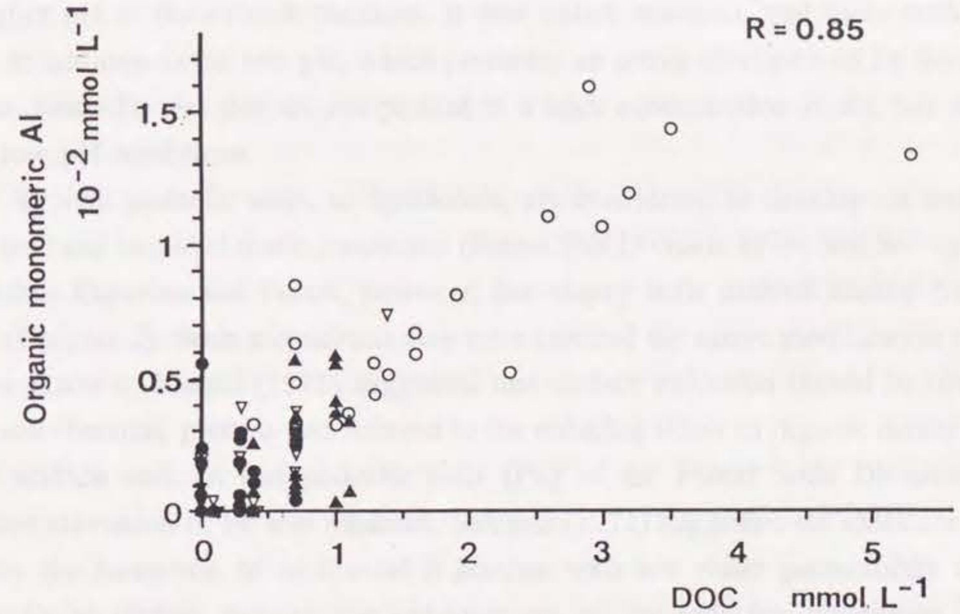


Fig. 4.5. Relationship between dissolved organic carbon and organic mono-meric Al concentrations in the soil solution.

○ H–1b; ▽ N–4b; ● H–2; ▲ S–3

Chapter 5
Dynamics of Fe in the forest soils:
Physical characteristics of the fine-textured forest soils

5.1 General

In Chapter 3, the soil solution study showed that concentrations of Al and Fe were high when the solution pH was below 5. Based on this, it was considered that acidity would be the major factor in the on-going process of podzolization; that is, the eluviation of Fe and Al is promoted by the low pH in the surface horizons and their illuviation is controlled by the higher pH in the subsoil horizons. It was noted, however, that there could be another factor, in addition to the low pH, which promotes an active eluviation of Fe from the surface horizon, since Fe was not always present at a high concentration in the soil solution even under low pH conditions.

Typical podzolic soils, or Spodosols, are considered to develop on sandy materials under cool and humid climatic conditions (Forest Soil Division 1976; Soil Survey Staff 1975). The Ashiu Experimental Forest, however, has clayey soils derived mainly from paleozoic shales (Chapter 2). Such a condition may have affected the active mobilization of Fe through a redox reaction. Matsui (1972) suggested that surface reduction should be considered as a forest soil-forming process and referred to the reducing effect of organic matter accumulated in the surface soil. In wet podzolic soils (P_W) of the Forest Soils Division (1976), the reductive eluviation of Fe was assumed. Sakuma (1971) suggested the existence of a process whereby the formation of an illuvial B horizon with low water permeability may promote further Fe eluviation through the enhancement of the reducing conditions in the upper horizons. These studies emphasize the importance of reductive eluviation of Fe in the surface horizon.

In this chapter, we will focus on the physical properties and morphological characteristics of podzolic soils and brown forest soils in the Experimental Forest. Moreover, the pedogenetic processes specific to fine textured forest soils will also be discussed.

5.2 Experimental methods

5.2.1 Brief description and physico-chemical and mineralogical characteristics of the sampled soils

Eight soil profiles were investigated. Based on the Classification of Forest Soils in Japan (Forest Soil Division 1976), N-4b, H-1b, Sw-1, and Sw-4 were classified as Podzolic soils (P_D or $P_{W(i)}$), whereas Sw-2, N-1b, H-2, and S-3 were classified as typical Brown Forest soils (B_D). Descriptions of the sampled soils are given in Chapter 2 and Appendix 1 and briefly summarized in Table 5.1. The A and AB horizons of the brown forest soils had mostly a crumb structure, while the E (H-1b, Sw-1, and Sw-4) and the AB (N-4b) horizons of the podzolic soils had a normally sub-angular blocky structure. As for the B horizons, the

Fe-illuviated Bs horizons of the podzolic soils had a sub-angular blocky structure and were more friable than the Bw horizons of the brown forest soils.

The general physico-chemical and mineralogical characteristics are given in Chapter 2 and Table 5.1, and the following comments can be made.

1) In the clay fraction, 2:1 type minerals were dominant. The detailed mineralogical characteristics were discussed by Hirai et al. (1989).

2) The pH of the sample soils was generally very low.

3) The clay content was generally high. In the well-developed B horizons, the clay content was higher than 40 %, whereas, in the E horizons of the podzolic soils, the clay content was usually lower than that in the B horizons (H-1b, Sw-1, and Sw-4), suggesting that the clay had been destroyed.

4) Based on the fact that the amorphous Al (Alo) content was higher in the B horizons than in the surface horizons, it appeared that Al translocation may have been more or less involved in the pedogenetic process of the soils of the area (Hirai et al. 1988). In the podzolic soil profiles, Fe translocation was remarkable.

5.2.2 Experimental methods

Determination of physical properties: The samples were taken using 100 cm^3 cores from the middle part of each horizon with 7 replications for the bulk density and 4 replications each for the hydraulic conductivity and the moisture characteristic curve.

1) Bulk density and true particle density: The samples were oven-dried at 105°C for at least 3 days to measure the bulk density. The true particle density was measured using the pycnometer method.

2) Saturated hydraulic conductivity: After water-saturation under decreasing pressure, the saturated hydraulic conductivity was measured using the falling-head method.

3) Determination of the moisture characteristic curve: The moisture contents at varying suctions were measured using the following methods: sand column method (1 and 3 kPa), pressure plate method (10, 30, and 100 kPa), centrifugal method ($1.6*10^3$ kPa), and air-drying at relative humidity ($3.2*10^4$ kPa).

Observation of the morphological characteristics: The soil clod samples were collected with Kubiena boxes. The samples were pre-treated by applying the modified acetone replacement method (Murphy 1986) to avoid shrinkage and, then, impregnated with polylite resin.

5.3 Physical properties and morphological features of the sampled soils

The physical properties of the sampled soils are given in Table 5.2. The moisture characteristic curves of the selected profiles (Sw-2, N-1b, N-4b, and Sw-1) are illustrated in Fig. 5.1, in which the cumulative volume of pores per 100 cm^3 was plotted against the water suction.

As evident from Table 5.2 and Fig. 5.1 for the brown forest soils (Sw-2, H-2, N-1b

and S-3), the bulk density was lower, while the volume of coarse pores (pore volume at 10 kPa) and the water permeability in terms of the saturated hydraulic conductivity were higher in the surface AB horizons than in the deeper B horizons. On the contrary, in the podzolic profiles (N-4b, H-1b, Sw-1, and Sw-4), the reverse was true. Thus, it can be concluded that the E or AB horizons of the podzolic soils are denser not only in comparison with the deeper B horizons of the same soil, but also in comparison with the AB horizons of the brown forest soils.

The thin sections of a few representative horizons (Fig. 5.2) showed a progressive compression of the surface horizons in the following order: brown forest soil (H-2) < weakly podzolized soil (N-4b) < podzolic soil (Sw-1). These findings are consistent with the physical properties of the soils described above. In Fig. 5.2c, the precipitation of oxidized Fe around the tree roots in the eluvial horizon of the podzolic soil was suggested the presence of a redox reaction.

Among the B horizons, the Bw horizons with amorphous Al accumulation had a well-developed subangular blocky structure (Fig. 5.2d), whereas the Bs horizons with Fe accumulation, in which Al was often eluviated to deeper horizons, did not have any definite structure (Fig. 5.2e), which is consistent with the field observation showing that the Bs horizons were more friable than the Bw horizons.

5.4 Formation of a dense podzolic E horizon

A comparison of the physical properties (Table 5.2) with the chemical and the mineralogical properties (Table 5.1) revealed the following aspects:

1) The dense E (H-1b, Sw-1, and Sw-4) or AB (N-4b) horizons of the podzolic soils contained either high-charge smectite or clay mica as the dominant clay minerals, whereas the 2:1-2:1:1 intergrade minerals predominated in the deeper horizons and most of the AB or BA horizons of the brown forest soils (N-1b, H-2, and S-3). Moreover, in the podzolic profiles, the clay content in the E horizon was lower than that in the well-developed B horizons, suggesting that clay was destroyed in the horizon.

2) The amorphous Al (Alo) content was remarkably lower in the podzol surface horizons (less than $0.5*10^{-2}$ kg kg^{-1}) than in the underlying B horizons or the AB horizons of the brown forest soils.

3) Horizons enriched with exchangeable Al (more than 10 cmol(+) kg^{-1}) extended deeper in the podzolic profiles than in the brown forest soils.

All these characteristics of the podzolic profiles indicated the presence of a strong soil acidification.

Based on the above discussion, it was assumed that the forming processes of the dense podzolic E horizons were as follows:

As the surface horizons became acidified, amorphous and/or interlayered compounds of Al were dissolved, resulting in an increase in the content of exchangeable Al and soil solution Al. The decrease in the content of amorphous Al, and the changes in the dominant clay mineral species from 2:1–2:1:1 intergrade to smectite resulted from this acid dissolution. As the amount of amorphous Al decreased, the crumb structure in the surface horizon became increasingly unstable.

Since the snow depth from December to April usually reaches one to three meters, it may be equivalent to a load corresponding to a 30 to 90 cm depth of soil with a bulk density of 1.0, assuming that the snow density is 0.3 g cm^{-3} (Takeuchi et al. 1969). This load may lead to the collapse of the weakened crumb structure, resulting in the formation of the dense surface horizon.

5.5 Fe translocation in the forest soil profiles

Based on the study on the soil solution composition carried out in July, 1990, since a negative correlation between the pH and Eh was detected in each horizon, the redox condition in the horizon may be expressed by the regression lines shown in Fig. 5.3. The figure indicates that the E horizon of Sw-1 and the AB horizon of N-4b displayed a more reduced condition than the B horizons of the respective soils or the AB and the Bw horizons of a brown forest soil, Sw-2. This fact suggests that Fe was eluviated under reduced conditions in the surface horizons and was illuviated in the relatively oxidative B horizons.

The soil solution study also indicated the presence of a positive correlation between the concentrations of Fe and DOC in the soil solution ($R = 0.62^{***}$, $n = 185$), suggesting the reducing effect of organic matter on Fe and/or complex formation of Fe by DOC.

Table 5.3 describes the moisture conditions at the sampling sites. The tensiometer data show that the forest soils of the area were kept at values of approximately 5 to 20 kPa. Based on Fig. 5.1 and Table 5.3, the volume of the gas phase in the E or AB horizons of the podzolic soils remained at or below 10 % during most of the year, whereas that in the AB horizon of the brown forest soils exceeded 20 % in most of the cases. Therefore, the dense features of the surface horizons of the podzolic soils may contribute to the maintenance of a relatively reduced condition.

In the AB horizon of N-4b, the concentration of Fe in the soil solution was very high ($7.9*10^{-3}$ mmol L^{-1}) (Chapter 3), but the value of Feo in the horizon was still high as compared to that in the distinctly Fe-eluviated horizons of H-1b, Sw-1, and Sw-4 (Table 5.1). Hence, this soil horizon was considered to be at an initial stage of Fe-eluviation, although it already displayed the dense and low permeability properties (the bulk density was 0.73 g cm^{-3}) in comparison with the underlying Bs horizon (the bulk density was 0.55 g cm^{-3}). These findings suggest that the formation of a dense surface horizon may precede active Fe-eluviation.

In conclusion, it was considered that the formation of the dense surface horizon enhanced active Fe-eluviation through surface reduction. A further study is necessary to demonstrate that this characteristic soil-forming process is also operating in fine-textured

podzols.

5.6 Conclusion

The physical properties and morphological characteristics of clayey podzolic soils and brown forest soils in the northern Kyoto region were studied.

These podzolic soils were characterized by dense eluvial horizons with a higher bulk density and a lower volume of coarse pores and a lower water permeability than the underlying B horizons or the surface horizons of brown forest soils. These observations suggested the presence of a close relationship between the formation of the dense surface horizons and active eluviation of Fe under reduced conditions in these horizons.

Based on the comparison of the physical properties with the chemical and mineralogical characteristics of the soils, it was assumed that the pedogenetic process of the podzolic soils in this region was as follows:

Al eluviation from the surface horizons due to strong acidification resulted in the decrease of the content of amorphous components of Al, followed by a weakening of the crumb structure. As a result, the dense surface horizons with low water permeability and relatively reduced conditions may have formed. This phenomenon may have promoted active eluviation of Fe from the surface horizons.

Table 5.1. Selected physico–chemical and mineralogical properties of the soils sampled.

Site and horizon	pH H_2O	pH KCl	ex.Al[a] (cmol(+) kg^{-1})	Alo[a] (*10^{-2} kg kg^{-1})	Feo[a] (*10^{-2} kg kg^{-1})	Particle size distribution (%) Clay	Silt	Sand	Clay mineral species[b]
Sw–2 (brown forest soil)									
A	3.82	2.91	10.8	0.69	0.95	41	47	12	H.C.Sm > Vt
AB	4.05	3.17	11.7	0.81	1.22	42	46	12	Vt > Ch, Mica
BA	4.35	3.53	8.1	0.81	1.40	45	46	10	2:1–2:1:1 int. > Ch, Mica, Kao, Gb
Bw	4.50	3.69	6.1	0.98	1.30	41	49	10	2:1–2:1:1 int. > Ch, Mica, Kao, Gb
BC	4.73	3.77	5.0	0.83	0.40	47	44	9	2:1–2:1:1 int. > Ch, Mica, Kao, Gb
C	4.68	3.70	4.7	0.48	0.33	32	39	29	2:1–2:1:1 int. > Ch, Mica, Kao, Gb
N–1b (brown forest soil)									
A	3.91	3.44	8.0	0.77	1.45	49	32	19	Vt > H.C.Sm, Mica, Kao, Ch
BA	4.22	3.80	6.3	1.01	2.07	41	39	20	2:1–2:1:1 int. > H.C.Sm, Mica, Kao, Gb
Bw	4.54	4.22	3.1	2.06	1.59	53	32	16	2:1–2:1:1 int. > Mica, Kao, Ch, Gb
BC	4.63	4.16	2.9	1.66	1.40	55	33	13	2:1–2:1:1 int. > Mica, Kao, Ch, Gb
C	4.65	4.03	3.0	0.60	0.72	34	35	31	2:1–2:1:1 int. > Mica, Kao, Gb
H–2 (brown forest soil)									
A	3.78	3.25	12.2	0.70	1.55	53	31	16	2:1–2:1:1 int., Vt > Mica, Kao
AB	4.00	3.47	12.1	0.88	1.86	55	33	12	2:1–2:1:1 int., Vt > Mica, Kao, Ch, Gb
BA	4.25	3.72	9.2	0.88	1.87	54	35	11	2:1–2:1:1 int. > Mica, Kao, Ch, Gb
Bw	4.50	3.90	6.4	0.70	1.08	52	33	15	2:1–2:1:1 int. > Mica, Kao, Ch, Gb
BC	4.65	3.95	5.3	0.52	0.55	46	33	21	2:1–2:1:1 int. > Mica, Kao, Ch, Gb
S–3 (brown forest soil)									
A	3.50	2.92	13.4	0.69	1.18	54	40	6	Sm > Kao
AB1	4.31	3.55	10.8	1.14	2.06	52	39	9	2:1–2:1:1 int. > Vt, Kao, Gb
AB2	4.56	3.89	6.4	1.51	2.08	43	46	11	2:1–2:1:1 int. > Vt, Kao, Gb
BA	4.67	4.01	4.5	1.68	1.68	48	43	8	2:1–2:1:1 int. > Vt, Kao, Gb
Bw	4.65	4.01	4.5	1.14	1.01	49	42	9	2:1–2:1:1 int. > Vt, Kao, Gb
BC	4.66	3.96	4.3	0.98	0.88	51	38	12	2:1–2:1:1 int. > Vt, Kao, Gb

[a]Oven dried basis. [b]Kao, kaolin minerals; Mica, clay mica; Sm, smectite; H.C.Sm, high charge smectite; Vt, vermiculite; Ch, chlorite; Gb, gibbsite; 2:1–2:1:1 int., 2:1–2:1:1 intergrade mineral; Mica–H.C.Sm, interstratified mineral of clay mica and high charge smectite; Mica–Vt, interstratified mineral of clay mica and vermiculite.

Table 5.1. (continued)

Site and horizon	pH H_2O	pH KCl	ex.Al[a] (cmol(+) kg^{-1})	Alo[a] (*10^{-2} kg kg^{-1})	Feo[a] (*10^{-2} kg kg^{-1})	Particle size distribution (%) Clay	Silt	Sand	Clay mineral species[b]
N–4b (podzolic soil)									
A	3.59	2.88	8.7	0.39	0.57	43	47	11	H.C.Sm > Mica, Kao
AB	3.76	2.94	14.6	0.51	1.44	43	46	11	H.C.Sm > Vt, Mica, Kao
BA	3.84	3.21	14.6	0.61	2.16	44	44	12	Vt > H.C.Sm, Kao
Bs	4.05	3.52	12.4	1.06	3.48	55	36	9	2:1–2:1:1 int. > Vt, Kao, Gb
Bw1	4.36	3.85	6.9	1.01	2.05	47	36	17	2:1–2:1:1 int. > Mica, Kao, Gb
Bw2	4.49	3.97	6.7	0.98	1.08	46	46	8	2:1–2:1:1 int. > Mica, Kao, Gb
BC	4.49	4.01	5.8	1.01	0.99	52	41	7	2:1–2:1:1 int. > Mica, Kao, Gb
C	4.57	4.05	4.7	1.12	1.10	47	37	16	2:1–2:1:1 int. > Mica, Kao, Gb
H–1b (podzolic soil)									
A	3.69	2.94	6.5	0.37	0.44	40	40	20	Mica > H.C.Sm, Vt, Kao
E	3.67	2.87	7.9	0.19	0.14	33	40	27	Mica > H.C.Sm, Kao
Bs1	3.88	3.24	16.7	0.67	2.20	40	29	31	H.C.Sm > Vt, Mica, Kao, Gb
Bs2	4.18	3.65	8.9	0.88	1.60	40	27	33	2:1–2:1:1 int. > Kao, Gb, Mica
BC	4.30	3.77	7.5	0.72	0.79	36	27	37	2:1–2:1:1 int. > Ch, Kao, Gb, Mica
Sw–1 (podzolic soil)									
A	3.43	2.37	6.9	0.27	0.24	31	35	34	Mica–H.C.Sm > Kao
E	3.65	2.60	13.4	0.30	0.44	33	36	31	Mica–H.C.Sm > Kao
EB	3.97	2.99	17.8	0.49	1.38	41	33	26	Mica–H.C.Sm, Mica–Vt > Kao
Bs	4.20	3.19	15.6	0.82	2.28	50	31	19	Vt, 2:1–2:1:1 int. > Mica, Kao, Gb
BC	4.58	3.58	6.3	0.92	1.44	34	28	38	2:1–2:1:1 int. > Mica, Kao, Gb
C	4.71	3.95	2.5	0.83	0.40	17	16	67	2:1–2:1:1 int., Mica > Kao, Gb
Sw–4 (podzolic soil)									
A	3.19	2.50	5.0	0.30	0.22	27	34	39	Mica > H.C.Sm, Kao
E	3.51	2.89	8.9	0.15	0.12	29	31	40	Mica > H.C.Sm, Kao
EB	3.73	3.06	15.0	0.37	0.49	32	29	39	Mica–H.C.Sm > Kao
Bs	3.90	3.35	16.8	0.79	1.77	41	27	32	2:1–2:1:1 int. > Mica, Kao, Gb
C	4.21	3.62	7.7	0.53	0.82	29	31	40	2:1–2:1:1 int. > Mica, Kao, Gb

[a]Oven dried basis. [b]Kao, kaolin minerals; Mica, clay mica; Sm, smectite; H.C.Sm, high charge smectite; Vt, vermiculite; Ch, chlorite; Gb, gibbsite; 2:1–2:1:1 int., 2:1–2:1:1 intergrade mineral; Mica–H.C.Sm, interstratified mineral of clay mica and high charge smectite; Mica–Vt, interstratified mineral of clay mica and vermiculite.

Table 5.2. Physical properties of sampled soils.

Site and horizon	Depth (cm)	Particle density[a] (g cm^{-3})	Bulk density[b] (g cm^{-3})	Saturated hydraulic conductivity[bc]	Coarse porosity[bd] (*10^{-2} m^3 m^{-3})
Sw-2 (brown forest soil)					
AB-BA	2-25	2.51	0.64	3.3	16.7
Bw	25-50	2.59	0.83	3.7	6.2
BC	50-73	2.64	0.87	5.4	6.0
N-1b (brown forest soil)					
BA	5-19	2.46	0.58	2.0	23.9
Bw	19-55	2.57	0.72	2.2	15.4
BC	55-86	2.64	0.81	2.6	15.2
H-2 (brown forest soil)					
AB	6-14	2.13	0.48	2.4	22.6
Bw	28-48	2.59	0.69	3.0	15.7
S-3 (brown forest soil)					
AB1	21-34	2.43	0.41	2.0	38.0
Bw	48-70	2.60	0.54	2.7	26.8
N-4b (podzolic soil)					
AB-BA	6-15	2.35	0.73	3.9	8.9
Bs	15-30	2.49	0.55	2.5	19.0
Bw2	40-52	2.60	0.78	3.1	7.9
H-1b (podzolic soil)					
E	9-19	2.49	0.96	3.5	9.3
Bs2	22-36	2.50	0.85	2.5	17.5
Sw-1 (podzolic soil)					
E	2-10	2.46	1.01	4.6	10.8
Bs	23-45	2.58	0.70	3.5	20.5
Sw-4 (podzolic soil)					
E	4-20	2.54	1.17	4.2	4.2
Bs	29-55	2.59	0.80	3.4	10.9

[a]Measured after oven dry treatment. [b]Bulk density was measured with seven replications and saturated hydraulic conductivity and coarse porosity with 4 replications. The values were averaged by omitting the highest and lowest values. [c]Saturated hydraulic conductivity was expressed as pKa value; pKa = - log [saturated hydraulic conductivity]

[d]Porosity greater than 0.03 mm, equivalent to retained water from 0 to 10 kPa.

Table 5.3. Moisture conditions of the profiles in 1991.

