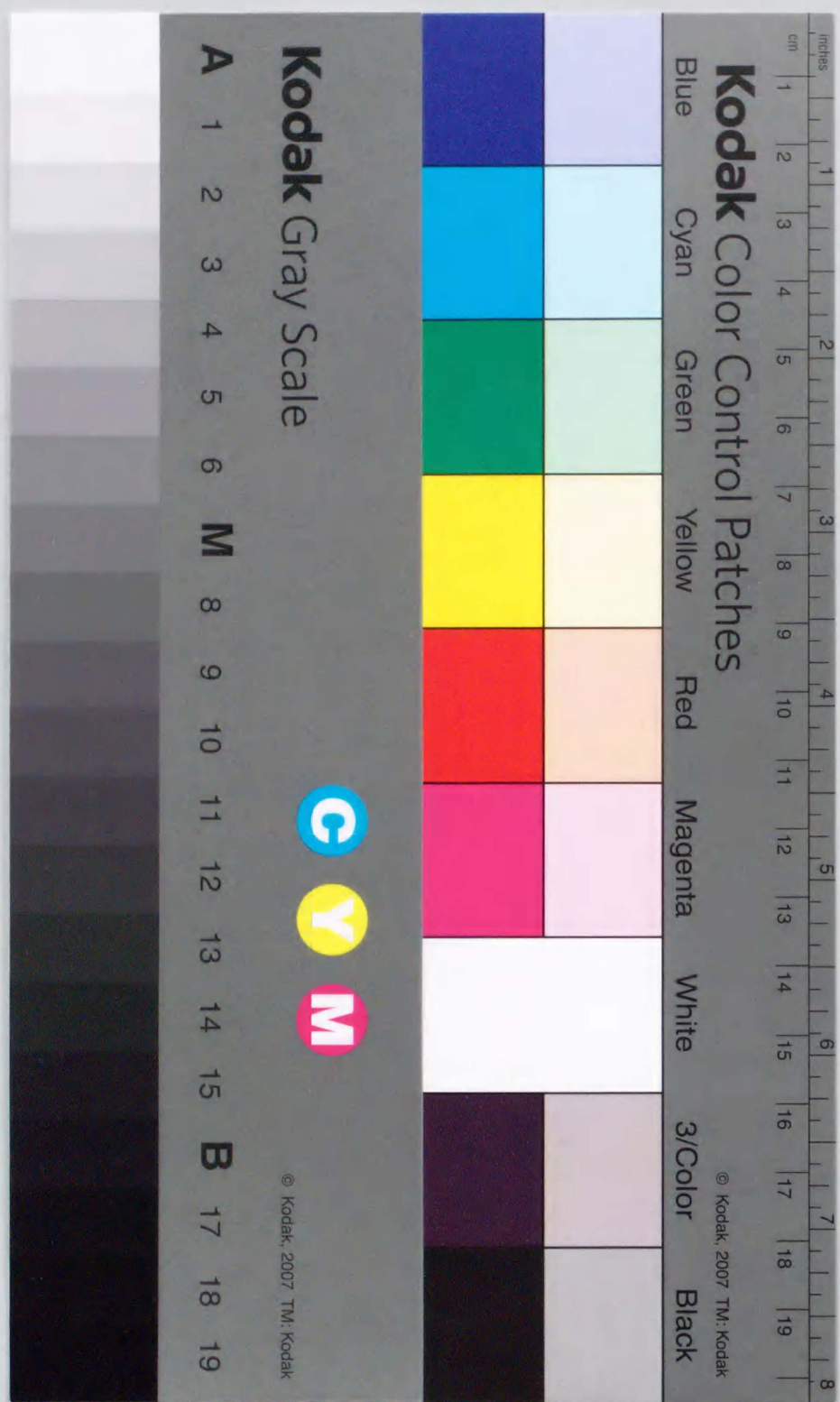# Acidification of Forested Andisols due to Acidic Deposition

1999.3

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（馬場　光久）

Acidification
of
Forested Andisols
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Acidic Deposition

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Content

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Chapter I

General Introduction

General Introduction

Acidic deposition is a global environmental issue and has its origin from the emission of pollutants to the atmosphere. Acidic deposition affects ecosystems directly and/or indirectly. In Europe and North America acidic deposition has seriously affected watercourses and forests in some areas are threatened (e.g. Babich *et al.*, 1980; Paces, 1985; Ulrich, 1986; Irwin and Williams, 1988; Cerny and Paces, 1995). The definition of the forest ecosystem and effects of acidic deposition was introduced by Papke and Krahl-Urban (1988). The major concern of this thesis is soil, an abiotic environmental factor of the forest ecosystems. Therefore, the theme of this thesis is

i) how precipitation chemistry contribute soil (solution) acidification?

ii) how soil acidification induce forest damage?

These subjects were examined by monitoring data for precipitation and soil (solution) chemistry.

Acidic deposition and its effects on forest ecosystems

Emitted sulfur dioxide and nitrogen oxides are transformed into sulfuric acid and nitric acid, respectively. These acids enter forest ecosystems as either wet deposition (precipitation and fog) or dry deposition (gas and aerosols). Acid rain is defined as rain in which pH values are less than 5.6 based on equilibria with the carbon dioxides (CO_2) concentration in the air (Babich et al., 1980; Okazaki, 1994). Taking natural sources of acid substances such as volcanos into consideration, it could be defined as acid rain when the pH is less than 5.0 (Charlson and Rodhe, 1982). Irwin and Williams (1988) and Hara (1994), for example, applied this criterion. The pH value is the strength of the acidity. Total amount of acidic substances, however, is important in estimating the chronic effects of acidification on the forest ecosystems. When forest canopies intercept acidic dry deposition, the intercepted substances are later washed down to the soil by rainfall. Therefore, the concentration and input of acidic substances are higher in throughfall than those in open bulk precipitation. Throughfall governs the soil acidification rate.

Since external ammonium contributes to soil acidification (Gundersen and Rasmussen, 1990), it is defined as a acidic substance in this thesis. Ammonium ions contribute to the neutralization of sulfuric and nitric acids in the atmosphere and form ammonium sulfate and ammonium nitrate. However, protons are released in soil profiles when ammonium ions are nitrified (van Breemen *et al.*, 1982). In addition, excess nitrogen input to the forest ecosystems induce nitrogen saturation (Aber *et al.*, 1989), although atmospheric

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nitrogen contributes to tree growth as the fertilizer in nitrogen poor ecosystems (Abrahamsen, 1980). Excess nitrogen causes a decrease in frost hardiness (Friedland et al., 1984; Soikkeli and Kärenlampi, 1984) and an increase in susceptibility to water stress (Dueck *et al.*, 1990). On the other hand, nitrate output from forest ecosystems increases with saturation. Simultaneously, base cation mobilization is accelerated. When base cation pools are exhausted, aluminum mobilization becomes the main acid sink.

Acid rain has been recorded in Japan since the 1960s (Komeiji *et al.*, 1975; Okita, 1976). Drizzle injured people's eyes and caused skin irritation in the Kanto district and Shizuoka Prefecture, Central Japan from 1973 to 1975 in spite of the enactment of the Air Pollution Acts in 1968 and the Water and Soil Pollution Act in 1970 (Hara *et al.*,1990). After this period, extraordinary injuries by air pollutants and oxidants have not been reported anywhere in the country. Based on the Acid Precipitation Chemistry Monitoring (Japan Environment Agency, Phase I study, 1983-1987, and Phase II study, 1988-1992), Japan Environment Agency (1989, 1994) stated that there were no serious problems caused by acidic deposition in Japan. However, abnormal growth and defoliation of coniferous trees have been recognized since the 1970s (Yoshizawa and Masuda, 1986). Yambe (1978) and Takahashi *et al.* (1986) have suggested that the Japanese cedar (*Cryptomeria japonica*) in the Kanto district might be suffering from acidic deposition. According to interim report on Acid Precipitation Chemistry Monitoring by Japan Environment Agency (Phase III study), relationship between forest decline and acidic deposition has not been elucidated (Japan Environment Agency, 1997). Dieback of other species has been reported in the northern Kanto district: Japanese birch (*Betula platyphylla var. japonica*) at Mt. Akagi (Tanimoto *et al.*, 1996) and northern Japanese hemlock (*Tsuga diversifolia*) and Erman's birch (*Betula ermanii*) in the Nikko mountains (Tanimoto *et al.*, 1996; Yoshitake 1996). Recently, diebacks of Momi fir at Mt. Homan, Fukuoka Prefecture (Suda *et al.*, 1992) and of Japanese red pine (*Pinus densiflora*) at Mt. Gokurakuji, Hiroshima Prefecture (Naemura *et al.*,. 1997) were also reported. Soil types of these regions were Dystrochrepts which developed on granite.

The soils in areas where forest ecosystems have been affected by acidic deposition have developed on alluvial sediments, glacial till, sandstone, and granite (Table I-1). These are poor in base cations. Soil acidification is an indirect cause of forest decline (e.g. Hauhs and Ulrich, 1988; Heij et al., 1991; Matzner and Murach, 1995). For example, yellowing of spruce needles was attributed to magnesium deficiency in needles due to magnesium depletion in soil profiles. Kolling *et al.* (1997) revealed that nitrogen fertilization enhanced magnesium deficiency. Acidic deposition accelerates soil acidification and induces aluminum dissolution.

Table I-1: Soil types in areas where forest ecosystems were affected by acidic deposition.

Site	Country	Soil type (Soil Taxonomy)	Parent materials	Vegetation	Condition	
Jizerske catchment	Czech Republic	Podzolic brown earth	biotitic granite	*Picea abies*	declined	1
Nacetin	Czech Republic	Cambic Podzols - Dystric Cambisols		*Picea abies*	declined	1
Sudety	Poland	Brown forest soils [Luvisols] - Podzols	granite, gneiss, slates	*Picea abies*	declined	1
Solling	Germany	Podzolic brown earth (Dystrochrept)	loess, red sandstone	*Picea abies*	yellowing	2
				Fagus silvatica		
Lange Bramke (Harz)	Germany	Cambisols and Podzols	sandstone	*Picea abies*	yellowing	3
					defoliation	
Oberwarmensteinach	Germany	(Spodosols, Inceptisols)	phyllitic solifluction material	*Picea abies*	chlorosis	4
Wulfersreuth	Germany	Podzolic brown earth	phyllitic solifluction cover	*Picea abies*	healthy	4
Selb	Germany	Eutrophic brown earth	basaltic solifluction cover	*Picea abies*	healthy	4
Bavarian Forest (opposite side of border: Bohemian Forest, Czech Republic)	Germany	Podzolic brown earth (Ochrept)	periglacial parageneiss sediments	*Picea abies*	damaged	5
Bavarian Alps (opposite side of border:Austria)	Germany	Moder-rendzina (Rendoll)	dolomite	*Picea abies*	damaged	6
Southern Black Forest (Kalbelescheuer)	Germany	Podzolic brown earth (Dystrochrept)	granite	*Picea abies*	yellowing/loss	7
Northern Black Forest (Freudenstadt)	Germany	(aquic Dystrochrept)	esozoic sandstone	*Abies alba*	defoliation	7
Northern Appalachians (Camels Hump)	NH, USA	(Ochrept - Spodosols - Folists) [low to high elevation]	glacial till	*Picea abies*	yellowing/loss	8
				Abies alba	defoliation	8
Adirondacks	NY, USA	(Spodosol (Humods)- Dysleptist)	glacial till	*Picea rubens*	defoliation	9
Southern Appalachians	USA	(Typic Hapla Umbrept)	Paleozoic granitic quartzite and sandstone	*Picea rubens*	defoliation and	10
				Abies fraseri	growth reduction	11

1: Cerny and Paces, 1995; 2: Ulrich and Matzner, 1988; 3: Hauhs and Ulrich 1988; 4 :Zech *et al.* 1988.; 5: Rehfuess 1988.; 6: Rehfuess 1988; 7: Zottl and Mies 1988; 8: Zottl and Aldinger 1988; 9: Johnson 1988; 10: Johnson 1988; 11:Bruck 1988

Aluminum adversely affects biota (Foy *et al.*, 1978; Cleveland *et al.*, 1989; Parker *et al.*, 1989; Godbold, 1994; Horst, 1995). Soil acidification is commonly defined as a decrease in acid neutralizing capacity (ANC) (van Breemen *et al.*, 1983). In this thesis, soil acidification is defined as the process of exchanging base cations by hydrogen and aluminum ions on soil surfaces. In addition, significant aluminum mobilization is the criteria needed to call it an acidified soil. Anthropogenic soil acidification due to acidic deposition has been added to the natural acidification due to carbonic acid, organic acid, nitrification and oxidation of pyrites (Ulrich, 1986; Okazaki, 1994). The decline in freshwater organisms has been related to increased water acidity in combination with increased concentrations of toxic aluminum species in the water (Abrahamsen *et al.*, 1989). It has been suggested that the uptake of aluminum from drinking water may cause the dementia as a result of accumulation of aluminum in the brain (McLachlan, 1989; Kuroda, 1992; Kuroda, 1998).

Andisols occupy 16 % of the total land area of Japan and 38 % of the Kanto area (Adachi, 1971). Melanudands and Hapludands are mainly distributed in the hilly lands in the Kanto district. Entisols, Haplaquents, developed in the lowlands. The Japan Environment Agency and Japanese Society of Soil Science and Plant Nutrition (1983) classified Andisols and Entisols as having high tolerance to acid substances. On the other hand, Dystrochrepts occupy mountainous areas and typic Cryaquods occupy the higher elevations. These soils are classified as moderately to poorly tolerant to acid. Soils in the southern Kanto district developed on basaltic ashes derived from Mt. Fuji, while soils in the northern Kanto district developed on dacitic or andesitic volcanic ashes derived from Mt. Asama and Mt. Shirane. Therefore, soils in the southern Kanto have higher tolerance to acid than those in the northern Kanto because of differences in base cation content. However, dieback of the Momi fir (*Abies firma*) forest at Mt. Oyama, Kanagawa Prefecture, southern Kanto district has occurred (Igawa *et al.*, 1991; Igawa, 1996). This was attributed to acid precipitation and acid fog.

Based on laboratory experiments, Andisols have a large acid neutralizing capacity, compared with Dystrochrepts and Hapludults (Okazaki, 1990; Oba, 1990). A previous study (Ishizuka *et al.*, 1990) shows that allophanes and high organic matter content contribute to the high neutralizing capacity of Andisols. Sulphate adsorption also contributes to the proton adsorptive capacity (Okazaki, 1989). It takes a long time to drop the pH of Andisols. However, larger amounts of aluminum can be dissolved from Andisols rich in allophane and imogolite than soils consisting of crystalline clay minerals at low pH range (Shioiri, 1952). Aluminum dissolution is regarded as a critical point of soil acidification in this thesis. The changes in composition of soil solutions are important in predicting the earlier stages of acidification of Andisols.

Aim and outline of this thesis

Monitoring studies on soil solution chemistry are the most useful and exact approach in evaluating the changes in pedogenetic processes (van Breemen and Brinkman, 1978). Based on long-term monitoring studies, the acidification processes and/or its effects on terrestrial ecosystems have been elucidated in Europe and North America (Likens, *et al.*, 1977; Paces, 1985; Mulder, 1988; Ulrich, 1989). The long-term monitoring of the forested catchment in the Tama Hills was started in 1990 to study soil acidification by atmospheric acid deposition at the Rolling Land Laboratory (RLL), Tokyo University of Agriculture and Technology, Hachioji, Tokyo.