Site and horizon		Moisture conditions (*10 kPa) 31,July	5,Sep.	5,Oct.	23,Nov.
N-1b	BA	0.82	1.22	1.88	0.94
	Bw	0.72	2.02	1.29	1.15
H-2	AB	0.73	0.79	1.21	1.52
	Bw	0.74	1.53	2.07	1.06
S-3	AB	0.62	1.05	1.46	1.11
	Bw	0.92	1.48	2.05	1.34
N-4b	AB	0.60	1.20	1.39	1.25
	Bs	0.47	1.53	1.74	0.79
H-1b	E	0.32	0.97	1.63	1.02
	Bs	0.34	1.04	1.59	0.94

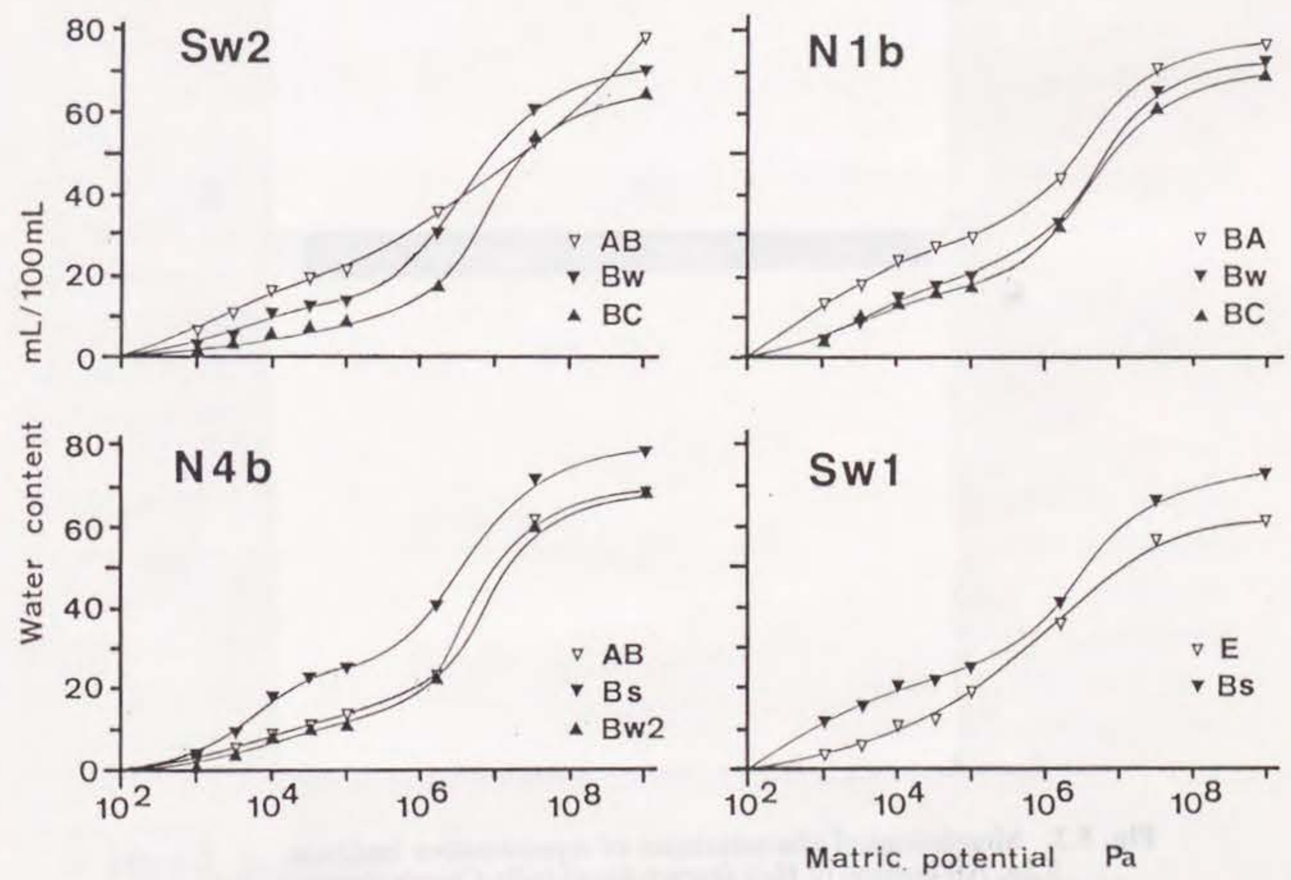
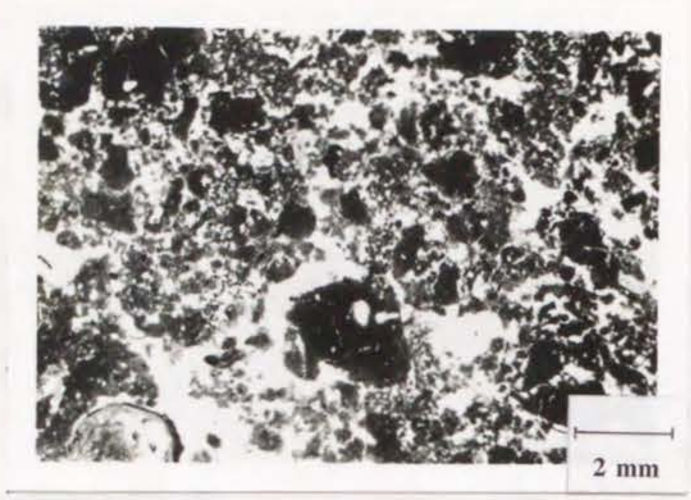


Fig. 5.1. Moisture characteristic curves of selected profiles.

a



b

c

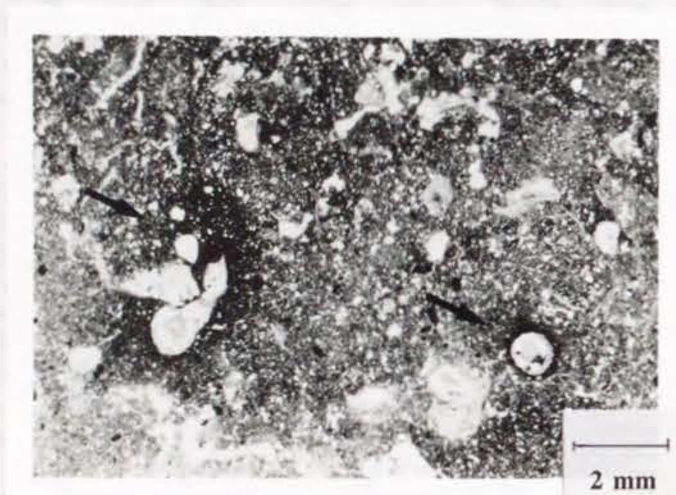


Fig. 5.2. Morphological characteristics of representative horizons.
5.2a. AB horizon of H–2 (brown forest soil). Crumb structure. Peds are separated by compound packing voids. PPL.
5.2b. AB horizon of N–4b (podzolic soil). No discrete peds. Dominant voids are vughs. PPL.
5.2c. E horizon of Sw–1 (podzolic soil). Massive structure. Relatively few vughs. Precipitation of oxidized Fe is observed around tree roots as indicated by arrows. PPL.

d

e

Fig. 5.2. (continued)
5.2d. Bw horizon of H–2. Subangular blocky structure. The solid material is divided into subangular aggregates by plain voids. Small vughs are often found in the interior of aggregates. PPL.
5.2e. Bs horizon of Sw–1. No discrete structure. Dominant voids are compound packing voids. PPL.

a

b

c

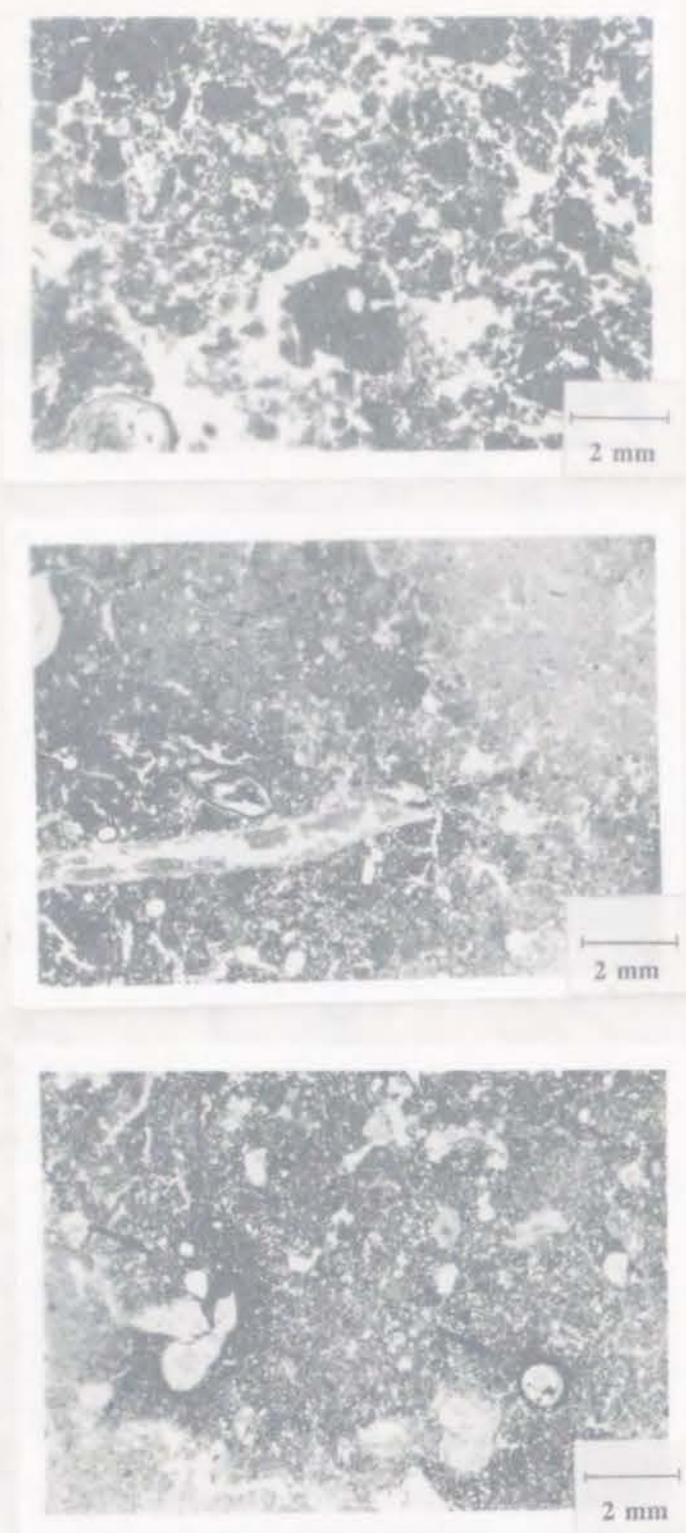


Fig. 5.2. Morphological characteristics of representative horizons.
5.2a. AB horizon of H–2 (brown forest soil). Crumb structure. Peds are separated by compound packing voids. PPL.
5.2b. AB horizon of N–4b (podzolic soil). No discrete peds. Dominant voids are vughs. PPL.
5.2c. E horizon of Sw–1 (podzolic soil). Massive structure. Relatively few vughs. Precipitation of oxidized Fe is observed around tree roots as indicated by arrows. PPL.

d

e

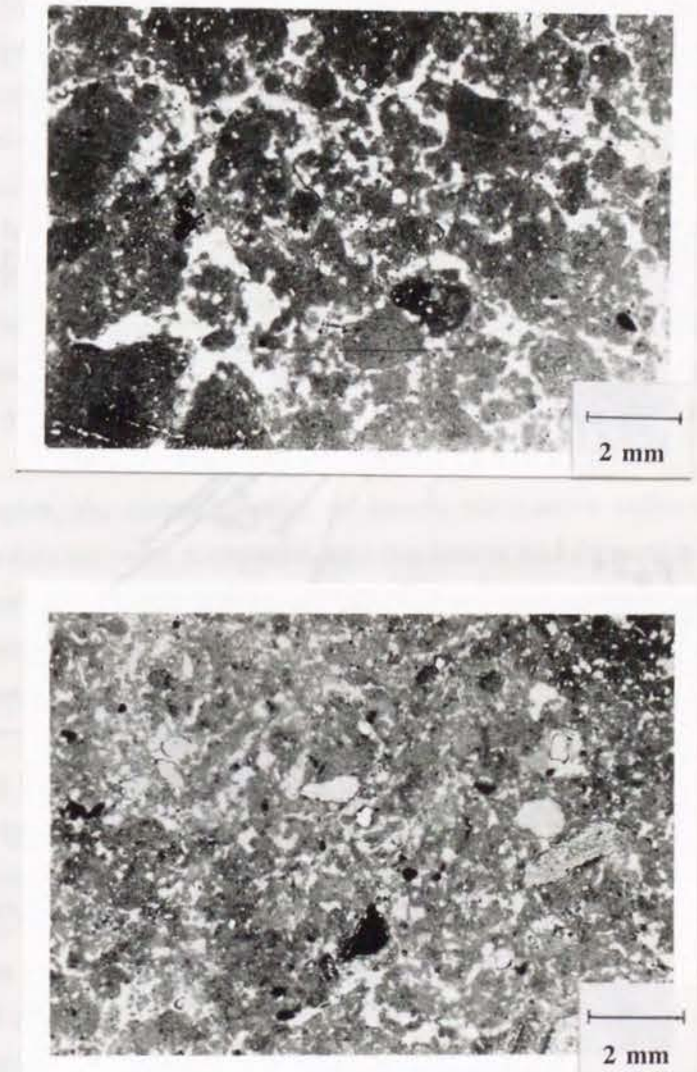


Fig. 5.2. (continued)
5.2d. Bw horizon of H–2. Subangular blocky structure. The solid material is divided into subangular aggregates by plain voids. Small vughs are often found in the interior of aggregates. PPL.
5.2e. Bs horizon of Sw–1. No discrete structure. Dominant voids are compound packing voids. PPL.

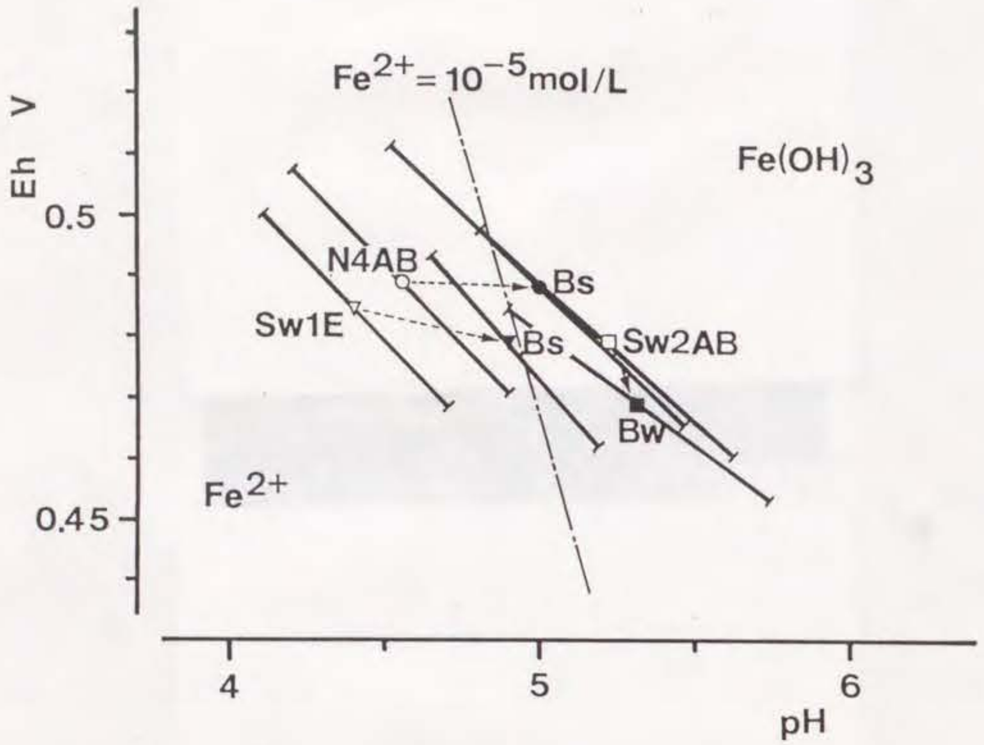


Fig. 5.3. Redox environment in the soil solution from each horizon in July, 1990.

Chapter 6
Characteristics and dynamics of organic matter in the forest soils

6.1 General

The nature and role of organic matter in the podzolization process have not been fully elucidated especially from the viewpoint of organo-mineral interactions. Hirai et al. (1988) reported that the Cp/(Fep+Alp) atomic ratio in the illuvial B horizons in the study area was often lower than that in typical spodic horizons, suggesting the presence of organo-mineral complexes with metal-rich, humus-poor characteristics. Moreover, as was shown in Chapter 2, amorphous Fe and/or Al compounds that did not form organo-mineral complexes generally increased in the B horizons compared with the surface horizons. Since forming processes of such Al-, Fe-illuvial B horizons without a concomitant accumulation of organic matter have been a controversial pedogenetic problem that could not be sufficiently explained by the organo-mineral theory (Farmer et al. 1980; Anderson et al. 1982), it is necessary to examine the characteristics of organic matter in the B horizons of this study in relation to interactions with metals.

In this chapter, the characteristics of humic substances collected from soils, litter extracts, and soil solutions were compared, and the nature and dynamics of dissolved organic matter in the soil profiles were examined with special reference to the interactions with metals both in the soil solution and on the soil particles for a comprehensive analysis of the pedogenetic processes of the forest soils in this study area.

6.2 Experimental methods

6.2.1 Brief description of the sample soils

Three brown forest soil profiles (Sw-2, N-1b, and H-2) and three podzolic soil profiles (N-4b, H-1a, and Sw-1) were investigated. The vegetation type is summarized as follows: Deciduous broad-leaved species such as *Fagus crenata* and *Quercus mongolica* are dominant in N-4b and N-1b. They also dominate in H-1a and H-2 with minor coniferous species, i.e. *Cryptomeria japonica*. In contrast, *Cryptomeria japonica* is the dominant vegetation in Sw-1 and Sw-2. General characteristics of the sampled soils are given in Table 6.1. The conspicuous characteristics of the sampled soils include a low pH especially in the surface horizons, high clay content, and Al translocation in most of the profiles and Fe translocation in the podzolic profiles.

6.2.2 Analytical methods

Air-dry fine earths (< 0.2 mm diameter) were used in the following analyses:

1) Humic substances were fractionated according to the method of Lowe (1980). The carbon content was determined by a wet combustion method with a reflux condenser (Tinsley 1947).

2) Purified humic substances for items 3) to 5) were prepared as follows: Samples from each of the A and B horizons of Sw–1, Sw–2, N–1b, and N–4b profiles were treated with a 1 : 1 mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ at 60°C five to six times. Soluble humic substances were acidified to pH 1.2 with 2 M H_2SO_4 and were fractionated into fulvic acid as supernatant and humic acid in the precipitate. The humic acid was further purified according to the method of Yonebayashi and Hattori (1988). On the other hand, the acidic supernatant was passed through a column of Amberlite XAD–8 resin and the adsorbed fraction was eluted with 0.1 M NaOH as fulvic acid. The fulvic and humic acid preparations were dialyzed against deionized water, resulting in retaining fractions with molecular weights > 500, thereafter passed through a column of Amberlite IR–120B resin in H^+ form, and then freeze–dried.

Colored fulvic substances from the litter layer of Sw–1 (mainly consisting of coarse litter of *Cryptomeria japonica*) and N–4b (mainly consisting of litter of *Fagus crenata* and *Sasa* sp.) were extracted with water after 1 week incubation at 25°C and then purified by XAD–8 resin treatment. The fulvic substances in the soil solution, which was collected from the surface AB or E and the B horizons of the three profiles (Sw–1, Sw–2, and N–4b) using porous cups in October, 1990, were also purified by the XAD–8 resin treatment. They were passed through a column of Amberlite IR–120B resin in H^+ form, and then freeze–dried.

3) Contents of acidic functional groups, that is, carboxyl and phenolic hydroxyl groups were determined by a nonaqueous titration method (Yonebayashi and Hattori 1985).

4) Contents of carbon, hydrogen, and nitrogen in the humic substances were determined by a dry combustion method at the Analytical Center of Kyoto University. Oxygen content was calculated by difference.

5) For ^{1}H–NMR analysis, a 10 mg portion of well–dried fulvic or humic acid sample was dissolved in 0.5 mL of deuterium dimethylsulfoxide (DMSOd_6–100% d) and a small amount of tetramethylsilane (TMS) was added as an internal reference. The ^{1}H–NMR spectra were obtained by Fourier transform–NMR spectroscopy (Hitachi 90H spectrometer, 90 MHz). Data points numbering 16,000 were collected using a 90° pulse and 200 transients were acquired with 5.0 s delays.

6) The soil solution was collected in 1988 through 1991 from ten forest soil profiles (six podzolic and four brown forest soils including Sw–2, N–1b, H–2, N–4b, H–1a, and Sw–1) in the area using porous cups and the solute composition was determined (Chapter 3). Mean annual concentration of DOC in each horizon was calculated as the average for four sampling dates in July (rainy season), August (summer), October (autumn), and November (after leaf–fall).

6.3 Characteristics of humic substances from the soils, soil solutions, and litter extracts

6.3.1 Fractionation of soil humic substances

Characteristics of humic substances after the fractionation scheme proposed by Lowe

(1980) are given in Table 6.2. According to the procedure, the soil humic substances were fractionated into humic (Ch) and fulvic (Cf) acids, and the latter was further divided into a polyvinylpolypyrrolidone–adsorbed fraction (Ca; consisting of polyphenolic acids) and a non–adsorbed fraction (consisting of polysaccharides). In all the B horizons, the characteristics of the humic substances were specific to the podzolic B horizon, that is, the Ch/Cf ratios were below 0.4 and the Ca/Cf ratios were above 0.3 (Lowe 1980; Schuppli and McKeague 1984), regardless of soil or vegetation types.

6.3.2 Elemental and acidic functional group composition

Table 6.3 gives the composition of elemental and acidic functional groups of the humic substances. Carboxyl group and oxygen contents were generally higher for fulvic acid than humic acid, that is, about 5 mmol/g organic matter and 45 to 51 %, respectively. Content of phenolic hydroxyl group was high in fulvic acid in the soil solution. In general, the contents of the acidic functional groups of the fulvic acids in this area were lower than typical values in the cool and temperate zones reported by Stevenson (1982), that is, 6.1 to 8.5 mmol/g of COOH and 2.8 to 5.7 mmol/g of acidic OH, respectively. These results indicated a relatively low chelating capacity of fulvic acids in this area, which may account for the fact that most of Al migrated through the soil profiles without forming firm organo–mineral complexes in this study area (see Chapter 4).

The 5 mmol/g content of the carboxyl group could explain the origin of the proton equal to about 0.1 mmol(+) L^{-1} through dissociation when the fulvic acid content in the soil solution was 1 mmol L^{-1}, and was considered to contribute to the acid dissolution of Al.