Response of the forest ecosystem to acidic deposition are dependent on soil properties and the nitrogen saturation status of the forest ecosystem. Several components work as acid sinks in forest ecosystems (Ulrich, 1986; Yoshida and Kawahata, 1988). The first objective of this study is to investigate acid deposition and characterize its chemistry (Chapter II). The main objective of this thesis was to elucidate the effects of acidic deposition on forested Andisols. This was individually analyzed in Chapter III-VI. The effect of sulfate adsorption on soil solution chemistry was discussed in Chapter III. Soil solution chemistry and soil solution acidification processes were examined in Chapter IV. Soil chemistry, especially the sources of soil solution aluminum was investigated in Chapter V. In Chapter VI, the effects of nitrogen saturation at RLL was determined based on stream water chemistry and elemental budgets.

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Chapter II

Acidic Deposition in Tama Hill Region

Abstract

Acidic precipitation has been observed in Japan. The cause of the decline of Japanese forests remains controversial. Since 1990, monitoring studies have been carried out at the Rolling Land Laboratory (RLL), Tokyo University of Agriculture and Technology, Hachioji, Tokyo to characterize precipitation chemistry and estimate ionic input. Open bulk precipitation, throughfall, and stemflow were sampled every two weeks and major ions were subsequently analyzed. The weighted mean pH values of open bulk precipitation were 4.5-4.8. Proton input was comparable to other study sites. Nitrogen input which was relatively high resulted in a lower S/N ratio (ratio of non-sea salt sulfate to nitrate). The high nitrate input was attributed to the high nitrogen oxide gas concentration in the air, which was derived from the non-point source. Coniferous canopies intercept large amounts of acidic substances. Coniferous throughfalls and stemflows were consequently abundant in protons and ammonium ions. In estimating acidic deposition in forest ecosystems, enriched ammonium ions were more important than protons. Estimation of nitrogen dynamics was essential for understanding forest response to atmospheric deposition at RLL.

II-1 *Introduction*

Acidic deposition is a global environmental issue and has its origin in the emissions of pollutants to the atmosphere. In Europe and North America, acidic deposition has seriously affected watercourses and forests in some areas may be threatened (Krahl-Urban *et al.*, 1988). The decline in number of organisms in freshwater has been related to increased water acidity in combination with increased concentration of toxic aluminum species in the water (Abrahamsen *et al.*, 1989). It has been suggested that the uptake of aluminum from drinking water may cause dementia as a result of accumulation of aluminum in the brain (Kuroda, 1992). The European atmospheric chemistry network was established in 1948 (Oden, 1976). Atmospheric monitoring networks have been organized in Europe and North America (e.g. European Monitoring and Evaluation Program (EMEP) (Okita, 1994a) and National Acid Precipitation Program (NADP) (Okita, 1994b)). A proposal for establishing a monitoring network in East Asia has been prepared (Yagishita, 1995). In order to elucidate the effects of acidic deposition

on terrestrial ecosystems, many projects also have been run (e.g. SWAP (UK and Scandinavian Surface Waters Acidification Programme) (Mason, 1990), the Dutch Priority Programme on Acidification (Heij and Schneider, 1991), NITREX (Nitrogen saturation experiments) (Wright and van Breemen, 1995)).

The term *acid rain* was first used by Smith over 100 years ago in and around Manchester (Oden, 1976; Irwin and Williams, 1988). Precipitation acidity has increased in Europe and North America (Irwin and Williams, 1988; Babich *et al.*, 1980). The atmospheric ammonium contributed to soil acidification (van Breemen *et al.*, 1982). When ammonium is nitrified in soil profiles, protons are released into soils and/or soil solutions. Ammonium, therefore, is regarded as a source of acidity. Precipitation chemistry has been monitored in Kobe, Japan since 1935 (Maruyama *et al.*, 1993). Acidic precipitation was observed using a glass electrode from at least 1957 (Maruyama *et al.*, 1994). Drizzle injured people's eyes and caused their skin irritation in the Kanto area and Shizuoka Prefecture, Central Japan, from 1973 to 1975 in spite of the enactment of the Air Pollution Protection Acts in 1968 and the Water and Soil Pollution Protection Act in 1970 (Okita, 1976). After their enactment, extraordinary injuries by air pollutants and oxidants have not been reported anywhere in the country. Based on a five-year Acid Precipitation Chemistry Study (Japan Environment Agency, Phase I study, 1983-1987), Japan Environment Agency (1989) stated that there were no serious problems caused by acid deposition in Japan. Abnormal growth and defoliation of coniferous trees, however, have been recognized since the 1970s (Yoshizawa and Masuda, 1986). Yambe (1978) and Takahashi *et al.* (1986) have suggested that Japanese cedar (*Cryptomeria japonica*) in the Kanto area might be suffering from acid deposition. Dieback of the Momi fir (*Abies firma*) forest at Mt. Oyama, Kanagawa Prefecture, was attributed to acid precipitation and acid fog (Igawa *et al.*,1991).

The monitoring networks on acidic precipitation were established in Japan (Chemical Society of Japan, 1997). Precipitation chemistry at the open space has been intensively studied. On the other hand, only the nutrient cycling aspect of throughfall chemistry has been investigated in forest ecosystems (e.g. Nishimura, 1973; Haibara and Aiba, 1982; Tsutsumi, 1987). Throughfall chemistry markedly varies due to vegetation and other factors. Therefore, comprehensive monitoring should be carried out when the effects of atmospheric deposition on the forest ecosystems are estimated.
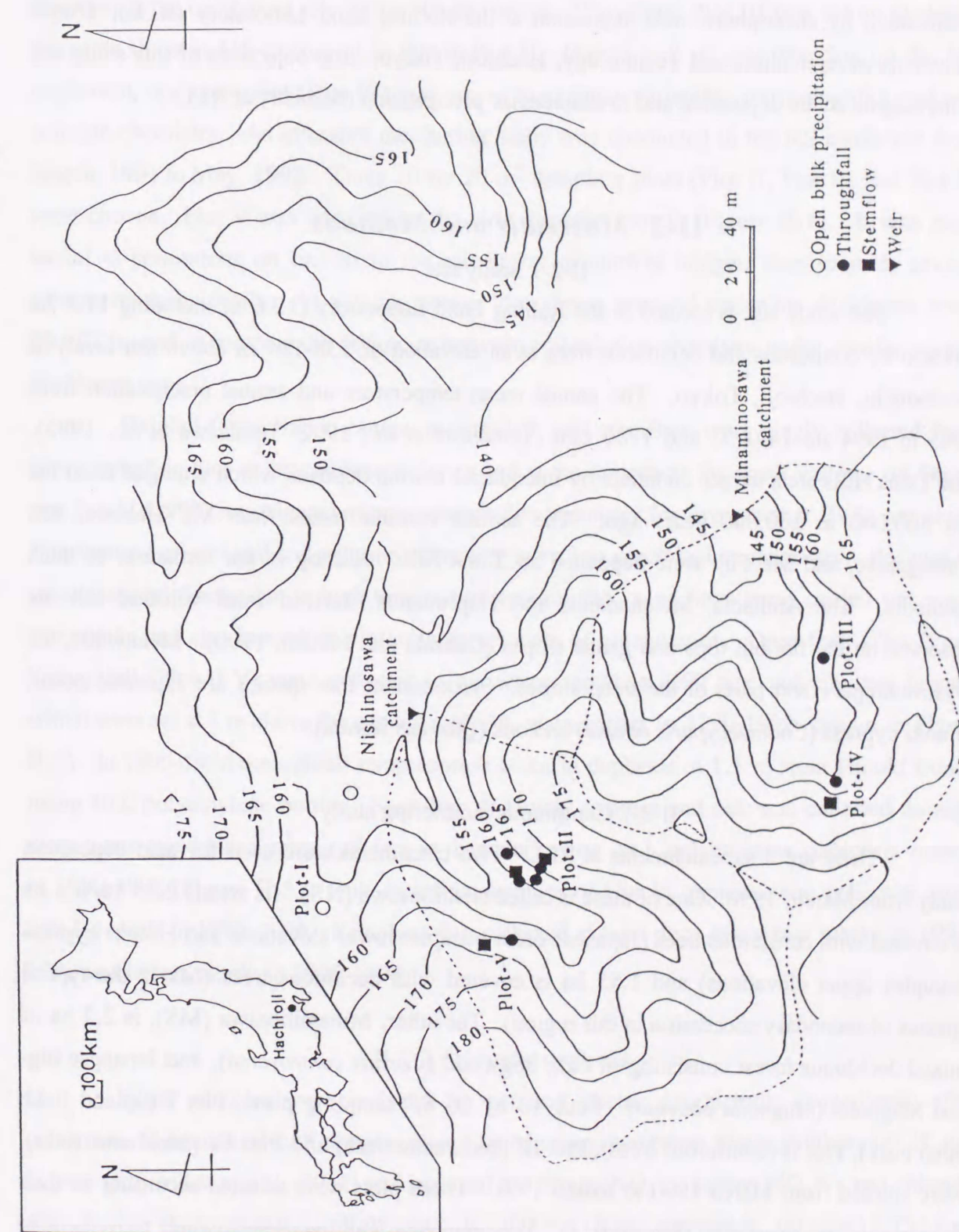