6.3.3 ^{1}H–NMR spectra

^{1}H–NMR spectra are presented in Fig. 6.1 for selected samples. Chemical shifts were measured in relation to the internal TMS. Each peak was interpreted based on the studies carried out by Wilson (1981), Wershaw (1985), and Yonebayashi and Hattori (1989). Remarkable characteristics of the fulvic and humic acids are summarized as follows:

The humic acids showed a relatively weak absorbance in the 6.0 to 9.5 ppm region of aromatic protons and strong absorbance in the region of the protons attached to aliphatic carbon atoms β (1.0 to 1.9 ppm) and γ (0.5 to 1.0 ppm) to aromatic rings as compared with α carbon protons (1.9 to 2.8 ppm). Therefore it was considered that the major part of their aromatic rings was substituted by groups with relatively long aliphatic chains.

The fulvic acids from the litter extract and the soil solution showed a strong broad absorbance in the aliphatic β and terminal proton zone (0.5 to 1.9 ppm) compared to that of α protons (1.9 to 2.8 ppm), suggesting that a certain quantity of aliphatic acids with high carboxyl content and/or polysaccharide components was involved. Judging from the relatively simple pulses observed in the aromatic and methoxyl proton zones (6.0 to 9.5 and 2.8 to 4.0 ppm) of the fulvic acids from the soil solution, these acids may consist of simple polyphenolic compounds. Thus, they were considered to be composed of mixtures of polyphenols, and aliphatic acids and/or polysaccharides.

The fact that the fulvic acids from the soil samples exhibited a high proportion of aliphatic protons α to aromatic rings compared with the β and γ protons, was attributed to their relatively short aliphatic side-chains. They showed a strong peak in the zone between 4.0 to 5.5 ppm, which was ascribed to lactone protons β to an aromatic ring formed among adjacent carboxyl and hydroxyl groups. Judging from the lack of this peak among the fulvic acids from the litter extract or the soil solution, it was assumed that a certain number of saccharide or aliphatic side-chains had been added to the simple polyphenolic compounds through bioactivity and/or chemical reaction on the soil particle surface, and then the soil fulvic acids with a high content of side-chains or functional groups were subsequently formed. Thus, it was considered that the fulvic acids from the soils showed a higher chelating capacity than those from the soil solution and litter extract, and that they displayed significant structural or compositional differences.

6.4. Nature and dynamics of dissolved organic matter in the soil profiles

6.4.1 Nature of DOC with special reference to its interaction with metal ions in the soil solution

The author examined the characteristics and dynamics of total dissolved organic matter in the soil solution, in which a fairly large amount of polysaccharides, organic acids with low molecular weight, and other organic compounds were involved in addition to the fulvic acid fraction.

In the soil solution, the sum of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Al^{3+}, and H^+) exceeded the sum of anions (Cl^-, NO_3^-, and SO_4^{2-}) in most cases. The positive correlation observed between the DOC concentration and the anion deficit in the soil solution from the surface horizons of six podzolic profiles (Fig. 6.2) suggested that a large part of the anion deficit originated in the dissociation of acidic functional groups of DOC in those horizons. This correlation was not, however, observed among the samples from the surface horizons of the brown forest soils and all the B horizons, presumably due to the elimination of the highly charged portion of DOC by amorphous compounds of the soil solid phase in these horizons, or to the error caused by the lack of measurement of HCO_3^- under relatively high pH conditions (HCO_3^- that equilibrates with 1 kPa of CO_2 accounts for about 10^{-2} to 10^{-1} mmol(−) L^{-1} when the pH values range from 5 to 6).

The content of the dissociated acidic functional groups ([R^-] in mmol(−)) in the soil solution from the surface horizons of the podzolic soils was expressed by the following regression equation:

$$[R^-] = 0.00115 + 0.0548 * [DOC] \quad (R = 0.53^{***}, n = 125) \qquad \text{(Eq. 6.1)}$$

where [DOC] is the amount of dissolved organic carbon (mmol). According to the equation, the content of dissociated acidic functional groups was estimated at about 2.2 mmol(−)/g organic matter, which is about half the amount of carboxyl groups of the fulvic acids (Table 6.2). This discrepancy may be due to the fact that the purified fulvic acids did not contain the

XAD-non-adsorbed fraction, as in the case of most of the organic acids with low molecular weight and polysaccharides, and also to the fact that the carboxyl groups of organic matter was not completely dissociated under acidic conditions (pH 4 to 5).

Based on Al and Fe concentrations in the soil solution, the degree of saturation of the dissociated acidic functional groups with metal ions (organically complexed Al^{3+} + total dissolved Fe^{2+})[5] was estimated to range from 20 to 40 % in each horizon. The amount of total dissolved Fe^{2+} was counted, even though there was no sound evidence concerning the complex formation of DOC with dissolved Fe^{2+} in the soil solution. It is difficult to determine whether this value was high enough relative to the critical level at which the complexes began to precipitate as postulated in the organo-mineral theory (De Coninck 1980). It is possible to consider, however, that a large part of the acidic functional groups was not saturated with metal ions and that the organic matter may act as anions in the soil solution.

6.4.2 Dynamics of dissolved organic matter in the forest soil profiles

Fig. 6.3 describes the relationship between amorphous compounds of the soil solid phase (Alo+1/2Feo)[6] and the average concentration of DOC in the soil solution. No significant variation of the DOC concentration was observed in the soil solution within the sampling seasons (July to November). The relative amount of DOC in the B horizons to that in the surface horizons must be lower than the amount of DOC estimated from the distribution pattern of the concentration, because a fairly large amount of evapotranspiration was responsible for the apparent increase in the solute concentration in the B horizons. The higher concentration of DOC in the B horizons compared to that in the upper horizons observed in the Sw-2 profile may be related to this factor.

It was interesting to note that the decrease of the DOC concentration in the illuvial B horizons, which was often observed in soil solution studies in podzolic soils (e.g. Ugolini et al. 1977; McDowell 1984), did not necessarily occur in this area. According to Fig. 6.3, a sharp decrease of the DOC concentration in the soil solution (more than 1 mmol L^{-1}) was observed in the horizons with a large amount of amorphous compounds, that is, the value of (Alo+1/2Feo) was higher than $2*10^{-2}$ kg kg^{-1} (N-4b Bs and H-1a Bs1 horizons). On the other hand, in the case of (Alo+1/2Feo) with less than $2*10^{-2}$ kg kg^{-1}, the larger part of DOC supplied from the overlying horizon appeared to run down through that horizon without retaining the soil solid phase. More than half of the amorphous compounds was considered

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[5]Organically complexed Al was estimated by Eq. 4.2 in Chapter 4:

$$Al_{org}\ (\text{mmol } L^{-1}) = 0.000737 + 0.00324 * DOC\ (\text{mmol } L^{-1}) \qquad \text{(Eq. 4.2)}$$

[6]Alo and Feo were considered to consist of amorphous compounds (Wada 1977; Schwertmann and Tayler 1977), while Alp and Fep of complexes with organic matter (McKeague et al. 1971; Farmer et al. 1983).

to form complexes with organic matter (Alp+1/2Fep)[6] in most of the horizons.

This figure strongly indicates the major contribution of amorphous compounds in the soil solid phase to the dynamics of dissolved organic matter with a certain amount of dissociated acidic functional groups through adsorption onto oxide surfaces or organo-mineral complexes, in spite of other factors that could influence the DOC dynamics such as the rate of biodegradation of DOC, structural or compositional variation of DOC with vegetational or topographical factors, rate of drainage, etc.

6.5 Characteristics of the organo-mineral complexes in the B horizons of the forest soils

Table 6.1 gives the characteristics of the free oxides and organo-mineral complexes in the soil profiles. The Alp/Alo and Fep/Feo ratios often decreased in the B horizons compared with the A horizons, suggesting that there was an increase in the content of amorphous compounds that were not present as organic complexes in the B horizons. The Cp/(Alp+Fep) atomic ratio in the B horizons in this study area was often low compared with the reported values typical for the spodic horizon, that is, with a value exceeding 5 in most of the cases (Higashi et al. 1981; Mokma and Buurman 1982; Buurman 1985). These results indicated that the amorphous compounds in the B horizons in this area exhibited metal-rich, humus-poor characteristics.

Table 6.4 shows the calculated total acidity of humic substances and molar ratio of the total acidity of humus / organic complexes with metal ions in the selected horizons. The values of the molar ratios were very low in the B horizons, that is, lower than 0.4. As positive charges originating from free oxides were hardly observed in these horizons (unpublished data), the low ratios were attributed to the presence of hydrolyzed metals, and may be consistent with the forming processes of the B horizons in this area, that is, hydrolysis and illuviation of metals as inorganic forms followed by additional precipitation of organic matter.

In Chapter 4 and 5, the author concluded that Al migrated mainly in inorganic monomeric forms, whose solubility was regulated by the soil solution pH, and Fe subsequently migrated through a redox reaction from dense surface horizons lacking in amorphous Al. The results of this study showed that organic matter in the soil solution may play a certain role in Al translocation through the supply of protons, but as a strong complexing agent such as the typical soil fulvic acid with higher acidic functional groups reported in cool and temperate zones. Redistribution of Fe and/or Al oxides, on the other hand, was considered to control the dynamics of dissolved organic matter through adsorption onto them.

The amorphous compounds formed through these processes in the illuvial B horizons in this area may consist of organo-mineral compounds with a low molar ratio of acidic functional groups of humus / metal ions. These processes may account for the formation of the Bs horizons with insufficient accumulation of organic matter.

6.6 Conclusion

Characteristics of humic substances extracted from soils, litter extracts, and soil solutions in forest soils in the northern Kyoto area were investigated, and the nature and dynamics of dissolved organic matter in the forest soil profiles were discussed with special reference to their pedogenetic processes.

Based on fractionation, the humic substances in the B horizons showed typical characteristics for the podzolic B horizon and no significant differences were detected among the soil or vegetation types. The contents of carboxyl and phenolic hydroxyl functional groups of the fulvic acids which corresponded to about 5 and 1 mmol/g organic matter, respectively, were lower than the reported values of soil fulvic acids in cool and temperate zones. According to ^{1}H-NMR analysis, the fulvic acids from litter extracts and soil solutions were considered to consist of mixtures of polyphenols, aliphatic acids, and/or polysaccharides. In contrast, those from the soils consisted of polyphenols with a high degree of substitution by relatively short aliphatic or saccharide chains. Thus, it was considered that the fulvic acids in this area, especially those from soil solutions and litter extracts, exhibited a low metal-chelating capacity and played a certain role in pedogenesis through the supply of protons.

On the other hand, the content of dissociated acidic functional groups of dissolved organic matter in the soil solution was about 2.2 mmol(−)/g organic matter as estimated from the DOC concentration and anion deficit in the soil solution. It was considered that acidic functional groups were not fully saturated with metal ions. The dynamics of dissolved organic matter with certain negative charges in the profiles was considered to be controlled by the adsorbing capacity of amorphous compounds of Al and Fe in the soil solid phase, which had previously been translocated mainly as inorganic forms.

The amorphous compounds derived through these processes in the illuvial B horizons were often rich in compounds which did not form complexes with organic matter compared to the surface horizons, and the organo-mineral compounds showed a low molar ratio of acidic functional groups of humus / metal ions.

Table 6.1. Selected physico-chemical properties and characteristics of free oxides.

Site and horizon	Depth (cm)	Texture[a]	pH (H_2O)	Total carbon[b] (*10^{-2} kg kg^{-1})	Cp[b]	Fep[b]	Feo[b]	Alp[b]	Alo[b]	Fep/ Feo	Alp/ Alo	Cp/ (Fep+Alp)[c]
					(*10^{-2} kg kg^{-1})							
Sw-2 (brown forest soil)												
A	0-2	C	3.82	22.9	4.63	0.91	0.95	0.59	0.69	0.96	0.86	10.1
AB	2-11	C	4.05	12.7	3.51	1.31	1.22	0.72	0.81	1.07	0.89	5.8
BA	11-25	C	4.35	4.9	1.80	1.01	1.40	0.66	0.81	0.72	0.81	3.5
Bw	25-50	C	4.50	4.1	1.61	0.89	1.34	0.60	0.92	0.66	0.65	3.5
BC	50-73	C	4.73	1.4	0.64	0.27	0.36	0.45	0.85	0.75	0.53	2.5
C	73-80	CL	4.68	0.9	0.32	0.15	0.26	0.23	0.45	0.58	0.51	2.4
N-1b (brown forest soil)												
A	0-5	C	3.91	12.2	3.81	1.32	1.45	0.66	0.77	0.91	0.86	6.6
BA	5-19	C	4.22	5.5	2.61	1.62	2.07	0.81	1.01	0.78	0.80	3.7
Bw	19-55	C	4.54	3.3	1.90	0.71	1.59	0.93	2.06	0.45	0.45	3.4
BC	55-86	C	4.63	2.3	1.29	0.51	1.40	0.78	1.66	0.36	0.47	2.8
C	86-99	CL	4.65	1.0	0.54	0.40	0.72	0.39	0.60	0.56	0.65	2.1
H-2 (brown forest soil)												
A	0-6	C	3.78	11.5	3.37	1.12	1.66	0.57	0.79	0.67	0.72	6.8
AB	6-14	C	4.00	7.5	3.11	1.37	1.82	0.68	0.83	0.75	0.82	5.2
BA	14-28	C	4.25	4.9	1.99	1.83	1.95	0.79	0.90	0.94	0.87	2.7
Bw	28-48	C	4.50	1.8	1.03	1.00	1.15	0.71	0.77	0.87	0.93	1.9
BC	48-60	C	4.65	1.3	0.67	0.64	0.67	0.57	0.66	0.96	0.87	1.7
N-4b (podzolic soil)												
A	0-6	C	3.59	21.3	4.35	0.60	0.57	0.24	0.39	1.05	0.62	18.5
AB	6-12	C	3.76	10.2	3.77	1.18	1.44	0.37	0.51	0.82	0.73	9.0
BA	12-15	C	3.84	5.8	2.65	1.44	2.16	0.40	0.61	0.67	0.66	5.4
Bs	15-30	C	4.05	5.3	3.06	1.42	3.48	0.72	1.06	0.41	0.68	4.9
Bw1	30-40	C	4.36	2.1	1.10	0.84	2.05	0.59	1.01	0.41	0.58	2.5
Bw2	40-52	C	4.49	1.5	1.04	0.58	1.08	0.55	0.98	0.54	0.56	2.8
BC	52-83	C	4.49	1.5	1.01	0.51	0.99	0.59	1.01	0.52	0.58	2.7
C	83-100	C	4.57	1.3	0.75	0.42	1.10	0.57	1.12	0.38	0.51	2.2
H-1a (podzolic soil)												
A	0-1		3.56	24.4	4.37	0.15	0.18	0.26	0.26	0.83	1.00	29.6
E	1-14	CL	3.91	2.1	0.64	0.20	0.27	0.13	0.16	0.74	0.81	6.3
BE	14-21	C	4.26	4.0	1.87	1.18	1.92	0.56	0.67	0.61	0.84	3.7
Bs1	21-36	C	4.73	6.5	3.38	1.34	2.86	1.17	1.42	0.47	0.82	4.2
Bs2	36-58	CL	4.82	6.0	3.64	0.87	1.57	1.48	1.79	0.55	0.83	4.3
BC	58-60	CL	4.71	6.1	3.67	0.78	0.93	1.59	1.62	0.84	0.98	4.2
Sw-1 (podzolic soil)												
A	0-2	CL	3.43	24.6	4.02	0.19	0.24	0.23	0.27	0.79	0.85	28.1
E	2-10	CL	3.65	5.7	1.33	0.37	0.44	0.22	0.30	0.84	0.73	7.5
EB	10-23	C	3.97	3.7	1.37	1.33	1.38	0.38	0.49	0.96	0.78	3.0
Bs	23-45	C	4.20	3.7	1.69	1.56	2.28	0.56	0.82	0.68	0.68	2.9
BC	45-60	CL	4.58	2.9	1.49	0.70	1.44	0.62	0.92	0.49	0.67	3.5
C	60-73	L	4.71	1.2	0.59	0.16	0.40	0.49	0.83	0.40	0.59	2.3

[a]According to USDA system. [b]Oven dried basis. [c]Atomic ratio.

Table 6.2. Fractionation of humic substances.

Site and horizon	Ch[a]	Cf[a]	Ca[a]	Ch/Cf	Ca/Cf
	Fractionation of humic substances (*10^{-2} kg kg^{-1})				
Sw-2 (brown forest soil)					
A	3.62	3.27	1.38	1.11	0.42
AB	2.02	2.11	0.98	0.96	0.46
BA	0.71	1.50	0.66	0.47	0.44
Bw	0.43	1.31	0.53	0.33	0.40
BC	0.15	0.58	0.26	0.26	0.45
C	0.09	0.39	0.14	0.23	0.36
N-1b (brown forest soil)					
A	1.87	2.78	1.08	0.67	0.39
BA	0.77	1.84	0.80	0.42	0.43
Bw	0.36	1.52	0.56	0.24	0.37
BC	0.26	0.95	0.46	0.27	0.48
C	0.09	0.38	0.16	0.24	0.42
H-2 (brown forest soil)					
A	1.92	2.73	0.55	0.70	0.20
AB	1.16	2.19	0.76	0.53	0.35
BA	0.60	1.63	0.59	0.37	0.36
Bw	0.19	0.77	0.37	0.25	0.48
BC	0.13	0.57	0.30	0.23	0.53
N-4b (podzolic soil)					
A	4.91	3.64	0.45	1.35	0.12
AB	2.07	2.17	0.78	0.95	0.36
BA	0.84	1.51	0.68	0.56	0.45
Bs	0.74	2.15	0.99	0.34	0.46
Bw1	0.22	0.84	0.29	0.26	0.35
Bw2	0.17	0.67	0.24	0.25	0.36
BC	0.11	0.69	0.27	0.16	0.39
C	0.16	0.75	0.36	0.21	0.48
Sw-1 (podzoli soil)					
A	5.22	3.93	1.05	1.33	0.27
E	1.19	0.89	0.01	1.34	0.01
EB	0.64	1.17	0.54	0.55	0.47
Bs	0.50	1.38	0.72	0.36	0.53
BC	0.50	1.49	0.79	0.34	0.53
C	0.27	0.91	0.51	0.30	0.56

[a]Oven dried basis.

Table 6.3. Elemental and acidic functional group composition.

Sample	Acidic functional group COOH	Ph-OH	Total acidity	Elemental composition C	H	O	N	Atomic ratio H/C	O/C	N/C
	(mmol/g organic matter)			(%)	(%)	(%)	(%)			
Fulvic acid from soil										
Sw-2 A	4.76	0.92	5.68	47.05	4.19	46.94	1.82	1.07	0.75	0.033
Bw	6.04	0.76	6.80	45.49	3.79	49.20	1.52	1.00	0.81	0.029
N-1b A	5.35	0.76	6.11	48.01	4.36	45.22	2.41	1.09	0.71	0.043
Bw	5.39	0.65	6.04	46.36	4.28	46.45	2.91	1.11	0.75	0.054
N-4b A	4.36	0.97	5.33	47.11	4.05	46.53	2.31	1.03	0.74	0.042
Bs	5.43	0.97	6.40	46.63	3.92	47.71	1.73	1.01	0.77	0.032
Bwl	5.33	0.62	5.95	45.12	4.12	48.31	2.45	1.10	0.80	0.047
Sw-1 A	4.36	0.93	5.29	47.37	4.08	46.73	1.82	1.03	0.74	0.033
Bs	5.16	0.71	5.87	44.32	3.70	50.35	1.63	1.00	0.85	0.032
Fulvic acid from litter extract										
Sw-1 L	4.22	1.03	5.25	51.38	4.48	42.95	1.19	0.96	0.63	0.020
N-4b L	4.67	0.84	5.51	49.80	3.97	44.88	1.35	0.96	0.68	0.023
Fulvic acid from soil solution										
Sw-2 A	4.73	1.21	5.94	.	.	.	.	.	.	.
N-4b AB	5.20	1.20	6.40	49.54	4.02	45.76	0.68	0.97	0.69	0.012
Bs	4.75	1.07	5.82	.	.	.	.	.	.	.
Sw-1 E	5.03	1.33	6.36	48.88	4.35	46.20	0.57	1.07	0.71	0.010
Bs	4.91	1.17	6.08	48.99	4.35	46.08	0.58	1.07	0.71	0.010
Humic acid from soil										
Sw-2 A	2.41	1.19	3.60	54.45	5.43	37.05	3.07	1.20	0.51	0.048
Bw	2.96	0.91	3.87	55.80	6.13	33.88	4.19	1.32	0.46	0.064
N-1b A	2.83	0.70	3.53	53.31	5.56	37.30	3.83	1.25	0.53	0.062
Bw	3.00	0.73	3.73	53.45	5.79	36.48	4.28	1.30	0.51	0.069
N-4b A	2.86	0.71	3.57	54.18	5.52	36.75	3.55	1.22	0.51	0.056
Bs	.	.	.	.	.	.	.	.	.	.
Bwl	.	.	.	51.95	5.96	37.83	4.26	1.38	0.55	0.070
Sw-1 A	2.78	1.08	3.86	54.05	5.21	37.79	2.95	1.16	0.52	0.047
Bs	3.09	0.95	4.04	52.84	5.35	37.94	3.87	1.21	0.54	0.063

Table 6.4. Characteristics of organo-mineral complexes in the selected horizons.

Site and horizon	Alo[a]	Alp[a]	Feo[a]	Fep[a]	Cp[a]	Ch+Cf	Alp /Alo	Fep /Feo	Cp/[b] (Fep+Alp)	TA[c]	TA/[d] (Fep+Alp)
	($*10^{-2}$ kg kg^{-1})									(cmol(-) kg^{-1})	
Sw-2 (brown forest soil)											
A	0.69	0.59	0.95	0.91	4.63	6.89	0.86	0.96	10.1	40.6	1.06
Bw	0.92	0.60	1.34	0.89	1.61	1.74	0.65	0.66	3.5	10.9	0.29
N-1b (brown forest soil)											
A	0.77	0.66	1.45	1.32	3.81	4.64	0.86	0.91	6.6	26.1	0.54
Bw	2.06	0.93	1.59	0.71	1.90	1.88	0.45	0.45	3.4	9.8	0.21
N-4b (podzolic soil)											
A	0.39	0.24	0.57	0.60	4.35	8.56	0.61	1.06	18.5	37.4	1.01
Bs	1.06	0.72	3.48	1.42	3.06	2.89	0.68	0.41	4.9	19.0	0.36
Bwl	1.01	0.59	2.05	0.84	1.10	1.06	0.58	0.41	2.5	5.5	0.15
Sw-1 (podzolic soil)											
A	0.27	0.23	0.24	0.19	4.02	9.15	0.85	0.79	28.1	49.0	4.11
Bs	0.82	0.56	2.28	1.56	1.69	1.88	0.68	0.68	2.9	13.4	0.27

[a]Oven dried basis. [b]Atomic ratio. [c]Total acidity of humic substances (TA) was calculated using the humic (Ch) and colored fulvic (Ca) acids contents, their carbon contents, and their total acidity. Since the total acidity and carbon content of HA from the B horizons of N-4b were not determined, the average value in the B horizons was used in the calculation. [d]Molar ratio.

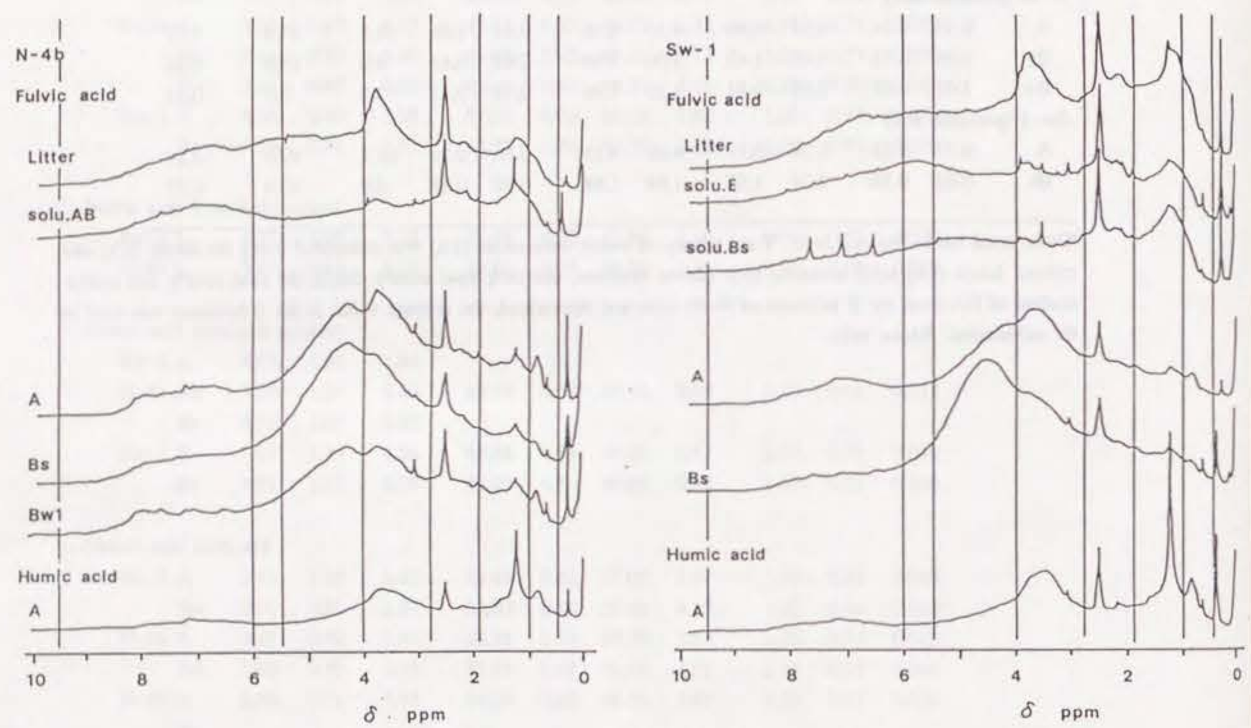

Fig. 6.1. ^{1}H-NMR spectra of the fulvic and humic acids from the N-4b and the Sw-1 profiles.

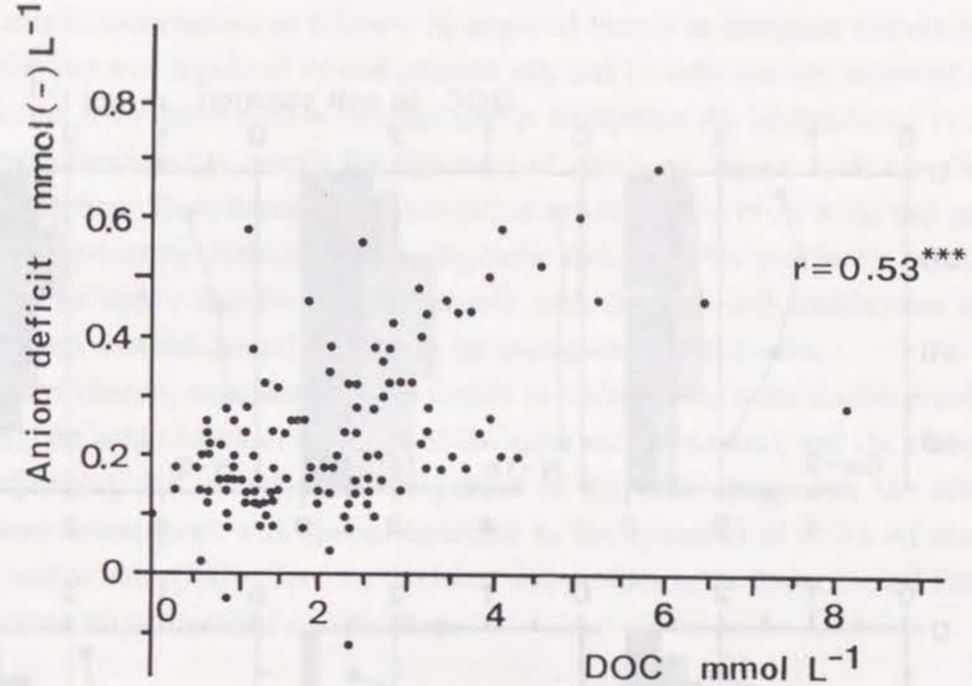

Fig. 6.2. Relationship between dissolved organic carbon (DOC) concentration and the anion deficit in the soil solution from the eluvial horizons of the six podzolic profiles (1988, 1989, and 1991).

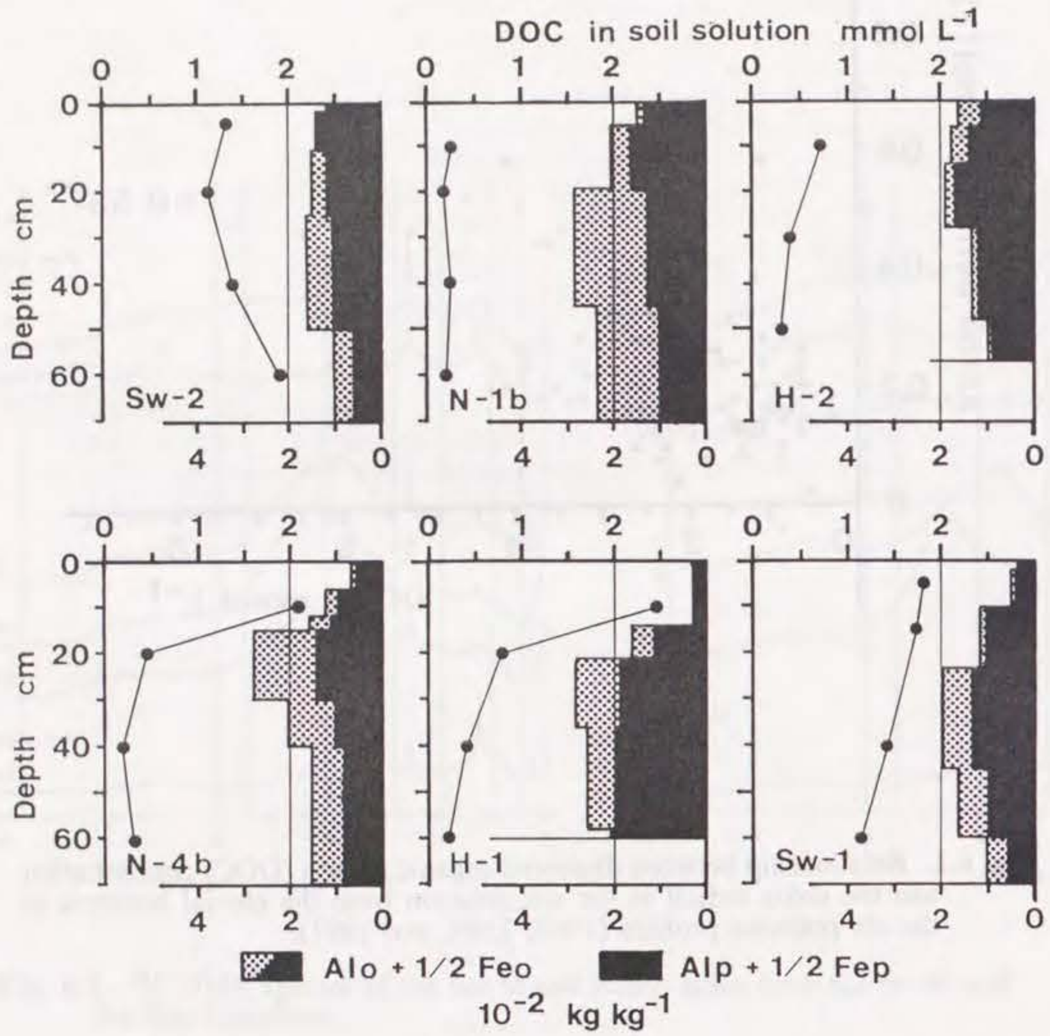

Fig. 6.3. Relationship between the concentration of dissolved organic carbon (DOC) in the soil solution and the amorphous compounds in the soil solid phase.

Chapter 7

Pedogenetic acidification process of the forest soils

7.1 General

The soil–forming processes in the Experimental Forest discussed in the previous chapters may be summarized as follows: Al migrated mainly as inorganic monomeric forms, whose solubility was regulated by soil solution pH, and Fe subsequently migrated through a redox reaction from dense surface horizons low in amorphous Al. Redistributed Fe and/or Al oxides were considered to control the dynamics of dissolved organic matter in the profiles through adsorption. Thus, the degree of eluviation and illuviation of Al in the soil profile was considered to primarily determine the pedogenetic feature of the profile by controlling the dynamics of Fe and/or dissolved organic matter, and, thus, the soil acidification in relation to Al dynamics was the central process in the pedogenesis in this area.

In this chapter, to understand the details involved in the acidification process of the forest soils, the acid and alkali titrations of the soils were performed, and the changes in the physico–chemical and mineralogical properties of the soils along with the acidification process were investigated with special reference to the dynamics of active Al components. Then, the author attempted to describe the forest soil profiles in the Experimental Forest based on the process of *pedogenetic acidification*.

7.2 Experimental methods

Acid and alkali titrations of the soils: Four brown forest soil profiles (Sw–2, N–1b, H–2, and S–3) and four podzolic soil profiles (N–4b, H–1b, Sw–1, and Sw–3) were investigated.

4.0 g of the sample soil was suspended in 40 mL of 0.10 M NaCl solution as the supporting electrolyte. After the pre–equilibration for 2 min, which could replace longer equilibration time (Sakurai et al. 1989), the suspension was titrated with 0.10 M HCl or NaOH using a potentiometric automatic titrator (HSS/HTS–10A, Toa Denpa Kogyo) with stirring, keeping the titration rate at 0.07 mL min^{-1}. The titratable acidity was determined as OH^- consumption by pH 8.3 following to Kinniburgh (1986), whereas the titratable alkalinity was determined as H^+ consumption by pH 3.0.

To examine an effect of exchangeable Al, organic matter, or amorphous oxides on titratable acidity, the alkali titration was performed with the above–stated method for the N–1b Bw and the Sw–1 Bs samples treated with 0.1 M KCl, hydrogen peroxide, or 0.2 M acid ammonium oxalate after hydrogen peroxide treatment.

Results of the acid and alkali titrations are discussed in relation to the physico–chemical properties of the sample soils, which are presented in Chapter 2.

7.3 Titratable acidity and alkalinity of the sample soils

The acid and alkali titration data are given in Table 7.1 and 7.2 and the titration curves are in Fig. 7.1 and 7.2. In general, the titratable alkalinity by pH 3.0 was high in the B horizons, whereas the titratable acidity by pH 8.3 was highest in the surface horizons for the brown forest soils and in the upper B horizons for the podzolic soils. It was well documented that results of these titrations are highly dependent on the analytical conditions, that is, concentration of supporting electrolyte, titration rate, so on (e.g. Kinniburgh 1986; Sakurai et al. 1989), so that the data presented here might not be directly compared with data in other papers.

The titratable acidity of the soil samples from the A horizon was generally much greater than the others, probably due to a great contribution of dissociation of the organic matter. This may hinder other important relationships between the titration data and physico-chemical properties, so that we arbitrarily choose the soils with less than 10 % of total carbon content in the following discussion on the titration data, excluding those for Fig. 7.4.

Table 7.3 gives a correlation matrix among the titration data and the selected chemical properties of the soil. The titratable alkalinity by pH 3.0 had a high correlation with the content of amorphous Al (Alo) (Fig. 7.3.1; $R = 0.90^{***}$, n = 35). This correlation was also reported for the brown forest soils by Kamosita et al. (1979), and considered to suggest a significance of amorphous Al compounds as an active acid buffering component through partial monomerization in the low pH region (pH 3 to 4) especially among the forest soils with low base saturation, expressed as follows:

$$Al(OH)_x^{(3-x)+} + H^+ \rightarrow Al(OH)_{(x-1)}^{(3-x+1)+} + H_2O \qquad \text{(Eq. 7.1)}$$

Fig. 7.4 showed relationships between the distribution pattern of the titratable alkalinity in the profile and soil solution composition (Chapter 3), and appeared to well describe the *in situ* acid neutralization, i.e. a gradual rise of solution pH with depth. Roughly speaking, the figure showed that pH of the soil solution rose to above 5, that is, a large part of supplied H^+ from the overlying horizon was neutralized, in the horizon with a titratable alkalinity greater than 10 cmol kg^{-1}.

In the alkali titration curves for determining the titratable acidity, some samples from the upper B horizon of the podzols displayed a noticeable pH buffer zone in the range of pH 4.5 to 5.5 (Fig. 7.1). Judging from the facts that the volume of this buffer zone (AC45) was highly correlated with the exchangeable Al content (ex.Al) (Fig. 7.3.2; Eq. 7.2 with the variables in cmol(+) kg^{-1}; $R = 0.95^{***}$, n = 35) and that the buffer zone disappeared after 1 M KCl treatment (Fig. 1-2, Sw-1 Bs), it might be attributed to a hydrolytic reaction of exchangeable Al.

$$AC45 = 0.545 + 0.563 * ex.Al \quad (R = 0.95^{***}) \qquad \text{(Eq. 7.2)}$$

Eq. 7.2 showed that more than half of the exchange acidity derived from Al ion (Al^{3+}) was neutralized in the range of pH 4.5 to 5.5 in the alkali titration, suggesting that at least two steps of hydrolytic reactions as expressed in Eq. 7.3 and 7.4 proceeded. Although $Al(OH)_{2.5}^{0.5+}$ species were often presumed to be a product of the hydrolytic reactions in this pH range (Yoshida 1979; Matijevic et al. 1961), it was difficult to judge whether a following polymerization of $Al(OH)_2^+$ (Eq. 7.5) occurred in this titration, because the experimental conditions in determining the exchange (in 1 M KCl solution) and titratable acidity (in 0.1 M NaCl solution) were different.

$$Al^{3+} + OH^- \rightarrow Al(OH)^{2+} \quad (pKa = 5.0) \qquad \text{(Eq. 7.3)}$$

$$Al(OH)^{2+} + OH^- \rightarrow Al(OH)_2^+ \qquad \text{(Eq. 7.4)}$$

$$2nAl(OH)_2^+ + nOH^- \rightarrow [Al_2(OH)_5]_n^{n+} \qquad \text{(Eq. 7.5)}$$

On the other hand, the OH^- consumption above pH 5.5 to 8.3 (AC58) correlated with the total carbon content or Cp (Fig. 7.3.3; Eq. 7.6 with the variables in cmol kg^{-1}; $R = 0.96^{***}$, n = 35), suggesting some buffering reactions accompanying with dissociation of acidic functional groups of the organic matter complexed with metal ions. Fig. 7.2 showed each contribution of organic matter, amorphous compounds, and crystalline components of the samples on the titratable acidity in this pH region estimated based on difference of the titration curves. According to them, about 10 cmol kg^{-1} of acidity was derived from crystalline components of the soils, which was almost consistent with the intercept of Eq. 7.6, whereas the additional part of the acidity was composed of those from organic matter and amorphous compounds. The OH^- consumption by these components might be expressed as following reactions (Eq. 7.7 to 7.9). The reaction in Eq. 7.8 was considered to accompany with that in Eq. 7.9.

$$AC58 = 7.44 + 0.0977 * Cp \qquad \text{(Eq. 7.6)}$$

$$R\text{-}COOH + OH^- \rightarrow R\text{-}COO^- + H_2O \quad (\text{or } R\text{-}OH) \qquad \text{(Eq. 7.7)}$$

$$\rangle M^+\text{-}^-OOC\text{-}R + OH^- \rightarrow \rangle M\text{-}OH + ^-OOC\text{-}R \qquad \text{(Eq. 7.8)}$$

$$\rangle M\text{-}OH + OH^- \rightarrow \rangle M\text{-}O^- + H_2O \qquad \text{(Eq. 7.9)}$$

where $\rangle M-$ represents metal ions on the surface of soil particles such as Fe or Al and R-COOH and R-OH are acidic functional groups of organic matter.

Some C or E horizon soils with a low content of amorphous or organo-mineral compounds showed OH^- consumption almost equivalent to that of crystalline components. Thus an increase of the titratable acidity in this pH region was considered to be attributable to an increase of amorphous compounds and/or organo-mineral complexes.

Table 7.1 showed that the strong acidity (AC45) due to exchangeable Al (ex.Al) was especially high in the upper B horizon soils of the podzol, whereas the weak acidity originated from the organo-mineral complexes was dominant among most of the brown forest soil profiles and the lower horizons of the podzols. The ratio of the former to the latter had a negative correlation with the soil pH (Fig. 7.3.4; $R = -0.77^{***}$, n = 35), that is, it increased with pH lowering. The total titratable acidity by pH 8.3 (TAC) is expressed by the following multiple regression equation with all the variables in cmol kg^{-1}:

$$TAC = 5.22 + 0.100 * Cp + 3.24 * ex.Al \quad (R = 0.97^{***}) \qquad \text{(Eq. 7.10)}$$

Thus an increase of titratable acidity from the C to surface horizon was considered to involve two processes, that is, (1) the formation of organo–mineral complexes in the lower B to C horizons under relatively weak acidic condition and (2) the monomerization of amorphous Al to exchangeable Al in the upper B horizons under severely acidified condition. It should be noted that an increase of amorphous Al during the former process accompanied an increase of active alkalinity of the soil.

The titratable acidity of the E horizon samples of the podzols decreased relative to that of the underlying B horizons. This would be a reflection of depletion of both organo–mineral complexes and exchangeable Al in the E horizon under most severely acidified condition.

7.4 Discussion on the pedogenetic acidification process of the forest soils

Based on the physico–chemical and mineralogical characteristics, the soil solution composition, and the titration data of the soils, a pedogenetic acidification process may be described as follows:

In *the initial acidic weathering stage* of the parent materials with a certain amount of micaceus minerals, the soil acidification could be brought about by an excess of cation uptake by plant roots, Al accumulation with weak podzolization, or dissociation of carbonic acid (Ugolini and Dahlgren 1987) as well as by direct proton load from the overlying horizon. Dominant clay mica gradually changes to 2:1–2:1:1 intergrade minerals and amorphous Al and/or Fe increases. These amorphous compounds adsorbs organic matter supplied from the overlying horizon (Chapter 6), and a larger part of them forms organo–mineral complexes (Alp/Alo or Fep/Feo often exceeds 0.5). They are not easily recrystallized because of low temperature or the inhibitory effect of organic matter (Schwertmann 1966; Inoue 1986) and tend to be preserved in that horizon. Some of the C horizons in the present study show this feature.

The first stage of soil acidification is characterized by an accelerated increase of amorphous Al (reaching > $1.0*10^{-2}$ kg kg^{-1}) caused by an Al illuviation with weak podzolization and a secondary adsorption of organic matter onto them. This results in an increase both of the titratable acidity and alkalinity. The increased active alkalinity would have a high capacity to neutralize H^+ in the soil solution, bring about a sharp rise of the solution pH, and promote a further precipitation of soluble Al through a partial hydrolytic reaction (Fig. 7.4; Eq. 7.3, 7.4, and 7.5). At this stage, 2:1–2:1:1 intergrade minerals are the dominant clay species. The upper B to Bw horizons of the brown forest soils and the lower B or BC horizons of the podzolic profiles represent this stage.

The H^+ adsorption or neutralization in the soil solution by amorphous Al hydroxides is, however, their partial monomerization process. So that if the supply of H^+ exceeds Al precipitated from the solution phase under higher acidic condition, the amorphous Al is gradually monomerized (with lowering of x for $Al(OH)_x^{(3-x)+}$), resulting in a decrease of the titratable alkalinity and an increase of the titratable acidity originated from exchangeable Al.

The second stage of acidification is characterized by a successive monomerization of amorphous Al hydroxides by an increased acid load, resulting in a further decrease of amorphous Al ($0.5*10^{-2}$ to $0.8*10^{-2}$ kg kg^{-1}) and an increase of exchangeable monomeric Al (greater than 10 cmol(+) kg^{-1}). A clear decrease in the titratable alkalinity and a simultaneous increase in the acidity are observed. As a result of increased supply of H^+ in spite of a lowered alkalinity, neutralization of H^+ and precipitation of Al from the solution phase decreases and monomerization and eluviation of Al from the solid phase is accelerated. At this stage, the dominant clay mineral species gradually shifts from 2:1–2:1:1 intergrade to vermiculite. The surface horizons of the brown forest soil and the upper B horizons of the podzolic soil represent this stage.

The third stage of acidification is characterized by a decreased amorphous Al (less than $0.5*10^{-2}$ kg kg^{-1}) and an active eluviation of Al from that horizon. Dominant clay mineral species are vermiculite and/or smectite, and gibbsite almost disappears. The titratable alkalinity is low, whereas the titratable acidity gradually decreases with a depletion of organo–mineral complexes and exchangeable Al as acidic components. H^+ in the solution is scarcely neutralized and Al in the solid phase is eluviated (Fig. 7.4). At this stage, a surface horizon gradually undergoes a compaction due to a decrease in amorphous Al and weakening of crumb structure, and an eluviation of Fe is enhanced under a reducing condition (Chapter 5). The podzolic E and EB horizons are typical for this stage.

The above–characterized stages might be typical for subhorizons, in which an acidification process is relatively slow. The initial and first stage is considered to be involved in the forming process of the B horizons of cool temperate forest soils, which are characterized by a relatively large amount of amorphous oxide, particularly Al–, Fe–humus complexes (Hirai et al. 1991). In this process, organo–mineral complexes or exchangeable Al could be regarded as a temporary storage of acidity that would be finally lost from that horizon through dissolution and eluviation to deeper horizons as a result of further acidification. In the case of a very surface horizon with intensive acidification, the initial and second stage might simultaneously proceed without a typical first stage.

Each profile in the Experimental Forest may be described with a combination of the above–characterized horizons, and podzolic soil in this area could be regarded as a highly acidified brown forest soil (Fig. 7.4). It is noteworthy that upper Fe–illuvial Bs horizons already show an eluvial feature with respect to Al (stage 2), because of an intensive H^+ load from the overlying horizons with a low titratable alkalinity. So that illuvial horizons of a podzolic profile would differentiate into an upper Fe illuvial Bs and a lower Al illuvial Bw or BC horizons, and eventually lose a clear Al illuvial horizon below a lithic or paralithic contact.