Figure II-1: Location of Rolling Land Laboratory (RLL, Hachioji, Tokyo) and topographical map of RLL.

The long-term monitoring of the forest catchment was started in 1990 to study soil acidification by atmospheric acid deposition at the Rolling Land Laboratory (RLL), Tokyo University of Agriculture and Technology, Hachioji, Tokyo. The objectives of this study are to investigate acidic deposition and to characterize precipitation chemistry at RLL.

II-2 *Materials and Methods*

II-2-1 Study site

The study site is located in the Rolling Land Laboratory (12.6 ha including 11.3 ha covered by coniferous and deciduous trees at an elevation of 138-184 m above sea level) in Horinouchi, Hachioji, Tokyo. The annual mean temperature and annual precipitation from 1985 to 1994 are 14.0 °C and 1780 mm (Tomizawa *et al.*, 1992; Tomizawa *et al.*, 1995). The Tama Hills are a terrace underlain by interglacial marine deposits which emerged from the sea 300,000 to 500,000 years ago. The aeolian volcanic ashes from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji were deposited on Tama Hills resulting in the formation of thick Andisols. The Andisols, Melanudands and Hapludands, derived from volcanic ash are observed on the flat hill tops and gentle slopes (Okazaki and Matsui, 1990). Meanwhile, the Dystrochrepts cover parts of the steep slopes. Predominant tree species are Japanese cedar, Hinoki cypress (*Chamaecyparis obtusa*) and oak (*Quercus serrata*).

II-2-2 Continuous monitoring study

There are 3 subcatchments at RLL. Two catchments were used for acid deposition study from March, 1990. One of these is called Nishinosawa (NS). Its area is 2.15 ha, 0.6 ha is covered with coniferous trees (Japanese cedar occupies lower elevations and Hinoki cypress occupies upper elevations) and 1.55 ha is covered with deciduous trees (oak is the typical species of secondary succession in this region). The other, Minaminosawa (MS), is 2.2 ha of mixed deciduous forest consisting of oak, dogwood (*Cornus controversa*), and Japanese big-leaf Magnolia (*Magnolia obovata*). Four 10 by 20 m^2 sampling plots, Plot I (upland field; open bulk), Plot II (coniferous trees), Plot III (deciduous trees) and Plot IV (deciduous trees), were studied from March 1990 to March 1991. These plots were selected according to their topography and vegetation (Figure II-1). Topographical features control water movement in

soil layers. However, it was impossible to install the deciduous site on the same slope direction as the coniferous site in the NS catchment. Therefore, Plot III was set up at almost the same slope in MS catchment as that in Plot II. Due to lack of available data on the MS catchment, one more plot (Plot IV) was set up to examine variability on throughfall and soil solution chemistry. An intensive monitoring study was conducted in the NS catchment from March, 1991 to May, 1992. Three 10 by 20 m^2 sampling plots (Plot II, Plot III and Plot V) were chosen. Plot V was installed on the side opposite Plot II (Figure II-1). It was more useful to concentrate on one basin for calculation of nutrient budgets than to study several catchments individually. As a consequence, Plot V was installed under the deciduous trees. Plot III is used to compare the difference between soil solution chemistry under coniferous and deciduous trees.

Rainfall (open bulk), canopy throughfall, and stemflow were singly collected from every sampling plot at the catchment slopes and at the bottom of the small valley. As Ogura and Sasaki (1990) investigated minute precipitation chemistry for two years at RLL, our study was focused on soil and soil solution chemistry related to precipitation chemistry. Because of great seasonal fluctuation in both temperature and rainfall, samplings were carried out every two weeks and also immediately after large amounts of precipitation. Open bulk (Plot I) and throughfall (Plot II-V) were collected in the water samplers (200 cm^2 polyethylene funnels which were set at 1 m above the ground with 5 L glass bottles in 1990-1992: shown in Figure II-2). In 1995-1996 throughfall samples were taken in duplicate at 1.5 m from Hinoki trunks using 10 L polyethylene bottles. Stemflow of Hinoki cypress and oak was collected through vinyl tubes glued into a spiral (28 mm in diameter) using 20 L polyethylene collection vessels in 1990-1992 (Figure II-3). Only stemflow samples of Hinoki cypress were collected using 200 L vessels in 1995-1996. Samples were collected at least once every two weeks in 1990-1992 and once a month in 1995-1996.