7.5 Conclusion

A natural process of soil acidification in the pedogenesis of the forest soils (i.e. brown forest soil and podzolic soil) in the northern Kyoto area was studied with special reference to dynamics of amorphous and exchangeable Al in the profiles.

The very low base saturation with low pH of the sample soils showed that all the profiles were highly acidified. Exchangeable Al was highest at the surface in the brown forest soil profiles, whereas it was highest at E to B horizons in the podzolic profiles. This suggested that an effect of soil acidification reached to deeper horizons in the podzolic profiles.

To understand the details involved in the pedogenetic acidification process, the acid and alkali titrations of the sample soils were conducted. The titratable alkalinity was highly correlated with amorphous Al content (Alo) among various soil properties, suggesting its importance in the *in situ* acid buffering by the solid phase of the forest soils. On the other hand, the titratable acidity was contributed by the contents of exchangeable Al and organic carbon, the latter forming complexes with amorphous Fe and/or Al. The pedogenetic acidification was considered to involve both increasing and a following decreasing processes of the titratable acidity; that is, an increase of the organo-mineral complexes in the C to B horizons, an increase of exchangeable Al in the upper B horizons, and a depletion of both organo-mineral complexes and exchangeable Al in the E horizon of the podzolic profiles.

From the considerations of the physico-chemical properties and the titration data of the soil solid phase and the soil solution composition, the pedogenetic process of the respective horizon in this area in relation to the soil acidification is described as follows: *the first stage of soil acidification* characterized by an accelerated increase of amorphous Al compounds caused by Al illuviation with weak podzolization and a secondary adsorption of dissolved organic matter onto them, *the second stage of acidification* characterized by a successive monomerization of amorphous Al hydroxides by an increased acid load, and *the third stage of acidification* characterized by a decreased amorphous Al and an active eluviation of Al, and often of Fe, from that horizon.

Each profile may be described with a combination of the above-characterized horizons, and podzolic soil in this area could be regarded as a highly acidified brown forest soil.

Table 7.1. Titration data of the sample soils.

Site and horizon	Initial pH	Titratable alkalinity by pH 3.0	Titratable acidity by pH 8.3	OH⁻ consumption pH 4.5–5.5 (AC45)	OH⁻ consumption pH 5.5–8.3 (AC58)	AC45 /AC58
		(cmol kg^{-1})				
N-1b (brown forest soil)						
A	3.78	89.1	n.m.	n.m.	n.m.	n.d.
BA	4.23	11.9	31.8	4.7	26.2	0.18
Bw	4.58	19.3	29.3	3.2	25.3	0.13
BC	4.62	17.2	19.8	2.9	16.2	0.18
C	4.50	4.6	11.2	1.9	8.4	0.23
Sw-2 (brown forest soil)						
A	3.44	5.4	n.m.	n.m.	n.m.	n.d.
AB	3.81	7.6	40.6	9.2	27.3	0.34
BA	4.18	9.7	30.5	4.8	24.1	0.20
Bw	4.31	13.6	26.1	4.0	21.8	0.18
BC	4.38	13.5	14.3	2.3	12.0	0.19
C	4.31	6.9	11.3	2.8	8.3	0.34
H-2 (brown forest soil)						
A	3.73	6.8	n.m.	n.m.	n.m.	n.d.
AB	3.83	9.0	45.5	9.2	32.3	0.28
BA	4.07	8.8	35.7	6.0	27.8	0.22
Bw	4.34	7.6	17.8	3.2	14.3	0.22
BC	4.39	7.0	16.0	3.0	12.5	0.24
S-3 (brown forest soil)						
A	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
AB1	3.98	9.8	49.5	7.7	39.0	0.20
AB2	4.25	6.8	33.5	4.0	28.8	0.14
BA	4.42	20.0	30.7	3.3	27.3	0.12
Bw	4.38	15.3	19.0	3.5	15.3	0.23
BC	4.40	11.8	14.0	2.8	11.0	0.26
N-4b (podzolic soil)						
A	3.40	3.3	n.m.	n.m.	n.m.	n.d.
AB	3.56	5.1	47.5	11.0	29.7	0.37
BA	3.69	5.8	45.4	9.6	29.7	0.32
Bs	3.89	7.6	47.6	9.1	34.7	0.26
Bw1	4.24	11.9	26.1	5.3	19.7	0.27
Bw2	4.31	14.9	21.4	4.1	16.5	0.25
BC	4.32	14.1	22.1	4.0	17.6	0.23
C	4.40	12.3	20.9	3.3	17.2	0.19
Sw-1 (podzolic soil)						
A	3.14	0.2	n.m.	n.m.	n.m.	n.d.
E	3.32	1.6	33.3	8.6	18.4	0.47
EB	3.70	5.0	37.7	10.3	22.3	0.46
Bs	3.90	8.3	39.0	9.5	25.7	0.37
BC	4.32	10.3	23.2	2.8	20.2	0.14
C	4.53	6.7	9.5	0.8	8.8	0.08
H-1b (podzolic soil)						
A	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
E	3.52	1.3	19.3	5.3	10.3	0.52
Bs1	3.67	4.3	47.7	9.3	33.4	0.28
Bs2	4.05	5.5	38.8	6.3	30.6	0.21
BC	4.13	7.4	28.3	4.1	23.0	0.18
Sw-3 (podzolic soil)						
A	n.m.	n.m.	n.m.	n.m.	n.m.	n.d.
E	3.32	0.9	25.6	7.2	13.4	0.53
EB	3.48	1.9	29.2	9.8	14.7	0.67
Bs	4.01	4.3	25.0	4.7	19.0	0.25

n.m. = not measured. n.d. = not determined.

Table 7.2. Alkali titration data of the samples treated with different reagents.

Site and horizon	Initial pH	Titratable alkalinity by pH 3.0	Titratable acidity by pH 8.3	OH^- consumption pH 4.5–5.5 (AC45)	OH^- consumption pH 5.5–8.3 (AC58)
		----------	----------(cmol kg^{-1})----------	----------	
N-1b Bw					
Original	4.58	29.3	3.2	25.3	0.13
KCl	5.11	16.9	n.d.	16.4	n.d.
Peroxide	4.91	20.3	n.d.	19.6	n.d.
Oxalate	4.30	14.7	3.5	10.9	0.32
Sw-1 Bs					
Original	3.90	39.0	9.5	25.7	0.37
KCl	4.85	18.8	n.d.	17.8	n.d.
Peroxide	3.95	28.0	8.2	18.0	0.46
Oxalate	4.33	13.9	4.2	9.5	0.44

[a]Expressed as content in the untreated sample.
n.m. = not measured. n.d. = not determined.

Table 7.3. Correlation matrix among titration data and selected chemical properties.

	pH H_2O	pH KCl	pH NaF	Cp	Exchangeable Al	Exchangeable bases	Total bases	Alo	Alp	Feo	Fep
Titratable alkalinity	0.69***	0.76***	0.82***	0.11	−0.59***	−0.41**	0.70***	0.90***	0.73***	0.27	0.18
Titratable acidity	−0.59***	−0.34*	−0.42*	0.88***	0.70***	0.39**	−0.56***	0.06	0.30	0.75***	0.78***
AC45[a]	−0.84***	−0.75***	−0.77***	0.50***	0.95***	0.52***	−0.66***	−0.37*	−0.20	0.43*	0.47**
AC58[b]	−0.30	−0.08	−0.10	0.96***	0.44**	0.23	−0.37*	0.33*	0.57***	0.84***	0.86***
Ratio of (AC45/AC58)	−0.77***	−0.86***	−0.86***	−0.23	0.69***	0.43*	−0.44**	−0.70***	−0.68***	−0.31	−0.24

[a]OH^- consumption in the range of pH 4.5 to 5.5. [b]OH^- consumption in the range of pH 5.5 to 8.3.
*: significant at 5 %, **: significant at 1 %, ***: significant at 0.1 %.

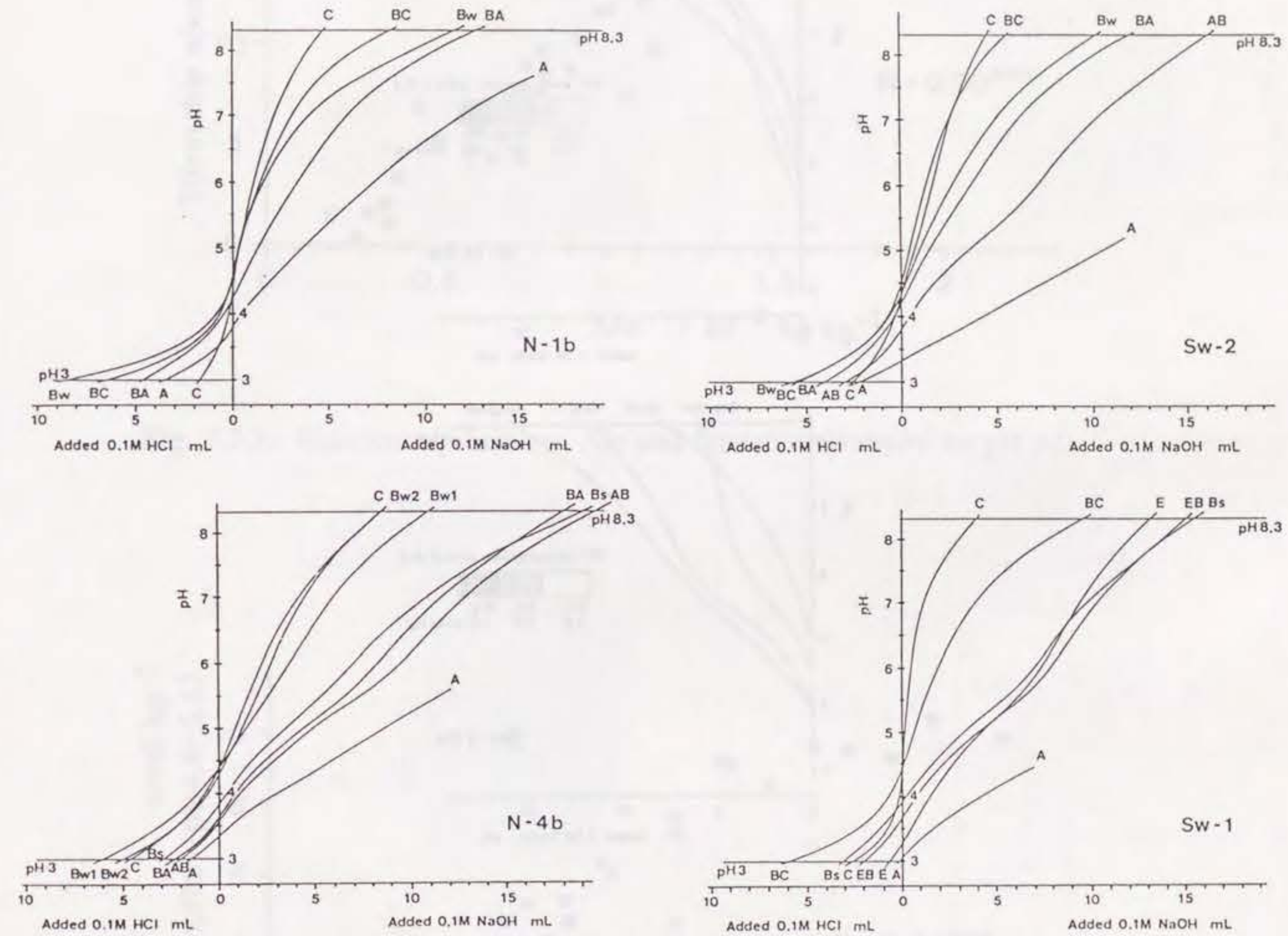

Fig. 7.1. Acid and alkali titration curves of the sample soils.

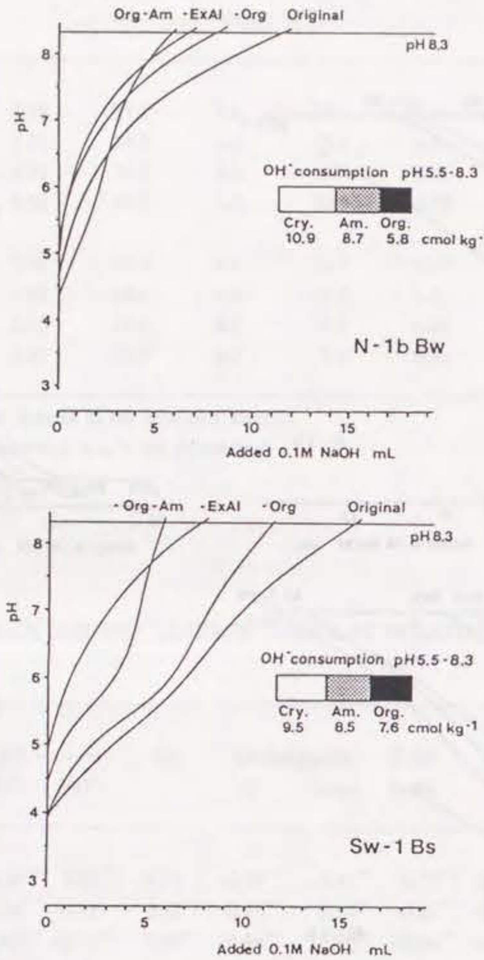

Fig. 7.2. Alkali titration curves of the N–1b Bw and the Sw–1 Bs samples treated with different reagents.

Original: original sample
- ExAl: treated with 1 M KCl to remove exchangeable Al
- Org: treated with H_2O_2 to remove organic matter
- Org – Am: treated with 0.2 M acid ammonium oxalate after H_2O_2 treatment to remove organic matter and amorphous compounds

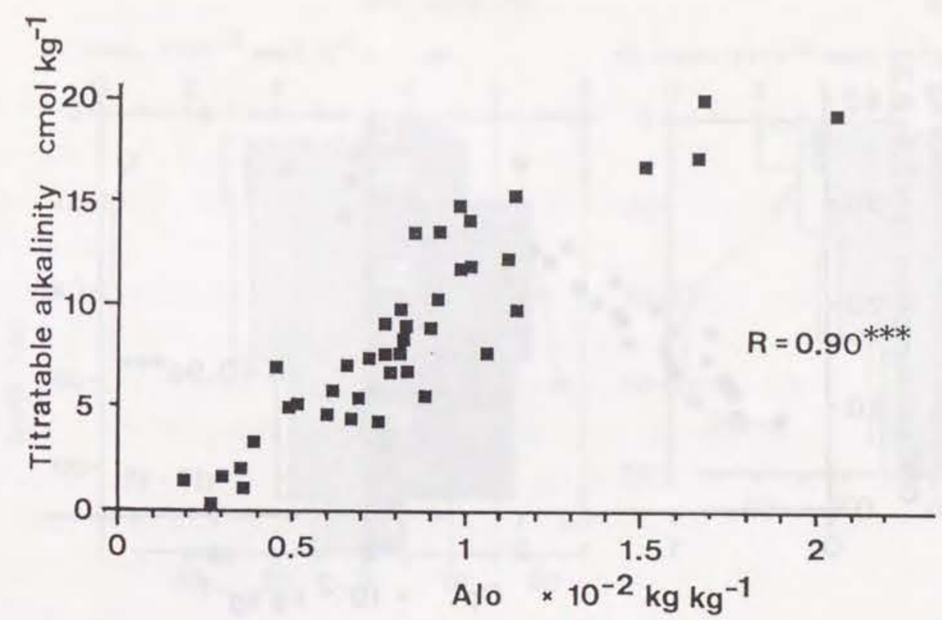

Fig. 7.3.1. Relationship between Alo and titratable alkalinity by pH 3.0.

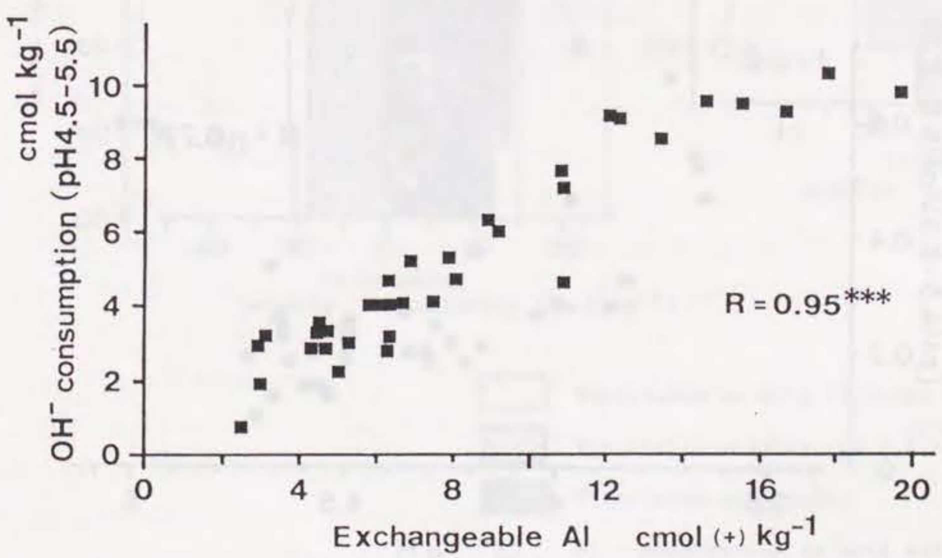

Fig. 7.3.2. Relationship between the content of exchangeable Al and OH^- consumption in the range of pH 4.5 to 5.5 in the alkali titration.

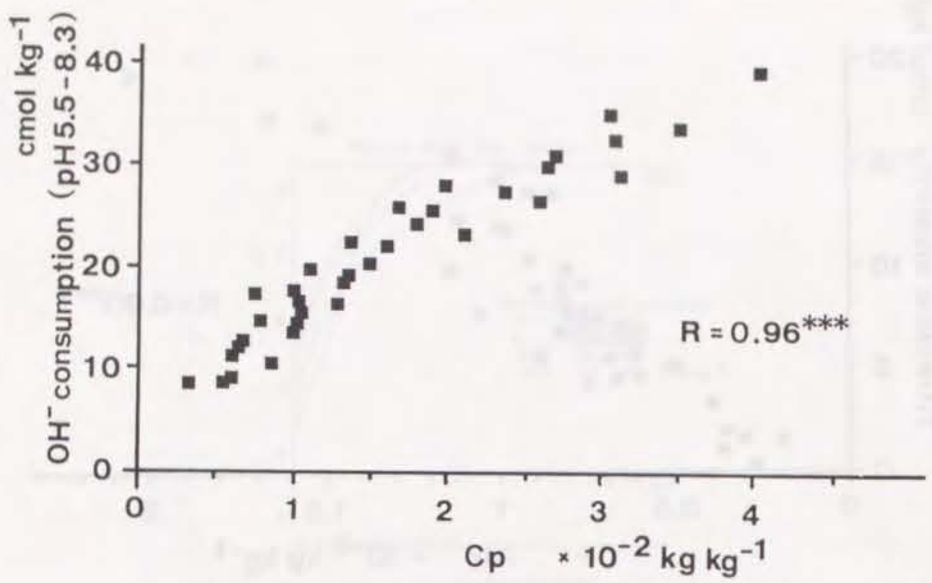

Fig. 7.3.3. Relationship between Cp and OH^{-} consumption in the range of pH 5.5 to 8.3 in the alkali titration.

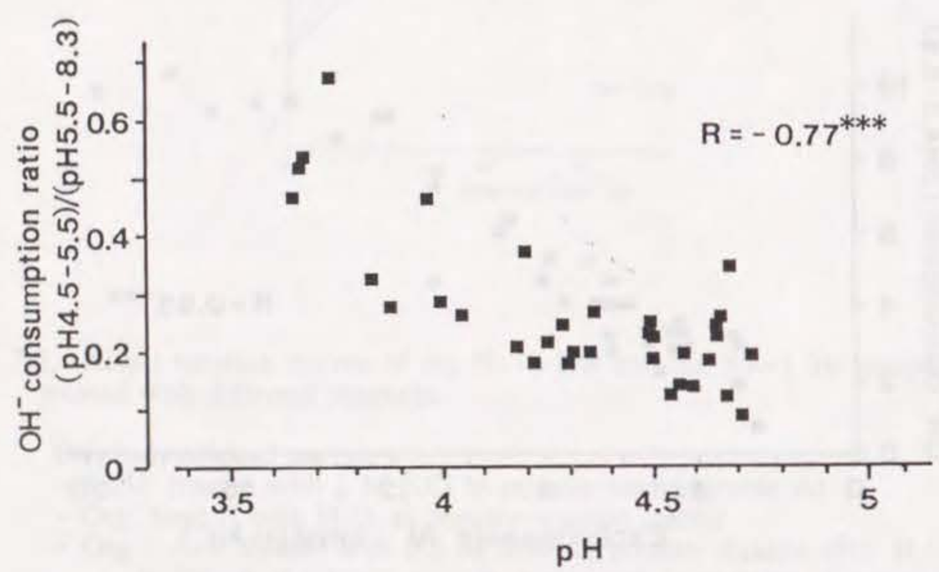

Fig. 7.3.4. Relationship between pH(H_2O) and the ratio of OH^{-} consumption from pH 4.5 to 5.5 to that from pH 5.5 to 8.3.

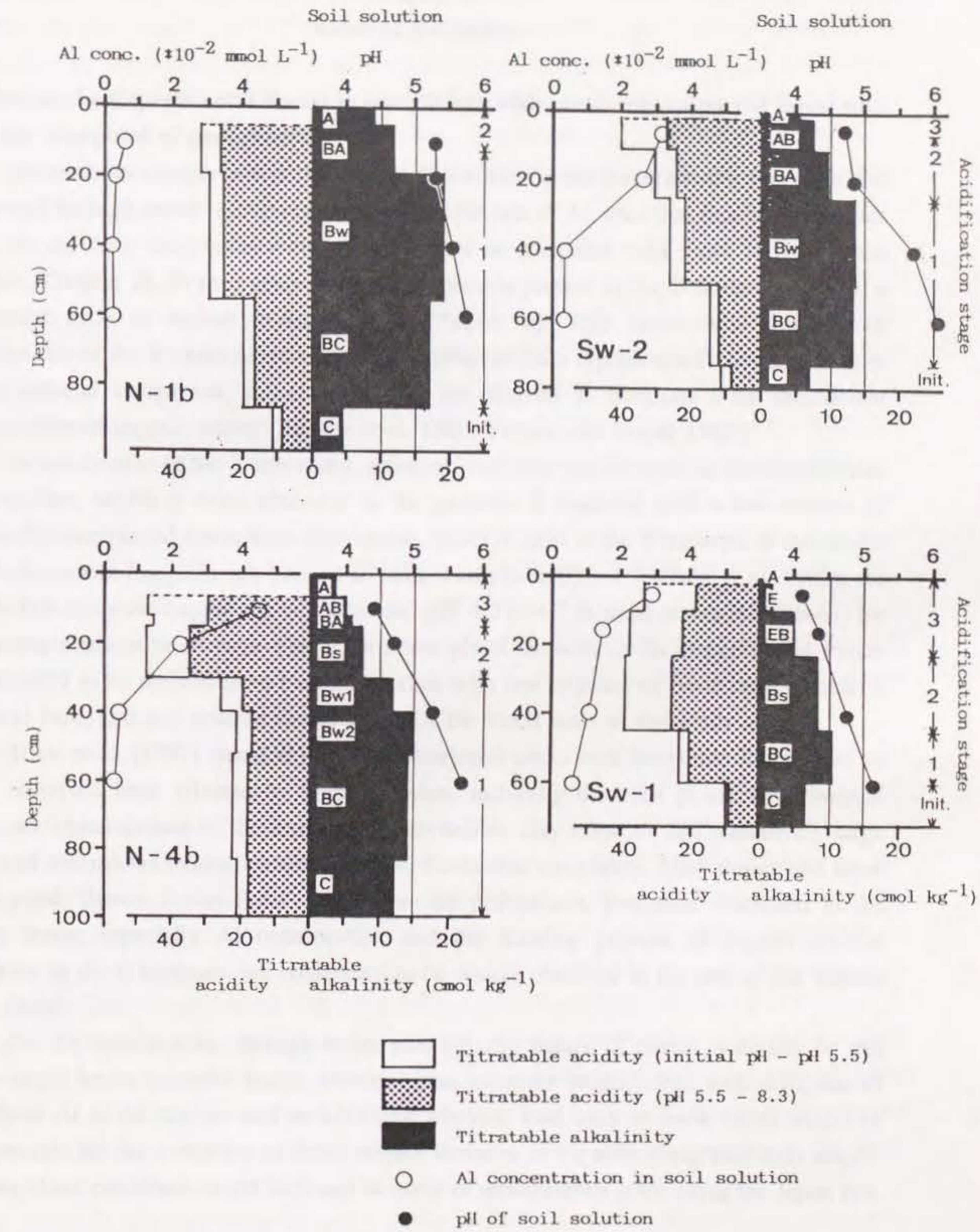

Fig. 7.4. Relationship among the soil solution composition and the titratable acidity and alkalinity of the soils in the profiles.

Chapter 8
General discussion

8.1 Soils in the Experimental Forest in comparison with previously-reported forest soils from the viewpoint of pedogenesis

Amorphous compounds in the illuvial B horizons in the Experimental Forest, which are formed through redox reaction of Fe and/or hydrolysis of Al, are often rich in compounds which do not form complexes with organic matter as compared with those in the surface horizons (Chapter 2). Even organo-mineral compounds present in the B horizons showed a low molar ratio of humus to metal ions (Chapter 6). This metal-rich, humus-poor characteristic of the B horizons was apparently different from typical spodic horizons rich in organo-mineral complexes, rather similar to the illuvial B horizons with insufficient accumulation of organic matter (Farmer et al. 1980; Farmer and Fraser 1982).

A low content of Si_o in this study, however, indicates that amorphous aluminosilicates or imogolites, which is often observed in the podzolic B horizons with a low content of organically-complexed amorphous compounds, scarcely exist in the B horizons of this study. As allophane and imogolite are present in soils with $pH(H_2O) > 4.9$ (Shoji et al. 1982), the soils in this study area appear to be too acidic (pH 4.2 to 4.7 in most of the B horizons) for these compounds to be formed. This quite a low pH of the soils in the Experimental Forest is considered to be derived from parent materials with low contents of basic cations under a high acid load, and is a notable characteristic of the forest soils in this study area.

Hirai et al. (1991) reported that soils developed under cool temperate forests and on parent materials little affected by volcanic ashes, including the soils in the Experimental Forest, are characterized by the formation of crystalline clay minerals and a relatively large amount of amorphous oxides, particularly Al-, Fe-humus complexes. They designated these soils typical 'Brown Forest Soils'. Therefore, the pedogenetic processes discussed in the present study, especially Al translocation and the forming process of organo-mineral complexes in the B horizons, are considered to be widely observed in the area of the 'Brown Forest Soils'.

For Fe translocation through redox reaction, the nature of parent materials or soil texture could be an essential factor. Moreover, an intensive acidification with depletion of amorphous Al in the surface and an additional physical load such as snow cover would be indispensable for the formation of dense surface horizons in the soils along mountain ridges. In Japan, these conditions could be found in many of mountainous areas along the Japan Sea.

8.2 Estimation of time needed for podzolization in the Experimental Forest

Some assumptions must be made for an estimation of time needed for podzolization. First, the author defines the degree of podzolization in terms of the amount of translocated Fe from E to Bs horizon (trFe*solid* in mol m^{-2}), as is computed by Eq. 8.1, assuming that translocation from/to another horizon is negligible and the initial total chemical composition of the parent material was homogeneous throughout the profile. Second, the rate of Fe translocation at present may be calculated from the difference of Fe concentration in the soil solution between the E and Bs horizon (trFe*solu* in mol m^{-2} yr^{-1}) (Eq. 8.2). Finally, it is assumed that Fe has been translocated at the same rate as today since the initial stage of podzolization. Then, time needed for translocation of Fe as observed today (Tp in yr) is calculated by Eq. 8.3.

$$\mathrm{trFe}\textit{soild} = 1/2 * (\mathrm{Fet(Bs)} * \mathrm{BD(Bs)} * \mathrm{Thick(Bs)} - \mathrm{Fet(E)} * \mathrm{BD(E)} * \mathrm{Thick(E)}) \qquad \text{(Eq. 8.1)}$$

where Fet, BD, and Thick represents total Fe content (mol kg^{-1}), bulk density (kg m^{-3}), thickness of the horizon (m), and (E) or (Bs) denotes a horizon.

$$\mathrm{trFe}\textit{solu} = (\mathrm{Fe}\textit{l}\mathrm{(E)} - \mathrm{Fe}\textit{l}\mathrm{(Bs)}) * (\mathrm{Ppt} - \mathrm{Evap}) \qquad \text{(Eq. 8.2)}$$

where Fe*l* represents mean annual concentration of Fe in soil solution, and Ppt and Evap is mean annual precipitation (2800 mm yr^{-1}) and evapotranspiration (800 mm yr^{-1}; Lake Biwa Research Institute 1985), respectively.

$$\mathrm{Tp} = \mathrm{trFe}\textit{solid} / \mathrm{trFe}\textit{solu} \qquad \text{(Eq. 8.3)}$$

The data used in this calculation and the estimated time for each podzolic profile are given in Table 8.1. It is concluded that, though quite rough, the podzolic soils in the Experimental Forest is considered to be formed for at least several thousand years with respect to Fe translocation.

8.3 Further studies needed for elucidating pedogenetic processes in the forest soils in the Experimental Forest

To investigate the soil-forming processes in the Ashiu Experimental Forest, this study was conducted through a comparative analysis of characteristics of the soils and soil solution composition. This kind of data or interpretations should be examined experimentally under the controlled conditions. Some problems appeared in the course of the present study are listed follows:

1) To elucidate the process of Al illuviation in the B horizons, the thermodynamic data about amorphous aluminosilicate minerals are indispensable. In the present study, the author concluded that hydrolyzed products in the B horizons are not amorphous aluminosilicates but amorphous aluminum hydroxides without supporting thermodynamic data (Chapter 4). This should be reexamined experimentally.

2) To analyze interactions between organic matter and metals in the soil solution, a comprehensive fractionation scheme of dissolved organic matter should be developed. Characterization of humic fractions is not sufficient (Chapter 6), and more reactive but unstable fractions such as low molecular weight organic acids must be characterized with special reference to their reaction with metals in the pedogenetic processes.

3) In order to apply the pedological information to forest management, it is necessary

to know distribution of soil acidification intensity in its relation to topographical and/or vegetational factors.

Table 8.1. Estimation of time needed for progress of podzolization in the Experimental Forest.

Site	Hor.	Fet[a] (mol kg^{-1})	B.D. (kg m^{-3})	Thick (m)	Fe*l* (mol L^{-1})	dFe*solid* (mol m^{-2})	dFe*solu* (mol m^{-2} yr^{-1})	Tp (yr)
N-4b	AB	0.69	730	0.06	$0.79*10^{-5}$			
	Bs	1.38	550	0.15	$0.13*10^{-5}$	41.9	0.0128	$3.2*10^{3}$
H-1a	E	0.28	960	0.13	$1.20*10^{-5}$			
	Bs	1.01	850	0.15	$0.20*10^{-5}$	47.2	0.0194	$2.4*10^{3}$
Sw-1	E	0.47	1010	0.08	$0.34*10^{-5}$			
	Bs	1.01	700	0.22	$0.13*10^{-5}$	58.7	0.0072	$14.0*10^{3}$

[a]Oven dried basis.

Chapter 9
Summary and conclusions

9.1 Soil-forming processes in the Experimental Forest

In order to investigate soil-forming processes in the Experimental Forest in reference to the theories of podzolization, on-going soil-forming processes were examined by a study of soil solution composition (Chapter 3). Two important results were obtained; (1) dynamics of Fe and/or Al appeared to be controlled by soil solution pH, (2) whereas dissolved organic carbon (DOC) did not necessarily illuviated simultaneously with metal ions in the B horizons. This phenomenon was apparently inconsistent with the organo-mineral theory and, thus, more detailed studies on the dynamics of Al, Fe, and DOC were conducted.

Dynamics of Al in the forest soils were investigated based on the speciation of Al in the soil solution (Chapter 4). More than 60 % of dissolved Al were inorganic monomeric species, whereas only a minor portion was organically-complexed or polymeric Al. The concentration of inorganic monomeric Al was controlled by the soil solution pH, that is, a higher concentration of Al was detected in soil solution with pH below 5. Based on the ionic activity of Al ions in the soil solution along with the thermodynamic data of the soil minerals, the soil solution was considered to be gradually saturated with amorphous $Al(OH)_3$ as it flew into the illuvial B horizons. A certain amount of Al was detected in a colloidal fraction without Si component, especially in the soil solution with a high Al saturation, suggesting that polymeric Al hydroxides may be the major products of hydrolytic reactions.

These results suggest that Al translocation in the soil profile in this region occurs mainly in the form of inorganic Al species. A large amount of NO_3 as well as organic acids may be responsible for a decrease of the pH of the soil solution in the surface horizons. Al is eluviated from the surface due to soil acidification, and precipitates as a result of hydrolytic reactions associated with an increase of the soil solution pH in the subsoil.

Dynamics of Fe in the forest soils were investigated in relation to soil physical properties (Chapter 5). The podzolic soils in the Experimental Forest were characterized by dense eluvial horizons with a higher bulk density and a lower volume of coarse pores and a lower water permeability in comparison with the underlying B horizons or the surface horizons of brown forest soils. This finding suggested a close relationship between the formation of the dense surface horizon and an active eluviation of Fe under a reduced condition in these horizons.

Based on a comparison of the physical properties with the chemical and mineralogical characteristics of the soils, the pedogenetic process of the podzolic soils in this region was assumed as follows: Al eluviation from the surface horizons due to strong acidification resulted in a decrease of the content of amorphous Al compounds, leading to a weakening of the crumb structure. As a result, the dense surface horizons with low water permeability and reduced condition were formed. This should have promoted active eluviation of Fe from the surface horizons.

Nature and dynamics of organic matter in the forest soils were examined based on the characterization of humic substances and their dynamics in the soil solution (Chapter 6). According to the functional group and ^{1}H-NMR analyses, the fulvic acids in this area, especially those from soil solutions and litter extracts, exhibited a low metal-chelating capacity and played a certain role in pedogenesis through the supply of protons. On the other hand, based on the estimated content of dissociated acidic functional groups of dissolved organic matter in the soil solution, it was considered that acidic functional groups were not fully saturated with metal ions. The dynamics of dissolved organic matter with negative charges in the profiles were considered to be controlled by the adsorbing capacity of amorphous compounds of Al and Fe in the soil solid phase, which had previously been translocated mainly in inorganic forms.

The amorphous compounds thus illuviated in the B horizons had a relatively low Alp/Alo or Fep/Feo ratio, suggesting abundance in compounds which do not form complexes with organic matter, as compared to the surface horizons, and the organo-mineral compounds showed a low molar ratio of acidic functional groups of humus to metal ions.

In conclusion, the soil-forming processes in the Experimental Forest may be described as follows: Al migrated mainly in inorganic monomeric forms as acidity increased, and Fe subsequently migrated in a reduced form from dense surface horizons poor in amorphous Al as a result of an intensive eluviation. Redistributed Fe and/or Al oxides were considered to control the dynamics of dissolved organic matter in the profile through adsorption. Therefore, the degree of eluviation and illuviation of Al in the soil profile was considered to primarily determine the pedogenetic features of the profile by controlling the dynamics of Fe and/or dissolved organic matter.

9.2 Pedogenetic acidification process in the Experimental Forest

The significance of soil acidification in the natural soil-forming processes was revealed in the course of the pedogenetic studies of the forest soils. In order to investigate the details involved in the pedogenetic acidification process of the forest soils, the acid and alkali titrations of the soils were conducted (Chapter 7). The titratable alkalinity was highly correlated with amorphous Al content (Alo), suggesting its importance in the in situ acid buffering by the soil solid phase. On the other hand, the titratable acidity, which generally increased from the C to the surface horizon, was correlated with both the contents of exchangeable Al and organic carbon that is complexed with amorphous Fe and/or Al (Cp). The pedogenetic acidification was considered to involve both increasing and a following decreasing processes of the titratable acidity; that is, an increase of the organo-mineral complexes in the C to B horizons, an increase of exchangeable Al in the upper B horizons, and depletion of both organo-mineral complexes and exchangeable Al in the E horizon of the podzolic profiles.

From the consideration of the physico-chemical properties and the titration data of the soil solid phase, the pedogenetic process which a subsoil horizon in this area undergoes in relation to the soil acidification may be described as follows: *The first stage of soil acidification* is characterized by an increase of amorphous Al compounds as a result of Al illuviation in a weak podzolization and a subsequent adsorption of dissolved organic matter onto the Al compounds. *The second stage of acidification* is characterized by a successive monomerization of amorphous Al hydroxides by an increase in acidity, and *the third stage of acidification* is characterized by a decreased amorphous Al and an active eluviation of Al, and often of Fe.

The above-characterized stages might be typical for subsoil horizons, in which an acidification process is relatively slow. In this process, organo-mineral complexes or exchangeable Al could be regarded as a temporary storage of acidity that would be finally lost from that horizon through dissolution and eluviation to deeper horizons as a result of further acidification. In the case of a very surface horizon that undergoes an intensive acidification, the initial and second stage might simultaneously proceed without a typical first stage because no Al illuviation occurs there.

Each profile may be described by a combination of horizons at one or another of the above-characterized stages, and a podzolic soil in this area may be regarded as a highly acidified brown forest soil.

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APPENDIX 1

Soil Profile Description

Sawadani-2 (Sw-2)

Soil type: Brown forest soil.

Vegetation: *Cryptomeria japonica*, *Quercus mongolica*, *Aucuba japonica*.

Topography: Gentle slope facing south, gradient 10°, on the crest stretching from southwest to northeast.

Altitude: 750 m.

Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	3–0	
A	0–2	Very dark brown (7.5YR2/3); moist; clay; moderate medium crumb; very friable; slightly sticky, very plastic; many roots; no stone; abrupt smooth boundary to
AB	2–11	Brownish black (7.5YR3/2); moist; clay; moderate medium crumb; friable; sticky, very plastic; many roots; no stone; clear wavy boundary to
BA	11–25	Brown (7.5YR4/4); moist; clay; moderate medium subangular blocky; friable; sticky, plastic; common roots; no stone; clear smooth boundary to
Bw	25–50	Bright brown (7.5YR5/6); moist; clay; moderate medium subangular blocky; friable; sticky, plastic; common roots; no stone; gradual smooth boundary to
BC	50–72	Yellowish brown (10YR5/6); moist; clay; moderate medium subangular blocky; friable; sticky, plastic; few roots; few moderately weathered pebbles; clear wavy boundary to
C	72–80	Yellowish brown (10YR5/6); moist; massive; no root

Nodabata-1b (N-1b)

Soil type: Brown forest soil.

Vegetation: *Fagus crenata*, *Quercus mongolica*, *Aucuba japonica*, *Cephalotaxus drupacea*, *Benzoin umbellatum*.

Topography: Convex slope facing west, gradient 15°, on the gentle hillslope.

Altitude: 750 m.

Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	3–0	
A	0–5	Dark brown (7.5YR3/4); moist; clay; moderate medium crumb; friable; slightly sticky, very plastic; many roots; few moderately weathered gravels; clear smooth boundary to
BA	5–19	Brown (7.5YR4/6); moist; clay; moderate fine crumb; very friable; slightly sticky, plastic; many roots; few moderately weathered gravels; clear smooth boundary to
Bw	19–55	Bright brown (7.5YR5/6); moist; clay; moderate fine subangular blocky; friable; sticky, plastic; common roots; few moderately weathered gravels; clear smooth boundary to
BC	55–86	Bright brown (7.5YR5/6); moist; clay; moderate coarse angular blocky; friable; sticky, very plastic; few roots; few moderately weathered gravels; clear smooth boundary to
C	86–99	Bright yellowish brown (10YR6/6); moist; clay; massive; few roots; many slightly weathered gravels to pebbles

Hatchu-2 (H-2)
Soil type: Brown forest soil.
Vegetation: *Cryptomeria japonica, Fagus crenata, Acer sieboidianum, Sasa* sp.
Topography: Gentle slope facing northeast, gradient 20°, on the crest stretching from northeast to southwest.
Altitude: 880 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
L	5-0	
A	0-6	Brownish black (7.5YR2/2); moist; clay; moderate medium crumb; loose; slightly sticky, very plastic; many roots; no stone; clear smooth boundary to
AB	6-14	Dark brown (7.5YR3/4); moist; clay; moderate medium crumb; very friable; sticky, very plastic; many roots; no stone; clear wavy boundary to
BA	14-28	Yellowish brown (10YR5/6); moist; clay; moderate fine subangular blocky; friable; sticky, very plastic; common roots; no stone; gradual wavy boundary to
Bw	28-48	Yellowish brown (10YR5/8); moist; clay; moderate medium subangular blocky; friable; sticky, very plastic; few roots; no stone; clear smooth boundary to
BC	48-60	Dull yellow orange (10YR6/3); moist; clay; weak coarse subangular blocky; friable; sticky, plastic; few roots; many moderately to strongly weathered pebbles; abrupt wavy boundary to
R	60+	

Sugio-3 (S-3)
Soil type: Brown forest soil.
Vegetation: *Cryptomeria japonica, Fagus crenata, Quercus mongolica, Sasa* sp., *Benzoin umbellatum*.
Topography: Gentle slope facing south, gradient 9°, on the small crest stretching from west to east.
Altitude: 760 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	3-0	
A	0-8	Brownish black (5YR2/2); clay; moderate crumb; many roots; common mycelia; few strongly weathered small pebbles; clear wavy boundary to
AB	8-34	Brown (7.5YR4/4); clay; moderate coarse subangular blocky, breaking into fine blocky; friable; common roots; few strongly weathered gravels; clear wavy boundary to
BA	34-48	Brown (7.5YR4/4); clay; moderate coarse subangular blocky; friable; common roots; few strongly weathered gravels; clear smooth boundary to
Bw	48-70	Bright brown (7.5YR5/6); clay; moderate coarse blocky; slightly firm; common roots; no gravel; clear smooth boundary to
BC	70-95	Bright brown (7.5YR5/6); clay; moderate coarse blocky; friable; few roots; no gravel

Nodabata-4b (N-4b)
Soil type: Podzolic soil.
Vegetation: *Fagus crenata, Quercus mongolica, Sasa* sp.
Topography: Flat, gradient 0°, on the crest stretching from south to north.
Altitude: 790 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
L	3-0	
A	0-6	Black (7.5YR2/1); moist; clay; moderate fine crumb; loose; slightly sticky, very plastic; many roots; no stone; clear smooth boundary to
AB	6-12	Dark brown (7.5YR3/3); moist; clay; moderate medium subangular blocky; very friable; slightly sticky, very plastic; many roots; no stone; clear wavy boundary to
BA	12-15	Dark brown (7.5YR3/4); moist; clay; moderate angular blocky; very friable; slightly sticky, very plastic; many roots; no stone; clear wavy boundary to
Bs	15-30	Brown (7.5YR4/6); moist; clay; moderate fine subangular blocky; friable; sticky, very plastic; many roots; no stone; clear wavy boundary to
Bw1	30-40	Bright brown (7.5YR5/8); moist; clay; moderate medium subangular blocky; friable; sticky, very plastic; common roots; no stone; clear smooth boundary to
Bw2	40-52	Bright brown (7.5YR5/6); moist; clay; moderate coarse subangular blocky; friable; sticky, vary plastic; common roots; no stone; clear smooth boundary to
BC	52-83	Bright brown (7.5YR5/8); moist; clay; moderate coarse angular blocky; friable; sticky, very plastic; common roots; no stone; clear smooth boundary to
C	83-100	Bright brown (7.5YR5/8); moist; clay; massive; sticky, very plastic; few roots; no stone

Hatchu-1a (H-1a)
Soil type: Podzolic soil.
Vegetation: *Magnolia salicifolia, Hydrangea paniculata, Quercus mongolica, Fagus crenata, Cryptomeria japonica, Daphniphyllum humile.*
Topography: Convex slope facing west, gradient 20°, on the crest stretching from south to north.
Altitude: 765 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	3-0	
A	0-1	Brownish black (7.5YR2/2); moist; clay; moderate medium crumb; many roots; no stone; clear wavy boundary to
E	1-14	Dull yellowish brown (10YR5/3); clay loam; weak fine subangular blocky; friable; few roots; few slightly to moderately weathered small pebbles; clear wavy boundary to
BE	14-21	Bright yellowish brown (10YR6/6); clay; moderate medium subangular blocky; friable; few roots; common mycelia; few slightly to moderately weathered small pebbles; clear wavy boundary to
Bs1	21-36	Brown (10YR4/6); clay; moderate fine to medium subangular blocky; very friable; many roots; few mycelia; few slightly to moderately weathered small pebbles; clear smooth boundary to
Bs2	36-58	Yellowish brown (10YR5/6); clay; weak fine to medium subangular blocky; very friable; few roots; many slightly to moderately weathered small pebbles; clear smooth boundary to
BC	58-60	Dark brown (10YR3/4); clay; dominant slightly to moderately weathered pebbles to cobbles; organic matter accumulated on the rock

Hatchu-1b (H-1b)

Soil type: Podzolic soil.

Vegetation: *Magnolia salicifolia*, *Hydrangea paniculata*, *Quercus mongolica*, *Fagus crenata*, *Cryptomeria japonica*, *Daphniphyllum humile*.

Topography: Convex slope facing west, gradient 20°, on the crest stretching from south to north.

Altitude: 765 m.

Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	3–0	
A	0–9	Brownish black (5YR2/2); moist; clay; moderate medium crumb; very friable; slightly sticky, plastic; many roots; no stone; clear smooth boundary to
E	9–19	Grayish brown (5YR4/2); moist; clay; weak medium subangular blocky; friable; slightly sticky, very plastic; common roots; common strongly weathered pebbles; clear wavy boundary to
Bs1	19–22	Dark reddish brown (5YR3/3); moist; clay; weak medium to fine subangular blocky; very friable; slightly sticky, very plastic; common roots; common strongly weathered pebbles; clear wavy boundary to
Bs2	22–36	Brown (7.5YR4/6); moist; clay; moderate fine subangular blocky; very friable; slightly sticky, very plastic; common roots; common moderately weathered pebbles; clear wavy boundary to
BC	36–49	Yellowish brown (10YR5/6); moist; clay; moderate medium subangular blocky; very friable; slightly sticky; very plastic; many moderately weathered pebbles

Sawadani-1 (Sw-1)

Soil type: Podzolic soil.

Vegetation: *Cryptomeria japonica*.

Topography: Convex slope facing east, gradient 26° on the crest stretching from southwest to northeast.

Altitude: 750 m.

Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LFH	4–0	
A	0–2	Reddish black (10R2/1); moist; clay; moderate medium crumb; very friable; slightly sticky, very plastic; many roots; no stone; abrupt smooth boundary to
E	2–10	Grayish brown (7.5YR4/2); moist; clay; moderate medium subangular blocky; friable; slightly sticky, plastic; common roots; few strongly weathered gravels to pebbles; clear wavy boundary to
EB	10–22	Brown (7.5YR4/4); moist; clay; moderate medium subangular blocky; friable; slightly sticky, plastic; common roots; few strongly weathered pebbles; clear wavy boundary to
Bs	22–45	Brown (7.5YR4/6); moist; clay; moderate medium subangular blocky; sticky, plastic; common roots; few strongly weathered pebbles; clear smooth boundary to
BC	45–60	Yellowish brown (10YR5/6 to 5/8); moist; clay; weak medium subangular blocky; friable; sticky, plastic; few roots; common moderately weathered pebbles; clear smooth boundary to
C	60–73	Yellowish brown (10YR5/8); moist; clay loam; massive; slightly sticky, plastic; few roots; abundant slightly weathered pebbles

Sawadani-3 (Sw-3)
Soil type: Podzolic soil.
Vegetation: *Cryptomeria japonica*, *Lindera umbellata*.
Topography: Convex slope facing northwest, gradient 25°, on the crest stretching from southwest to northeast.
Altitude: 745 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
LF	2–0	
A	0–6	Brownish black (5YR2/2); moist; clay; weak medium crumb; very friable; slightly sticky, plastic; many roots; no stone; abrupt wavy boundary to
E	6–12	Grayish brown (7.5YR4/2); moist; clay; weak medium subangular blocky; friable; slightly sticky, very plastic; few roots; few strongly weathered gravels; clear smooth boundary to
EB	12–20	Bright yellowish brown (10YR6/6); moist; clay; moderate medium subangular blocky; friable; sticky, plastic; few roots; few strongly weathered gravels; clear wavy boundary to
Bs	20–75	Bright brown (7.5YR5/6 to 5/8); moist; clay; weak fine subangular blocky; loose; sticky, plastic; few roots; many strongly weathered cobbles

Sawadani-4 (Sw-4)
Soil type: Podzolic soil.
Vegetation: *Cryptomeria japonica*, *Acer sieboldianum Miq.*
Topography: Steep slope facing west, gradient 30°, on the crest stretching from southwest to northeast.
Altitude: 750 m.
Parent rock: Paleozoic shale.

Hor.	Depth (cm)	Description
L	10–5	
FH	5–0	
A	0–4	Reddish black (2.5YR2/1); moist; clay loam; moderate medium crumb; very friable; slightly sticky, very plastic; many roots; no stone; clear smooth boundary to
E	4–22	Grayish brown (7.5YR4/2); moist; clay; moderate medium subangular blocky; friable; slightly sticky, plastic; few roots; many strongly weathered gravels; clear smooth boundary to
EB	22–29	Dark brown (7.5YR3/3); moist; clay; moderate coarse angular blocky; friable; slightly sticky, plastic; common roots; many strongly weathered gravels; clear smooth boundary to
Bs	29–50	Brown (7.5YR4/4); moist; clay; weak medium angular blocky; very friable; slightly sticky, plastic; common roots; many strongly weathered gravels; clear smooth boundary to
C	50–65	Bright yellowish brown (10YR6/6); moist; clay; massive; few roots; abundant slightly weathered cobbles

APPENDIX 2

Analytical Data

Table 1-1. General chemical properties (1).

Site and horizon	Depth (cm)	Na	K	Mg	Ca	Al	H	ECEC	Na+K+ Mg+Ca
		---------- Exchangeable cations ---------- (cmol(+) kg^{-1})							
Sw-2									
A	0-2	0.21	0.35	1.08	6.44	10.83	2.31	21.2	8.08
AB	2-11	0.10	0.23	0.39	0.75	11.71	0.76	13.9	1.47
BA	11-25	0.11	0.16	0.15	0.21	8.07	0.13	8.8	0.63
Bw	25-50	0.09	0.11	0.10	0.32	6.13	0.10	6.9	0.62
BC	50-73	0.12	0.10	0.08	0.17	5.04	0.06	5.6	0.47
C	73-80	0.04	0.08	0.07	0.09	4.72	0.00	5.0	0.28
N-1b									
A	0-5	0.17	0.41	0.73	0.86	8.03	2.08	12.3	2.17
BA	5-19	0.13	0.24	0.22	0.17	6.25	0.65	7.7	0.76
Bw	19-55	0.10	0.11	0.04	0.04	3.12	0.00	3.4	0.29
BC	55-86	0.11	0.13	0.05	0.05	2.92	0.00	3.3	0.34
C	86-99	0.09	0.08	0.04	0.06	2.95	0.23	3.5	0.27
H-2									
A	0-6	0.28	0.25	0.90	1.55	12.24	1.55	16.8	2.98
AB	6-14	0.16	0.21	0.35	0.44	12.12	1.68	15.0	1.16
BA	14-28	0.15	0.16	0.16	0.25	9.21	0.80	10.7	0.72
Bw	28-48	0.12	0.12	0.10	0.12	6.36	0.16	7.0	0.46
BC	48-57	0.13	0.11	0.10	0.16	5.26	0.00	5.8	0.50
S-3									
A	0-8	0.34	0.47	1.36	1.79	13.40	1.60	19.0	3.95
AB1	8-21	0.13	0.26	0.26	0.17	10.80	0.60	12.2	0.83
AB2	21-34	0.12	0.17	0.11	0.06	6.40	0.10	7.0	0.45
BA	34-48	0.13	0.12	0.08	0.06	4.50	0.00	4.9	0.37
Bw	48-70	0.12	0.15	0.52	0.06	4.50	0.70	6.1	0.86
BC	70-95	0.13	0.14	0.11	0.08	4.30	0.10	4.9	0.45

All the data are given on an oven dried basis.

Table 1-2. General chemical properties (1).

Site and horizon	Depth (cm)	Na	K	Mg	Ca	Al	H	ECEC	Na+K+ Mg+Ca
		---------- Exchangeable cations ---------- (cmol(+) kg^{-1})							
N-4b									
A	0-6	0.27	0.31	1.56	1.11	8.73	4.61	16.6	3.25
AB	6-12	0.18	0.15	0.66	0.31	14.64	3.69	19.6	1.30
BA	12-15	0.14	0.12	0.33	0.13	14.55	3.63	18.9	0.72
Bs	15-30	0.12	0.14	0.24	0.06	12.43	0.71	13.7	0.56
Bw1	30-40	0.11	0.15	0.14	0.04	6.89	0.61	7.9	0.44
Bw2	40-52	0.12	0.15	0.10	0.04	6.68	0.00	7.1	0.41
BC	52-83	0.12	0.13	0.09	0.03	5.78	0.14	6.3	0.37
C	83-100	0.12	0.12	0.08	0.02	4.70	0.13	5.2	0.34
H-1a									
A	0-1	0.20	0.84	5.56	5.82	5.80	2.20	20.4	12.39
E	1-14	0.06	0.07	0.22	0.14	9.20	0.70	10.4	0.49
BE	14-21	0.12	0.11	0.20	0.21	15.10	0.30	16.0	0.64
Bs1	21-36	0.11	0.14	0.17	0.15	9.30	0.00	9.9	0.58
Bs2	36-58	0.09	0.12	0.06	0.06	4.60	0.30	5.3	0.35
BC	58-60	0.08	0.08	0.04	0.06	3.70	0.40	4.4	0.27
H-1b									
A	0-9	0.28	0.37	1.38	1.79	6.54	4.15	14.5	3.82
E	9-19	0.08	0.09	0.24	0.25	7.94	1.92	10.5	0.66
Bs1	19-22	0.10	0.13	0.09	0.15	16.71	1.10	18.3	0.47
Bs2	22-36	0.11	0.13	0.20	0.13	8.93	1.39	10.9	0.57
BC	36-49	0.10	0.11	0.05	0.19	7.47	0.02	7.9	0.45
Sw-1									
A	0-2	0.34	0.38	1.69	1.02	6.88	4.63	14.9	3.43
E	2-10	0.10	0.17	0.27	0.22	13.36	1.87	16.0	0.76
EB	10-23	0.15	0.16	0.15	0.39	17.81	1.42	20.1	0.85
Bs	23-45	0.08	0.14	0.12	0.15	15.58	0.65	16.7	0.49
BC	45-60	0.17	0.10	0.05	0.17	6.33	0.05	6.9	0.49
C	60-73	0.04	0.02	0.02	0.27	2.52	0.04	2.9	0.35
Sw-3									
A	0-6	0.29	0.21	2.87	6.18	3.49	2.68	15.7	9.55
E	6-12	0.11	0.14	0.37	0.78	10.91	1.41	13.7	1.40
EB	12-20	0.04	0.10	0.21	0.24	19.69	0.41	20.7	0.59
Bs	20-75	0.16	0.13	0.13	0.63	10.90	0.07	12.0	1.05
Sw-4									
A	0-4	0.49	0.42	1.59	0.43	5.01	4.59	12.5	2.93
E	4-22	0.06	0.09	0.12	0.03	8.86	1.51	10.7	0.30
EB	22-29	0.13	0.10	0.12	0.04	15.03	0.93	16.4	0.39
Bs	29-50	0.21	0.12	0.11	0.03	16.78	1.39	18.6	0.47
C	50-65	0.09	0.09	0.04	0.03	7.67	0.72	8.6	0.25

All the data are given on an oven dried basis.

Table 2-1. General chemical properties (2).

Site and horizon	Depth (cm)	CEC* (cmol kg^{-1})	Base satur. (%)	ECEC /CEC (%)	Total* C (*10^{-2} kg kg^{-1})	Total* N (*10^{-2} kg kg^{-1})	Phosphate retention (%)	Moisture* content (*10^{-2} kg kg^{-1})
Sw-2								
A	0-2	62.3	12.97	34.1	22.9	1.16	60.0	10.0
AB	2-11	42.9	3.43	32.5	12.7	0.73	82.0	7.7
BA	11-25	29.6	2.13	29.8	4.9	0.29	83.1	6.2
Bw	25-50	28.2	2.20	24.3	4.1	0.23	81.7	6.4
BC	50-73	24.1	1.95	23.1	1.4	0.08	76.1	6.1
C	73-80	21.7	1.29	23.0	0.9	0.07	57.7	4.3
N-1b								
A	0-5	39.7	5.47	30.9	12.2	0.93	76.7	6.3
BA	5-19	26.3	2.89	29.1	5.5	0.40	82.0	5.2
Bw	19-55	19.9	1.46	17.1	3.3	0.23	93.1	5.7
BC	55-86	17.5	1.94	18.6	2.3	0.17	90.1	5.3
C	86-99	11.1	2.43	31.0	1.0	0.11	60.4	3.1
H-2								
A	0-6	37.3	7.98	44.9	11.5	0.60	81.0	6.6
AB	6-14	31.5	3.68	47.5	7.5	0.47	83.7	6.3
BA	14-28	23.5	3.07	45.8	4.9	0.30	84.8	6.0
Bw	28-48	15.8	2.91	44.2	1.8	0.11	77.8	4.7
BC	48-57	13.4	3.75	43.1	1.3	0.08	73.8	4.3
S-3								
A	0-8	63.7	6.21	29.8	22.6	1.24	61.8	9.0
AB1	8-21	38.6	2.14	31.6	8.8	0.45	93.6	7.3
AB2	21-34	30.0	1.52	23.3	6.1	0.32	97.7	7.0
BA	34-48	26.9	1.38	18.2	4.6	0.24	99.3	6.8
Bw	48-70	20.1	4.26	30.3	1.7	0.10	97.0	6.0
BC	70-95	16.0	2.82	30.7	1.1	0.07	91.5	4.9

*Oven dried basis.

Table 2-2. General chemical properties (2).

Site and horizon	Depth (cm)	CEC* (cmol kg^{-1})	Base satur. (%)	ECEC /CEC (%)	Total* C (*10^{-2} kg kg^{-1})	Total* N (*10^{-2} kg kg^{-1})	Phosphate retention (%)	Moisture* content (*10^{-2} kg kg^{-1})
N-4b								
A	0-6	62.2	5.22	26.7	21.3	1.36	53.0	8.0
AB	6-12	40.2	3.23	48.8	10.2	0.61	77.5	6.2
BA	12-15	34.4	2.09	55.0	5.8	0.35	87.3	5.4
Bs	15-30	30.8	1.82	44.5	5.3	0.32	93.8	6.7
Bw1	30-40	20.6	2.14	38.6	2.1	0.16	93.8	5.9
Bw2	40-52	19.8	2.07	35.8	1.5	0.12	85.1	5.0
BC	52-83	19.5	1.90	32.3	1.5	0.12	82.1	4.9
C	83-100	19.4	1.76	26.7	1.3	0.12	83.4	4.7
H-1a								
A	0-1	60.5	20.48	33.7	24.4	1.23	11.8	11.4
E	1-14	13.6	3.60	76.4	2.1	0.15	31.3	2.0
BE	14-21	25.0	2.56	64.2	4.0	0.24	86.1	5.0
Bs1	21-36	35.9	1.62	27.5	6.5	0.32	94.8	21.7
Bs2	36-58	31.3	1.12	16.8	6.0	0.32	98.8	7.6
BC	58-60	26.5	1.02	16.5	6.1	0.28	98.8	7.5
H-1b								
A	0-9	71.2	10.23	20.4	28.1	1.68	46.4	7.2
E	9-19	17.8	2.10	59.1	2.9	0.33	29.9	2.0
Bs1	19-22	33.7	2.00	54.3	5.4	0.29	86.5	4.6
Bs2	22-36	27.5	3.61	39.6	4.2	0.21	79.2	4.3
BC	36-49	19.0	3.37	41.9	3.3	0.18	68.4	3.4
Sw-1								
A	0-2	69.3	4.95	21.6	24.6	1.37	27.8	9.3
E	2-10	32.0	2.38	50.0	5.7	0.37	49.2	3.8
EB	10-23	29.9	2.84	67.2	3.7	0.26	76.2	4.0
Bs	23-45	33.9	1.45	49.3	3.7	0.25	82.4	6.3
BC	45-60	23.4	2.09	29.4	2.9	0.18	74.4	5.4
C	60-73	12.8	2.73	22.7	1.2	0.09	58.0	3.5
Sw-3								
A	0-6	66.0	14.47	23.8	27.5	1.38	24.0	7.6
E	6-12	32.6	4.29	42.1	4.4	0.24	35.8	3.2
EB	12-20	24.8	2.38	83.4	2.4	0.18	59.2	4.0
Bs	20-75	33.6	3.13	35.8	3.1	0.20	73.9	6.0
Sw-4								
A	0-4	63.0	4.65	19.9	20.2	1.07	20.4	6.0
E	4-22	17.9	1.68	59.7	2.6	0.15	33.4	2.1
EB	22-29	26.0	1.50	62.8	2.1	0.13	56.0	2.7
Bs	29-50	27.1	1.73	68.8	3.3	0.18	83.4	4.3
C	50-65	15.8	1.58	54.8	1.4	0.09	62.0	3.2

*Oven dried basis.

Table 3-1. General chemical properties (3).

Site and horizon	Depth (cm)	pH H_2O	pH KCl	pH NaF	STPT method ZPC	STPT method σ_p[a] (cmol kg^{-1})	PAT method ZPC	PAT method σ_p[a] (cmol kg^{-1})
Sw-2								
A	0-2	3.82	2.91	7.05	3.18	3.89	< 3.0	n.d.
AB	2-11	4.05	3.17	8.48	3.56	2.32	3.59	0.99
BA	11-25	4.35	3.53	9.68	3.98	0.87	3.89	0.15
Bw	25-50	4.50	3.69	10.35	3.99	1.32	4.24	0.42
BC	50-73	4.73	3.77	10.71	4.08	0.82	4.36	- 0.02
C	73-80	4.68	3.70	9.67	4.06	0.80	4.26	0.08
N-1b								
A	0-5	3.91	3.44	8.13	3.79	2.14	3.57	1.42
BA	5-19	4.22	3.80	9.69	4.03	1.82	4.15	0.00
Bw	19-55	4.54	4.22	11.64	4.59	0.22	4.46	0.07
BC	55-86	4.63	4.16	11.38	4.41	0.41	4.52	- 0.06
C	86-99	4.65	4.03	9.90	4.44	0.14	4.48	- 0.08
H-2								
A	0-6	3.78	3.25	7.89	3.77	1.39	< 3.0	n.d.
AB	6-14	4.00	3.47	8.69	3.76	1.96	3.78	0.52
BA	14-28	4.25	3.72	9.44	4.08	0.99	4.14	- 0.08
Bw	28-48	4.50	3.90	9.90	4.17	0.96	4.28	0.00
BC	48-57	4.65	3.95	9.92	4.36	0.31	4.28	0.22
S-3								
A	0-8	3.50	2.92	6.91	.	.	.	.
AB1	8-21	4.31	3.55	9.43	.	.	3.89	0.38
AB2	21-34	4.56	3.89	10.78	.	.	4.27	0.00
BA	34-48	4.67	4.01	11.12	4.32	0.27	4.42	- 0.10
Bw	48-70	4.65	3.95	10.66	4.11	0.65	4.24	0.54
BC	70-95	4.66	3.96	10.42	.	.	4.38	0.19

[a]Oven dried basis.

Table 3-2. General chemical properties (3).

Site and horizon	Depth (cm)	pH H_2O	pH KCl	pH NaF	STPT method ZPC	STPT method σ_p[a] (cmol kg^{-1})	PAT method ZPC	PAT method σ_p[a] (cmol kg^{-1})
N-4b								
A	0-6	3.59	2.88	6.72	< 3.0	n.d.	< 3.0	n.d.
AB	6-12	3.76	2.94	7.48	3.13	3.91	< 3.0	n.d.
BA	12-15	3.84	3.21	8.38	3.41	2.74	3.48	1.15
Bs	15-30	4.05	3.52	8.95	3.74	1.86	3.76	0.70
Bw1	30-40	4.36	3.85	10.16	4.06	1.00	4.16	0.85
Bw2	40-52	4.49	3.97	10.29	4.16	0.69	4.34	- 0.09
BC	52-83	4.49	4.01	10.35	4.16	0.76	4.29	0.31
C	83-100	4.57	4.05	10.81	4.41	0.08	4.25	0.69
H-1a								
A	0-1	3.56	2.75	6.13	.	.	.	.
E	1-14	3.91	2.90	7.31	.	.	< 3.0	n.d.
BE	14-21	4.26	3.33	8.61	.	.	.	.
Bs1	21-36	4.73	3.73	10.00	3.93	2.68	4.06	0.76
Bs2	36-58	4.82	4.00	11.36	4.16	0.67	.	.
BC	58-60	4.71	4.10	11.49	.	.	4.31	0.00
H-1b								
A	0-9	3.69	2.94	6.47	.	.	< 3.0	n.d.
E	9-19	3.67	2.87	7.24	< 3.0	n.d.	< 3.0	n.d.
Bs1	19-22	3.88	3.24	8.56	3.48	2.82	3.59	0.92
Bs2	22-36	4.18	3.65	9.62	3.86	1.68	3.94	0.23
BC	36-49	4.30	3.77	10.16	3.94	1.40	4.08	0.31
Sw-1								
A	0-2	3.43	2.37	6.43	< 3.0	n.d.	< 3.0	n.d.
E	2-10	3.65	2.60	7.38	3.04	1.49	< 3.0	n.d.
EB	10-23	3.97	2.99	8.51	3.58	1.16	< 3.0	n.d.
Bs	23-45	4.20	3.19	8.95	3.78	0.86	< 3.0	n.d.
BC	45-60	4.58	3.58	10.83	4.20	0.38	4.18	0.18
C	60-73	4.71	3.95	11.39	4.38	0.24	4.58	- 0.04
Sw-3								
A	0-6	3.73	2.63	6.54	< 3.0	n.d.	< 3.0	n.d.
E	6-12	3.68	2.53	7.24	< 3.0	n.d.	< 3.0	n.d.
EB	12-20	3.74	2.61	7.83	< 3.0	n.d.	< 3.0	n.d.
Bs	20-75	4.29	3.44	9.42	3.84	0.88	3.80	0.78
Sw-4								
A	0-4	3.19	2.50	6.17	.	.	.	.
E	4-22	3.51	2.89	7.30	.	.	.	.
EB	22-29	3.73	3.06	8.03	.	.	.	.
Bs	29-50	3.90	3.35	8.80	.	.	.	.
C	50-65	4.21	3.62	9.44	.	.	.	.

[a]Oven dried basis.

Table 4-1. Sesquioxidic properties.