II-2-3 Analytical methods

Water samples were analyzed for pH and electric conductivity immediately after collection. Subsequently, all samples were filtered using membrane filters (Millipore 0.45 μm in pore size) and stored at –20 °C and analyzed for nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-) by ion chromatography (Yokogawa, IC 200 Ion Chromatographic Analyzer). Calcium
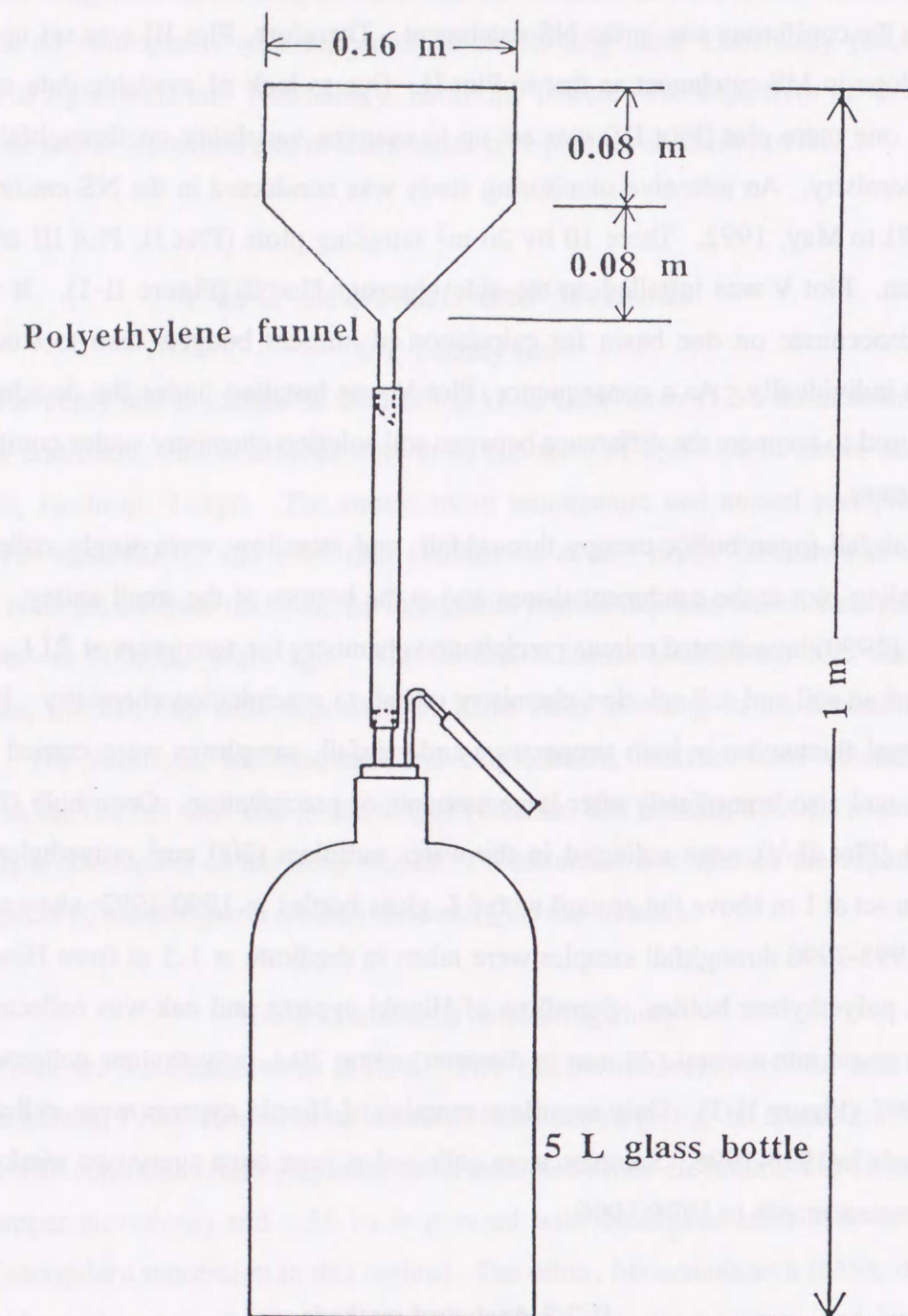
Figure II-2: Collecting equipment for open bulk precipitation and throughfall.

0.16 m

0.08 m

0.08 m

Polyethylene funnel

1 m

5 L glass bottle

Cave to canalize stemflow

Adhesive

Trunk

20 L polyethylene bottle
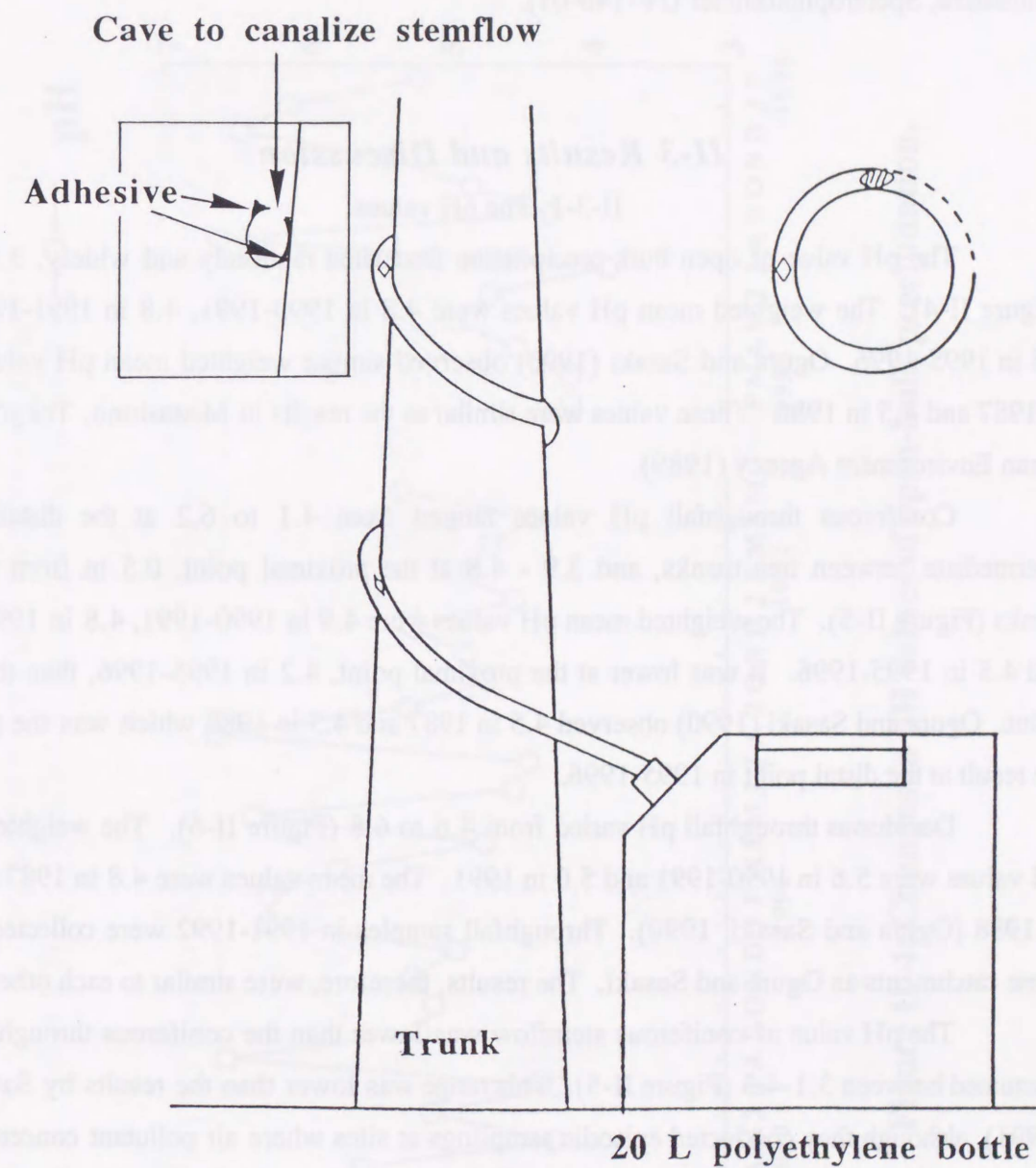
Figure II-3: Collecting equipment for stemflow.

(Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+) were determined by atomic absorption spectrophotometry (Shimadzu, 670/AA Atomic Absorption Spectrophotometer). Ammonium (NH_4^+) analysis was performed by the indophenol-blue colorimetric method (Shimadzu, Spectrophotometer UV-140-01).

II-3 Results and Discussion
II-3-1. The pH values

The pH value of open bulk precipitation fluctuated randomly and widely, 3.9 - 6.6 (Figure II-4). The weighted mean pH values were 4.8 in 1990-1991, 4.8 in 1991-1992 and 4.5 in 1995-1996. Ogura and Sasaki (1990) observed similar weighted mean pH values, 4.4 in 1987 and 4.5 in 1988. These values were similar to the results in Musashino, Tokyo by the Japan Environment Agency (1989).

Coniferous throughfall pH values ranged from 4.1 to 6.2 at the distal point, intermediate between tree trunks, and 3.9 - 4.8 at the proximal point, 0.5 m from the tree trunks (Figure II-5). The weighted mean pH values were 4.9 in 1990-1991, 4.8 in 1991-1992 and 4.5 in 1995-1996. It was lower at the proximal point, 4.2 in 1995-1996, than the distal point. Ogura and Sasaki (1990) observed 4.5 in 1987 and 4.5 in 1988 which was the same as the result at the distal point in 1995-1996.

Deciduous throughfall pH varied from 4.6 to 6.8 (Figure II-6). The weighted mean pH values were 5.6 in 1990-1991 and 5.0 in 1991. The mean values were 4.8 in 1987 and 5.2 in 1988 (Ogura and Sasaki, 1990). Throughfall samples in 1991-1992 were collected in the same catchments as Ogura and Sasaki. The results, therefore, were similar to each other.

The pH value of coniferous stemflow was lower than the coniferous throughfall and fluctuated between 3.1-4.3 (Figure II-5). This range was lower than the results by Sasa *et al.* (1991), although they conducted episodic samplings at sites where air pollutant concentrations were low. At RLL the weighted mean pH values were 3.7 in 1990-1991, 3.9 in 1991-1992 and 3.8 in 1995-1996. These values were 1 pH unit lower than those of the coniferous throughfall. That is, proton concentrations in the stemflow was 10 times as high as those in the throughfall. Therefore, proton input due to stemflow reached 31 % of the total input. The percentage was calculated as follows;

Figure II-4: Changes in pH values of open-bulk precipitation.

pH

Figure II-5: Changes in pH values of throughfall and stemflow under the coniferous forest.

pH

Figure II-6: Changes in pH values of throughfall and stemflow under the deciduous forest.

Percentage $= (H^+)s*Vs / \{(H^+)s*Vs + (H^+)t*Vt\}*100$

$\qquad\qquad\quad = 10*4.3 / \{10*4.3 + 1*95.7\}*100 = 31\ (\%)$

where parenthesis represents proton concentration, V is volume, s is stemflow and t is throughfall. Stemflow, therefore, is quan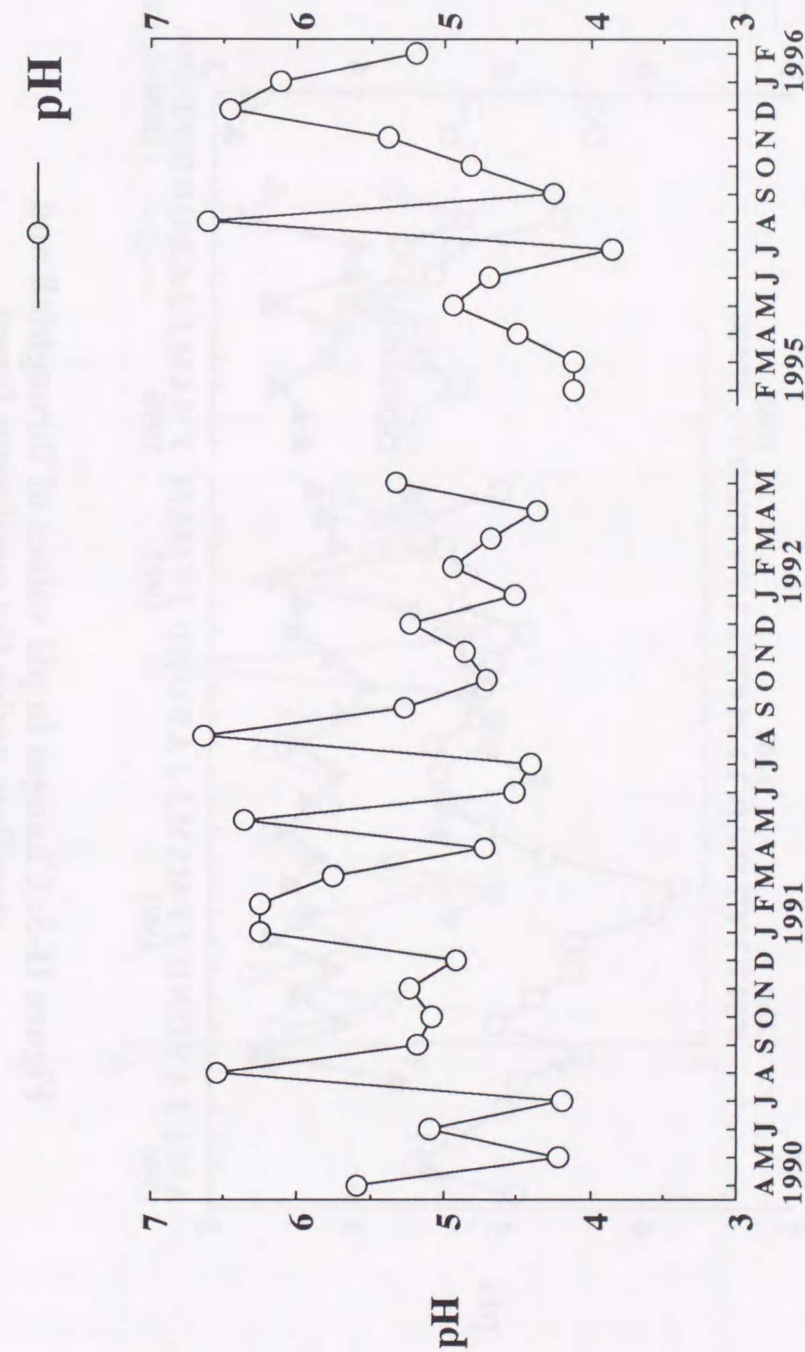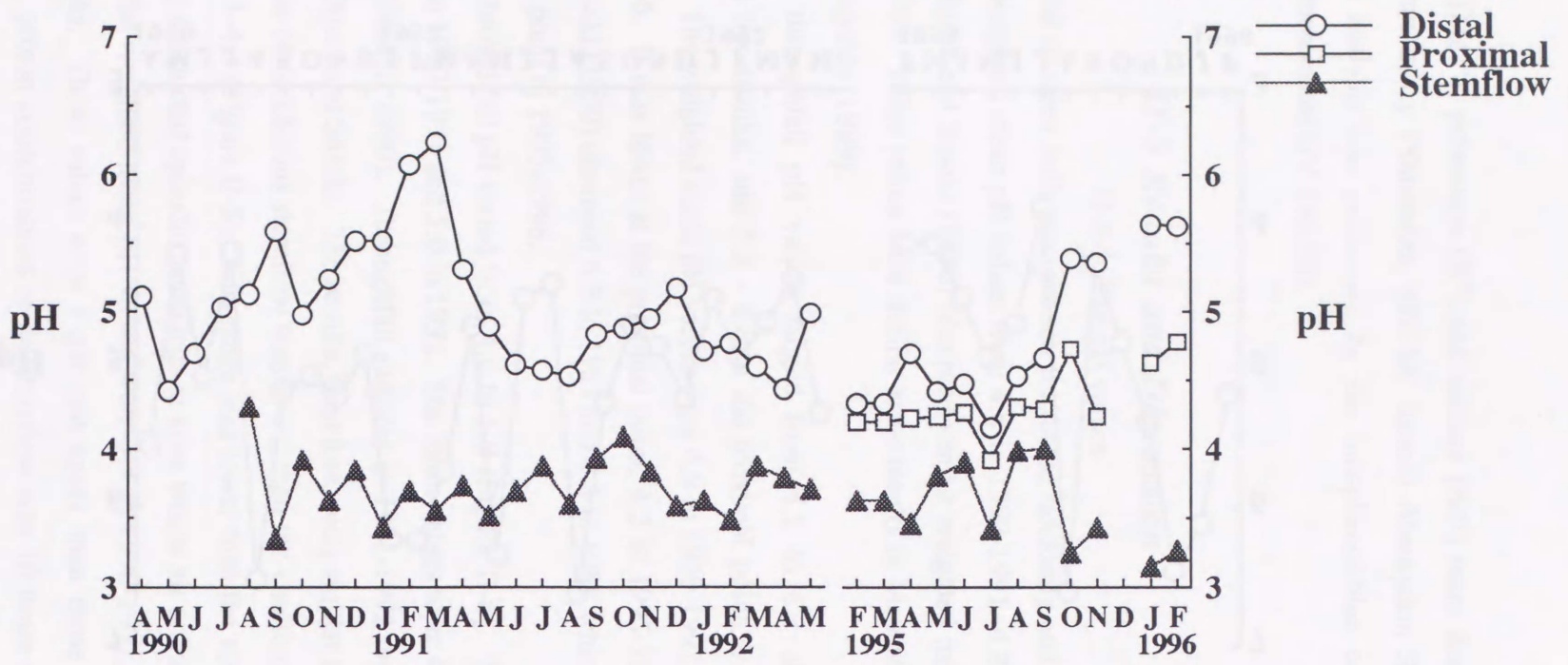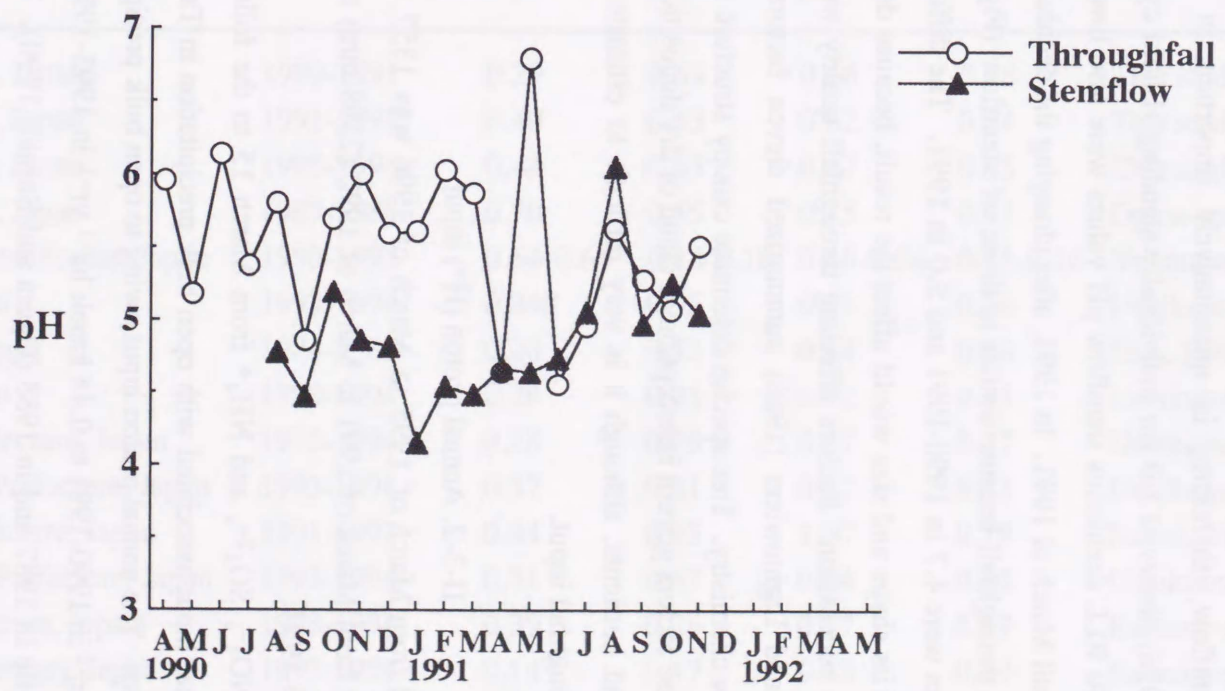titatively important in estimating soil acidification. Katou (1996) observed 3.9 for individually standing Hinoki cypress in Isogo, Kanagawa Prefecture. At RLL deciduous stemflow pH values were also lower than those of deciduous throughfall until March of 1991. In 1991, after changing the deciduous site, the pH values of the deciduous throughfall became similar to those of stemflow (Figure II-6). The weighted mean pH values were 4.7 in 1990-1991 and 5.0 in 1991. The difference in canopy structure with respect to its shape and size would affect the result, because deciduous trees at RLL grew in secondary succession. Factors affecting throughfall quality were reviewed by Parker (1983). Cape and Lightowlers (1988) summarized eleven factors which control throughfall and stemflow chemistry. Tree species determine canopy structure and morphology of leaves and bark. These factors govern interception of cloud or dry deposition, leaching, and distribution of water and nutrients, although it is very difficult to estimate how individual factors contribute to throughfall input.