Site and horizon	Depth (cm)	Alo[a]	Feo[a]	Sio[a]	Alp[a]	Fep[a]	Sip[a]	Cp[a]	Ald[a]	Fed[a]	Sid[a]	Fep /Feo	Alp /Alo	Cp /(Fep +Alp)[b]
		($*10^{-2}$ kg kg^{-1})			($*10^{-2}$ kg kg^{-1})				($*10^{-2}$ kg kg^{-1})					
Sw-2														
A	0-2	0.69	0.95	0.04	0.59	0.91	0.00	4.63	0.96	2.10	0.22	0.96	0.86	10.1
AB	2-11	0.81	1.22	0.04	0.72	1.31	0.00	3.51	1.01	2.98	0.17	1.07	0.89	5.8
BA	11-25	0.81	1.40	0.04	0.66	1.01	0.00	1.80	1.13	3.48	0.12	0.72	0.81	3.5
Bw	25-50	0.92	1.34	0.06	0.60	0.89	0.00	1.61	1.28	3.33	0.13	0.66	0.65	3.5
BC	50-73	0.85	0.36	0.10	0.45	0.27	0.01	0.64	1.04	2.08	0.18	0.75	0.53	2.5
C	73-80	0.45	0.26	0.05	0.23	0.15	0.00	0.32	0.77	2.28	0.12	0.58	0.51	2.4
N-1b														
A	0-5	0.77	1.45	0.04	0.66	1.32	0.10	3.81	0.79	2.60	0.17	0.91	0.86	6.6
BA	5-19	1.01	2.07	0.05	0.81	1.62	0.00	2.61	0.95	3.15	0.09	0.78	0.80	3.7
Bw	19-55	2.06	1.59	0.29	0.93	0.71	0.01	1.90	1.68	2.68	0.20	0.45	0.45	3.4
BC	55-86	1.66	1.40	0.23	0.78	0.51	0.05	1.29	1.35	2.48	0.16	0.36	0.47	2.8
C	86-99	0.60	0.72	0.06	0.39	0.40	0.07	0.54	0.67	2.19	0.07	0.55	0.65	2.1
H-2														
A	0-6	0.79	1.66	0.02	0.57	1.12	0.05	3.37	0.73	2.90	0.10	0.67	0.72	6.8
AB	6-14	0.83	1.82	0.04	0.68	1.37	0.01	3.11	0.85	3.22	0.05	0.75	0.82	5.2
BA	14-28	0.90	1.95	0.03	0.79	1.83	0.00	1.99	1.01	3.48	0.03	0.94	0.87	2.7
Bw	28-48	0.77	1.15	0.06	0.71	1.00	.	1.03	0.90	3.07	0.01	0.87	0.93	1.9
BC	48-57	0.66	0.67	0.07	0.57	0.64	0.04	0.67	0.81	2.50	0.05	0.96	0.87	1.7
S-3														
A	0-8	0.69	1.18	0.02	0.61	1.07	.	6.45	0.86	2.56	0.28	0.91	0.88	12.9
AB1	8-21	1.14	2.06	0.02	1.16	2.20	.	4.04	1.28	3.74	0.06	1.07	1.02	4.1
AB2	21-34	1.51	2.08	0.08	1.38	1.56	.	3.14	1.64	3.87	0.06	0.75	0.91	3.3
BA	34-48	1.68	1.68	0.14	1.38	1.25	.	2.39	1.83	3.70	0.12	0.74	0.82	2.7
Bw	48-70	1.14	1.01	0.11	0.72	0.49	.	1.06	1.30	3.27	0.10	0.49	0.63	2.5
BC	70-95	0.98	0.88	0.15	0.59	0.54	.	0.60	1.01	2.98	0.10	0.61	0.60	1.6

[a]Oven dried basis. [b]Atomic ratio.

Table 4-2. Sesquioxidic properties.

Site and horizon	Depth (cm)	Alo[a]	Feo[a]	Sio[a]	Alp[a]	Fep[a]	Sip[a]	Cp[a]	Ald[a]	Fed[a]	Sid[a]	Fep /Feo	Alp /Alo	Cp /(Fep +Alp)[b]
		($*10^{-2}$ kg kg^{-1})			($*10^{-2}$ kg kg^{-1})				($*10^{-2}$ kg kg^{-1})					
N-4b														
A	0-6	0.39	0.57	0.02	0.24	0.60	0.13	4.35	0.47	1.32	0.25	1.06	0.61	18.5
AB	6-12	0.51	1.44	0.06	0.37	1.18	0.05	3.77	0.58	2.60	0.14	0.82	0.72	9.0
BA	12-15	0.61	2.16	0.03	0.40	1.44	0.00	2.65	0.70	3.79	0.11	0.67	0.65	5.4
Bs	15-30	1.06	3.48	0.04	0.72	1.42	0.04	3.06	1.21	5.57	0.10	0.41	0.68	4.9
Bw1	30-40	1.01	2.05	0.06	0.59	0.84	0.07	1.10	1.23	4.43	0.10	0.41	0.58	2.5
Bw2	40-52	0.98	1.08	0.10	0.55	0.58	0.16	1.04	1.15	3.41	0.12	0.53	0.56	2.8
BC	52-83	1.01	0.99	0.06	0.59	0.51	0.07	1.01	1.14	3.16	0.10	0.52	0.58	2.7
C	83-100	1.12	1.10	0.15	0.57	0.42	0.02	0.75	1.16	2.80	0.15	0.38	0.51	2.2
H-1a														
A	0-1	0.26	0.18	0.00	0.26	0.15	.	4.37	0.51	1.80	0.17	0.83	1.00	29.6
E	1-14	0.16	0.27	0.00	0.13	0.20	.	0.64	0.15	1.32	0.05	0.74	0.81	6.3
BE	14-21	0.67	1.92	0.01	0.56	1.18	.	1.87	0.75	4.47	0.02	0.61	0.84	3.7
Bs1	21-36	1.42	2.86	0.04	1.17	1.34	.	3.38	1.60	5.26	0.04	0.47	0.82	4.2
Bs2	36-58	1.79	1.57	0.12	1.48	0.87	.	3.64	1.98	4.15	0.09	0.55	0.83	4.3
BC	58-60	1.62	0.93	0.07	1.59	0.78	.	3.67	1.90	3.42	0.09	0.84	0.98	4.2
H-1b														
A	0-9	0.37	0.44	0.02	0.36	0.39	0.17	6.36	.	.	.	0.88	0.98	26.1
E	9-19	0.19	0.14	0.03	0.16	0.12	0.07	0.87	0.19	0.97	0.09	0.84	0.83	9.0
Bs1	19-22	0.67	2.20	0.02	0.54	1.26	0.04	3.51	0.64	3.71	0.07	0.57	0.80	6.9
Bs2	22-36	0.88	1.60	0.05	0.66	0.89	0.04	2.71	0.95	3.52	0.10	0.56	0.75	5.6
BC	36-49	0.72	0.79	0.03	0.66	0.70	0.20	2.12	0.80	2.36	0.02	0.89	0.91	4.8
Sw-1														
A	0-2	0.27	0.24	0.03	0.23	0.19	0.08	4.02	0.33	0.51	0.22	0.79	0.85	28.1
E	2-10	0.30	0.44	0.03	0.22	0.37	0.06	1.33	0.34	1.63	0.13	0.84	0.73	7.5
EB	10-23	0.49	1.38	0.03	0.38	1.33	0.06	1.37	0.51	3.25	0.08	0.96	0.78	3.0
Bs	23-45	0.82	2.28	0.03	0.56	1.56	0.02	1.69	0.83	4.61	0.08	0.68	0.68	2.9
BC	45-60	0.92	1.44	0.03	0.62	0.70	0.00	1.49	0.96	2.82	0.09	0.49	0.67	3.5
C	60-73	0.83	0.40	0.12	0.49	0.16	0.00	0.59	0.78	1.35	0.14	0.40	0.59	2.3
Sw-3														
A	0-6	0.23	0.23	0.02	0.20	0.22	0.12	3.20	0.25	0.89	0.32	0.96	0.87	23.5
E	6-12	0.36	0.16	0.05	0.09	0.11	0.00	1.00	0.26	1.23	0.20	0.69	0.25	15.7
EB	12-20	0.35	0.54	0.02	0.26	0.31	0.06	0.79	0.42	3.32	0.10	0.57	0.74	4.3
Bs	20-75	0.75	1.36	0.03	0.45	0.56	0.00	1.35	0.89	4.01	0.08	0.41	0.60	4.2
Sw-4														
A	0-4	0.30	0.22	0.00	0.21	0.12	0.12	3.54	0.20	1.24	0.17	0.54	0.70	29.7
E	4-22	0.15	0.12	0.02	0.17	0.13	0.03	0.88	0.17	1.79	0.09	1.06	1.11	8.5
EB	22-29	0.37	0.49	0.01	0.24	0.31	0.05	1.11	0.28	2.39	0.09	0.63	0.65	6.4
Bs	29-50	0.78	1.77	0.02	0.55	1.06	0.04	1.94	0.66	4.16	0.09	0.60	0.70	4.1
C	50-65	0.53	0.83	0.03	0.46	0.67	0.02	0.91	0.73	3.52	0.09	0.81	0.87	2.6

[a]Oven dried basis. [b]Atomic ratio.

Table 5-1. Particle size distribution and clay mineral species.

Site and horizon	Depth (cm)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	Clay mineral species
Sw-2						
A	0-2	40.8	47.4	8.9	2.9	H.C.Sm > Vt, Ch, Mica, Kao
AB	2-11	42.1	46.0	9.7	2.3	Vt > Ch, Mica, Kao
BA	11-25	44.8	45.6	7.6	2.0	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
Bw	25-50	40.9	48.8	7.3	2.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
BC	50-73	46.8	44.2	6.1	2.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
C	73-80	32.4	39.0	12.2	16.5	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
N-1b						
A	0-5	49.1	32.3	14.7	3.9	H.C.Sm, Vt, 2:1-2:1:1 int. > Ch, Mica
BA	5-19	40.6	39.1	17.5	2.8	2:1-2:1:1 int. > H.C.Sm, Vt, Mica, Kao, Gb
Bw	19-55	52.6	31.8	13.1	2.5	2:1-2:1:1 int. > Mica, Kao, Gb
BC	55-86	54.6	32.8	11.5	1.2	2:1-2:1:1 int. > Mica, Ch, Kao, Gb
C	86-99	33.8	35.3	24.1	6.8	2:1-2:1:1 int. > Mica, Ch, Kao, Gb
H-2						
A	0-6	52.9	31.2	11.6	4.2	Vt, 2:1-2:1:1 int. > Mica, Kao, Gb
AB	6-14	54.6	33.1	8.3	4.0	2:1-2:1:1 int. > Vt, Mica, Kao Gb
BA	14-28	54.3	35.2	8.1	2.4	2:1-2:1:1 int. > Mica, Kao, Gb
Bw	28-48	52.4	33.0	9.9	4.7	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
BC	48-57	46.4	33.2	12.5	8.0	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
S-3						
A	0-8	53.7	40.3	5.8	0.2	Sm > Kao
AB1	8-21	52.2	38.6	8.3	0.9	2:1-2:1:1 int. > Vt, Kao, Gb
AB2	21-34	42.9	45.7	10.6	0.8	2:1-2:1:1 int. > Ch, Kao, Gb
BA	34-48	48.3	43.4	7.8	0.8	2:1-2:1:1 int. > Ch, Kao, Gb
Bw	48-70	49.3	41.7	7.7	1.3	2:1-2:1:1 int. > Ch, Kao, Gb
BC	70-95	50.7	37.5	10.6	1.2	2:1-2:1:1 int. > Ch, Kao, Gb

[a]Kao, kaolin minerals; Mica, clay mica; H.C.Sm, high charge smectite; Vt, vermiculite; Sm, smectite; Ch, chlorite; Gb, gibbsite; 2:1-2:1:1 int., 2:1-2:1:1 intergrade mineral; Mica-H.C.Sm, interstratified mineral of clay mica and high charge smectite; Mica-Vt, interstratified mineral of clay mica and vermiculite.

Table 5-2. Particle size distribution and clay mineral species.

Site and horizon	Depth (cm)	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	Clay mineral species
N-4b						
A	0-6	42.5	46.7	9.8	1.1	H.C.Sm > Mica, Kao
AB	6-12	43.2	45.8	10.3	0.6	H.C.Sm > Vt, Mica, Kao
BA	12-15	44.1	44.2	10.9	0.8	Vt > H.C.Sm, Mica, Kao
Bs	15-30	54.8	36.3	8.0	0.8	2:1-2:1:1 int. > Vt, Mica, Kao, Gb
Bw1	30-40	48.0	36.6	5.8	9.7	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
Bw2	40-52	46.3	45.5	6.3	1.9	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
BC	52-83	52.0	40.9	5.7	1.4	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
C	83-100	47.2	37.0	9.7	6.2	2:1-2:1:1 int. > Ch, Mica, Kao, Gb
H-1a						
A	0-1	.	.	.	.	H.C.Sm > Mica, Kao
E	1-14	32.1	39.1	18.5	10.4	Mica > H.C.Sm, Kao
BE	14-21	45.1	32.0	14.1	8.8	Vt > H.C.Sm, Kao
Bs1	21-36	53.2	29.3	12.9	4.6	Vt > 2:1-2:1:1 int., Kao, Gb
Bs2	36-58	37.3	29.8	15.5	17.3	2:1-2:1:1 int. > Vt, Kao, Gb
BC	58-60	32.4	19.5	16.9	31.2	2:1-2:1:1 int. > Vt, Kao, Gb
H-1b						
A	0-9	39.6	40.2	12.3	7.9	Mica > H.C.Sm, Vt, Kao
E	9-19	33.0	39.9	14.4	12.7	Mica > H.C.Sm > Vt, Kao
Bs1	19-22	40.1	28.7	15.0	16.2	H.C.Sm-Mica > Vt, Kao
Bs2	22-36	40.4	26.6	13.4	19.7	2:1-2:1:1 int. > Vt, Mica, Kao, Gb
BC	36-49	36.1	27.2	16.2	20.5	2:1-2:1:1 int. > Vt, Ch, Mica, Kao, Gb
Sw-1						
A	0-2	31.0	35.4	16.9	16.7	H.C.Sm-Mica > Kao
E	2-10	33.2	36.0	16.8	14.0	H.C.Sm-Mica > Kao
EB	10-23	40.7	33.0	14.7	11.6	H.C.Sm-Mica, Vt-Mica > Kao
Bs	23-45	49.6	31.2	10.4	8.9	Vt, 2:1-2:1:1 int. > Mica, Kao, Gb
BC	45-60	34.2	27.5	12.5	25.9	2:1-2:1:1 int. > Mica, Kao, Gb
C	60-73	17.0	16.2	18.5	48.4	2:1-2:1:1 int., Mica > Kao, Gb
Sw-3						
A	0-6	25.9	45.8	18.0	10.3	H.C.Sm-Mica > Kao
E	6-12	27.7	43.5	20.4	8.4	H.C.Sm-Mica > Kao
EB	12-20	35.7	40.0	18.4	6.0	H.C.Sm-Mica > Vt-Mica, Kao
Bs	20-75	33.4	32.7	14.0	19.9	Vt > 2:1-2:1:1 int., Mica, Kao
Sw-4						
A	0-4	27.0	33.6	26.5	12.8	H.C.Sm-Mica > 2:1-2:1:1 int., Kao
E	4-22	29.2	30.5	34.4	5.9	H.C.Sm-Mica > Kao
EB	22-29	32.1	29.3	33.5	5.1	H.C.Sm-Mica, Vt-Mica > Kao
Bs	29-50	40.7	27.1	28.0	4.2	2:1-2:1:1 int. > Vt, Mica, Kao, Gb
C	50-65	29.4	30.7	31.0	8.9	2:1-2:1:1 int. > Mica, Kao, Gb

[a]Kao, kaolin minerals; Mica, clay mica; H.C.Sm, high charge smectite; Vt, vermiculite; Sm, smectite; Ch, chlorite; Gb, gibbsite; 2:1-2:1:1 int., 2:1-2:1:1 intergrade mineral; Mica-H.C.Sm, interstratified mineral of clay mica and high charge smectite; Mica-Vt, interstratified mineral of clay mica and vermiculite.

Table 6-1. Total chemical composition.

Site and horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	Ignition[a] loss (%)
		($*10^{-2}$ kg kg^{-1})										
Sw-2												
A	0-2	68.19	17.08	8.12	1.32	0.05	0.48	1.03	1.74	0.71	0.08	45.1
AB	2-11	68.95	17.21	8.28	1.32	0.05	0.29	0.99	1.68	0.65	0.04	26.7
BA	11-25	68.34	17.82	8.43	1.32	0.05	0.24	0.97	1.64	0.59	0.01	14.7
Bw	25-50	66.35	19.58	8.88	1.27	0.05	0.24	1.07	1.63	0.61	0.01	13.5
BC	50-73	63.06	23.02	8.23	1.10	0.07	0.18	1.45	1.87	0.53	0.00	10.3
C	73-80	64.50	22.09	7.76	1.07	0.05	0.08	1.34	2.44	0.29	0.00	8.7
N-1b												
A	0-5	65.85	17.33	8.13	1.18	0.03	0.27	1.06	2.08	0.73	0.27	30.2
BA	5-19	67.77	17.78	8.58	1.20	0.03	0.23	1.08	2.05	0.72	0.19	17.1
Bw	19-55	64.24	24.41	8.36	1.08	0.05	0.27	1.42	2.10	0.77	0.13	13.4
BC	55-86	61.90	22.27	8.18	1.06	0.05	0.29	1.52	2.16	0.80	0.10	11.6
C	86-99	69.77	17.66	6.28	1.06	0.03	0.08	1.09	2.21	0.63	0.07	7.1
H-2												
A	0-6	65.26	18.66	9.12	1.20	0.03	0.28	1.22	1.93	0.55	0.22	27.6
AB	6-14	65.00	19.42	9.26	1.24	0.03	0.21	1.22	1.90	0.51	0.18	20.6
BA	14-28	63.63	20.79	9.59	1.24	0.03	0.17	1.25	1.87	0.49	0.13	15.7
Bw	28-48	61.13	22.33	9.44	1.15	0.02	0.11	1.44	2.06	0.32	0.09	11.0
BC	48-57	61.93	22.33	7.85	1.11	0.02	0.08	1.46	2.39	0.28	0.08	9.5
S-3												
A	0-8	67.91	17.39	8.32	1.19	0.06	0.51	1.14	1.87	0.88	0.12	53.1
AB1	8-21	66.28	19.16	9.27	1.26	0.06	0.29	1.17	1.86	0.77	0.05	22.4
AB2	21-34	64.29	20.63	9.29	1.20	0.06	0.28	1.26	1.85	0.74	0.03	18.2
BA	34-48	63.21	22.20	8.89	1.14	0.07	0.29	1.42	1.88	0.72	0.02	10.6
Bw	48-70	62.47	22.30	8.45	1.08	0.08	0.23	1.68	2.02	0.66	0.00	10.6
BC	70-95	61.91	22.97	7.91	1.02	0.08	0.28	1.64	2.11	0.76	0.00	9.7

All the data except for ignition loss are given on an ignition basis. [a]Oven dried basis.

Table 6-2. Total chemical composition.

Site and horizon	Depth (cm)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO_2	CaO	MgO	K_2O	Na_2O	P_2O_5	Ignition[a] loss (%)
		($*10^{-2}$ kg kg^{-1})										
N-4b												
A	0-6	73.84	14.17	6.12	1.32	0.02	0.34	0.86	1.51	0.76	0.26	49.1
AB	6-12	73.38	13.70	7.17	1.49	0.02	0.20	0.78	1.50	0.66	0.13	23.5
BA	12-15	71.24	13.61	8.91	1.59	0.02	0.17	0.77	1.39	0.59	0.09	15.2
Bs	15-30	63.19	17.34	13.22	1.53	0.02	0.16	0.95	1.45	0.48	0.09	16.6
Bw1	30-40	60.85	21.57	11.18	1.28	0.04	0.19	1.33	1.70	0.54	0.07	11.5
Bw2	40-52	61.52	22.56	9.53	1.20	0.05	0.18	1.51	1.97	0.52	0.06	10.6
BC	52-83	60.51	22.78	9.57	1.18	0.05	0.16	1.50	2.00	0.51	0.06	10.7
C	83-100	58.94	23.86	8.69	1.08	0.04	0.26	1.48	1.91	0.69	0.05	10.9
H-1a												
A	0-1	73.57	13.08	4.52	1.38	0.01	0.20	0.70	2.79	1.11	0.20	.
E	1-14	78.73	13.43	2.40	1.36	0.02	0.09	0.52	2.67	0.37	0.00	6.5
BE	14-21	67.52	18.62	7.98	1.29	0.02	0.02	0.72	2.70	0.29	0.01	13.2
Bs1	21-36	61.51	23.01	10.03	1.20	0.03	0.07	0.84	2.62	0.33	0.03	19.2
Bs2	36-58	58.42	27.07	8.34	1.06	0.03	0.06	1.00	2.90	0.33	0.03	19.8
BC	58-60	57.18	28.18	6.94	1.05	0.02	0.01	0.97	4.03	0.24	0.03	18.2
H-1b												
A	0-9	.	.	.	.	.	.	.	.	.	.	53.1
E	9-19	76.16	14.98	2.52	1.32	0.01	0.07	0.64	3.17	0.37	0.06	8.2
Bs1	19-22	62.31	20.89	9.12	1.14	0.01	0.03	0.87	3.47	0.25	0.10	16.9
Bs2	22-36	60.29	23.75	8.47	1.07	0.02	0.04	0.97	3.10	0.27	0.09	15.2
BC	36-49	61.16	24.78	6.52	1.07	0.01	0.04	0.98	3.39	0.32	0.09	13.0
Sw-1												
A	0-2	73.30	15.85	3.94	1.24	0.02	0.20	0.77	2.93	0.44	0.10	49.1
E	2-10	72.84	16.46	4.28	1.24	0.02	0.05	0.75	3.17	0.28	0.03	13.2
EB	10-23	68.01	18.31	6.69	1.21	0.02	0.03	0.80	3.25	0.23	0.02	11.1
Bs	23-45	62.08	22.07	9.23	1.17	0.02	0.02	0.92	3.41	0.21	0.03	12.9
BC	45-60	61.44	24.84	6.94	1.05	0.02	0.00	0.94	3.47	0.17	0.03	12.4
C	60-73	65.27	23.83	3.61	0.95	0.02	0.00	0.81	3.99	0.12	0.02	8.1
Sw-3												
A	0-6	76.08	12.36	3.56	1.24	0.03	0.61	0.74	2.14	0.66	0.08	50.7
E	6-12	77.69	12.42	3.42	1.25	0.02	0.06	0.66	2.21	0.30	0.01	10.5
EB	12-20	68.31	18.38	7.44	1.14	0.02	0.01	0.97	3.18	0.14	0.02	9.0
Bs	20-75	61.65	23.04	8.82	1.02	0.02	0.00	1.05	3.60	0.11	0.04	14.0
Sw-4												
A	0-4	.	.	.	.	.	.	.	.	.	.	46.3
E	4-22	.	.	.	.	.	.	.	.	.	.	8.1
EB	22-29	.	.	.	.	.	.	.	.	.	.	8.0
Bs	29-50	.	.	.	.	.	.	.	.	.	.	12.1
C	50-65	.	.	.	.	.	.	.	.	.	.	9.8

All the data except for ignition loss are given on an ignition basis. [a]Oven dried basis.

Publications

Chapter 3

Funakawa, S., Hirai, H., and Kyuma, K. 1992: Soil-forming processes under natural forest north of Kyoto in relation to soil solution composition. *Soil Sci. Plant Nutr.*, **38,** 101–112

Chapter 4

Funakawa, S., Hirai H., and Kyuma K. 1993: Speciation of Al in soil solution from forest soils in northern Kyoto with special reference to their pedogenetic process. *Soil Sci. Plant Nutr.*, **39,** in press

Chapter 5

Funakawa, S., Nambu, K., Hirai. H., and Kyuma, K. 1993: Physical properties of forest soils in northern Kyoto with special reference to their pedogenetic processes. *Soil Sci. Plant Nutr.*, **39,** in press

Chapter 6

Funakawa, S., Yonebayashi, K., and Kyuma, K. 1993: Characteristics of humic substances and dynamics of dissolved organic matter in forest soils in northern Kyoto with special reference to their pedogenetic processes. *Soil Sci. Plant Nutr.*, **39,** in press

Chapter 7

Funakawa, S., Nambu, K., Hirai, H., and Kyuma, K. 1993: Pedogenetic acidification process of forest soils in northern Kyoto. *Soil Sci. Plant Nutr.*, submitted