II-3-2. Annual proton (H$^+$) input

Annual rainfall from March of 1995 to March of 1996 was 1357 mm, which was 1000 mm less than that from March of 1991 to March of 1992 (2398 mm) and 400 mm less than the average in 1985-1994.

Input of H^+, NO_3^-, SO_4^{2-}, and NH_4^+ from March 15 to the following March 15 were shown as the annual input associated with open bulk precipitation in Table II-1 with the results at other study sites. The annual proton input owing to open bulk precipitation increased from 0.29 kmol$_c$ ha^{-1} yr^{-1} in 1990-1991 to 0.44 kmol$_c$ ha^{-1} yr^{-1} in 1995-1996, although they were still lower than those in 1987 and in 1988 (Ogura and Sasaki, 1990). The proton input was comparable to other study sites and less than half of those at polluted sites. Using data in Table II-1 except data in Chongqing, China where sulfate input was extremely high, relationship between proton input and nitrate input or proton input and sulfate input is shown Figure II-7. Proton input was proportional to nitrate input or sulfate input. However, proton

Table II-1 Annual input of proton, nitrate, sulfate and ammonium by open bulk precipitation.

Site, Country	Period	H$^+$	NO$_3^-$	nss-SO$_4^{2-}$	NH$_4^+$	References
			kmol$_c$ ha^{-1} yr^{-1}			
RLL, Hachioji, Tokyo, Japan	1990-1991	0.29	0.64	0.66	0.48	This study
RLL, Hachioji, Tokyo, Japan	1991-1992	0.40	0.53	0.62	0.54	This study
RLL, Hachioji, Tokyo, Japan	1995-1996	0.44	0.43	0.47	0.63	This study
RLL, Hachioji, Tokyo, Japan	1987-1988	0.70	0.55	0.75	0.45	Ogura and Sasaki, 1990
Tomakomai Experimental Forest, Japan	1990-1992	0.64-0.66	0.14-0.18	0.48-0.54	0.15-0.16	Shibata and Sakuma, 1996
Setagaya, Tokyo, Japan	1993-1994	0.048	0.55	0.81	0.36	Ushikubo and Okamoto, 1995
Musashino, Tokyo, Japan	1984-1987	0.20	0.53	0.64	0.56	JEA, 1989
Okutama, Tokyo, Japan	1993-1994	0.20	0.25	0.22	0.14	Ushikubo and Okamoto, 1995
Atsugi, Kanagawa Prefecture, Japan	1993-1994	0.28	0.29	0.37	0.27	Ushikubo and Okamoto, 1995
Ninomiya, Kanagawa Prefecture, Japan	1993-1994	0.37	0.31	0.27	0.23	Ushikubo and Okamoto, 1995
Isogo, Kanagawa Prefecture, Japan	1991-1992	0.44	0.45	1.07	0.78	Katou, 1996
Fujinomiya, Shizuoka Prefecture, Japan	1993-1994	0.31	0.37	0.24	0.42	Ushikubo and Okamoto, 1995
Nagiso, Nagano Prefecture, Japan	1993-1994	0.39	0.26	0.47	0.19	Katsuno et al., 1995
Nagano Prefecture (average), Japan	1993-1994	0.14	0.17	0.33	0.19	Katsuno et al., 1995
Tottori-city, Japan	1991-1993	0.36	0.29	0.79	0.35	Iimura, 1994
Daiei, Tottori Prefecture, Japan	1991-1993	0.28	0.28	0.90	0.54	Iimura, 1994
Sekikane, Tottori Prefecture, Japan	1991-1993	0.29	0.30	0.84	0.43	Iimura, 1994
Sakaiminato, Tottori Prefecture, Japan	1991-1993	0.43	0.32	1.00	0.50	Iimura, 1994
Japanese average	1983-1987	0.34	0.27	0.78	0.38	JEA, 1989

Table II-1 (*Continued*)

Site, Country	Period	H+	NO3-	SO4 2-	NH4+	References
Japanese average	1988-1992	0.24	0.19	0.52	0.26	JEA, 1994
Japanese average	1995	0.26	0.24	0.50	0.31	JEA, 1994
Chongqing, Southwest China	1991-1992	0.31	0.56	5.77	1.32	Ogura, 1994
Janow, Southeastern Poland	1990-1991	0.17	0.36	0.63	0.33*	Vogt et al., 1994
Trnavka river basin, Czech Republic	1976-1982	0.37-0.42	0.26-0.31	0.65-0.76	0.35-0.40	Paces, 1985
Krusne hory (Erzgebirge), Czech Republic	1978-1982	0.46	0.39	1.21	0.54	Paces, 1985
Uhlirska, Jizerske hory, Czech Republic	1994	0.97	0.59	1.66	0.51	Cerny and Paces, 1995
Grunewald, Berlin, Germany	1986-1989	0.34	0.58	1.49	0.52	Marschner et al., 1991
Solling, FRG	1969-1985	0.82	0.62	1.41	0.85	Hauhs, 1989
Lange Bramke, FRG	1981-1988	0.72	0.64	1.33	0.94	Hauhs, 1989
Harste, FRG	1982-1985	0.34	0.40	0.78	0.45	Bredemeier et al., 1990
Spanbeck, FRG	1982-1985	0.35	0.44	0.89	0.53	Bredemeier et al., 1990
Lueneburger Heide, FRG	1980-1985	0.44	0.48	0.98	0.74	Bredemeier et al., 1990
Oberbarenburg, FRG	1985-1994	0.35	0.53	1.71	0.66	Cerny and Paces, 1995
Gerritsfles, Netherlands	1983-1987	0.18	0.42	0.85	0.89	Mulder et al., 1987b
Gerritsfles, Netherlands	1982-1984	0.31	0.41	0.78	0.77	van Dobben et al., 1992
Tongbersven, Netherlands	1981-1984	0.33	0.37	0.89	0.81	van Dobben et al., 1992
Kliplo, Netherlands	1982-1984	0.29	0.40	0.74	0.71	van Dobben et al., 1992
Strodam Reserve, Denmark	1986-1987	0.24	0.32	0.45	0.41	Beier et al., 1993
Birkenes, Norway	1973-78+81-83	0.77	0.53	0.88	0.54	Abrahamsen, 1989
Storgma, Norway	1975-78+80-84	0.52	0.28	0.53	0.27	Abrahamsen, 1989

*Calculated based on charge balance

Table II-1 (*Continued*)

Site, Country	Period	H+	NO3-	SO4 2-	NH4+	References
Langtjern, Norway	1975-1983	0.33	0.19	0.38	0.21	Abrahamsen, 1989
Karvatn, Norway	1978-1984	0.16	0.06	0.14	0.09	Abrahamsen, 1989
Sogndal, Norway	1983-1991	0.16	0.09	0.19	0.10	Wright et al., 1994
Berg, Sweden	1986-1992	0.54	0.48	0.61	0.51	Lofgren and Kvarnas, 1995
Tiveden, Sweden	1986-1992	0.31	0.22	0.35	0.22	Lofgren and Kvarnas, 1995
Reivo, Sweden	1986-1992	0.12	0.07	0.16	0.07	Lofgren and Kvarnas, 1995
Gårdsjon, Sweden	1989-1991	0.51	0.40	0.60	0.33	Moldan et al., 1995
Beddgelert Forest, Wales, UK	1982-1984	0.53-1.31	0.28-0.36	1.31-1.65	0.36-0.48	Stevens et al., 1989
Strengbach catchment, France	1986-1989	0.47	0.45	0.64	0.41	Probst et al., 1992
Bllinzago, Italy	1985-1988	0.38	0.56	1.05	0.63	Lucia et al., 1996
Bllinzago, Italy	1989-1993	0.36	0.56	0.75	0.72	Lucia et al., 1996
S.M. Orta, Italy	1985-1988	0.59	0.88	1.37	1.02	Lucia et al., 1996
S.M. Orta, Italy	1989-1993	0.56	0.79	1.00	0.96	Lucia et al., 1996
Pallanza, Italy	1985-1988	0.81	0.98	1.56	1.11	Lucia et al., 1996
Pallanza, Italy	1989-1993	0.69	0.99	1.26	1.16	Lucia et al., 1996
Lunecco, Italy	1989-1993	0.62	0.79	1.08	0.94	Lucia et al., 1996
Domodossola, Italy	1985-1988	0.52	0.53	0.91	0.53	Lucia et al., 1996
Domodossola, Italy	1989-1993	0.36	0.41	0.56	0.41	Lucia et al., 1996
Lake Toggia, Italy	1985-1988	0.13	0.20	0.40	0.23	Lucia et al., 1996
Lake Toggia, Italy	1989-1993	0.07	0.14	0.20	0.13	Lucia et al., 1996
HBEF, NH, USA	1963-1974	0.96	0.31	0.78	0.16	Likens et al., 1977

Table II-1 (*Continued*)

|						
HIFS, ME, USA	1989	0.42	0.23	0.37	0.098	Lawrence and Fernandez, 1991
HIFS, ME, USA	1988-1993	0.32	0.20	0.29	0.090	McLaughlin et al., 1996
Arbutus, Adirondack Mountains, NY, USA	1983-1992	0.43	0.24	0.41	0.11	Mitchell et al., 1996
Cree Lake, Sask., Canada	1985	0.061	0.033	0.059	0.023	Brydges and Summers, 1989
McCrear, Manit., Canada	1985	0.028	0.063	0.072	0.098	Brydges and Summers, 1989
Island Lake, Manit., Canada	1985	0.053	0.041	0.062	0.050	Brydges and Summers, 1989
Ela, Ont., Canada	1985	0.095	0.11	0.14	0.13	Brydges and Summers, 1989
Pickle Lake, Ont., Canada	1985	0.11	0.075	0.13	0.081	Brydges and Summers, 1989
Algoma, Ont., Canada	1985	0.64	0.40	0.66	0.33	Brydges and Summers, 1989
Dorset, Ont., Canada	1985	0.67	0.39	0.55	0.21	Brydges and Summers, 1989
Priceville, Ont., Canada	1985	0.62	0.45	0.64	0.34	Brydges and Summers, 1989
Longwoods, Ont., Canada	1985	0.70	0.43	0.69	0.27	Brydges and Summers, 1989
Sutton, Que., Canada	1985	0.79	0.42	0.63	0.23	Brydges and Summers, 1989
Chalk River, Que., Canada	1985	0.54	0.28	0.42	0.14	Brydges and Summers, 1989
Montmorency, Que., Canada	1985	0.52	0.26	0.47	0.17	Brydges and Summers, 1989
Nitchequon, Que., Canada	1985	0.087	0.037	0.087	0.0334	Brydges and Summers, 1989
Bay D'espoir, Que., Canada	1985	0.29	0.088	0.21	0.069	Brydges and Summers, 1989
Goose, Que., Canada	1985	0.12	0.043	0.080	0.021	Brydges and Summers, 1989
Harcourt, Que., Canada	1985	0.30	0.12	0.20	0.047	Brydges and Summers, 1989
Jackson, Que., Canada	1985	0.37	0.16	0.27	0.075	Brydges and Summers, 1989
Kejimkujik, Que., Canada	1985	0.51	0.19	0.35	0.092	Brydges and Summers, 1989
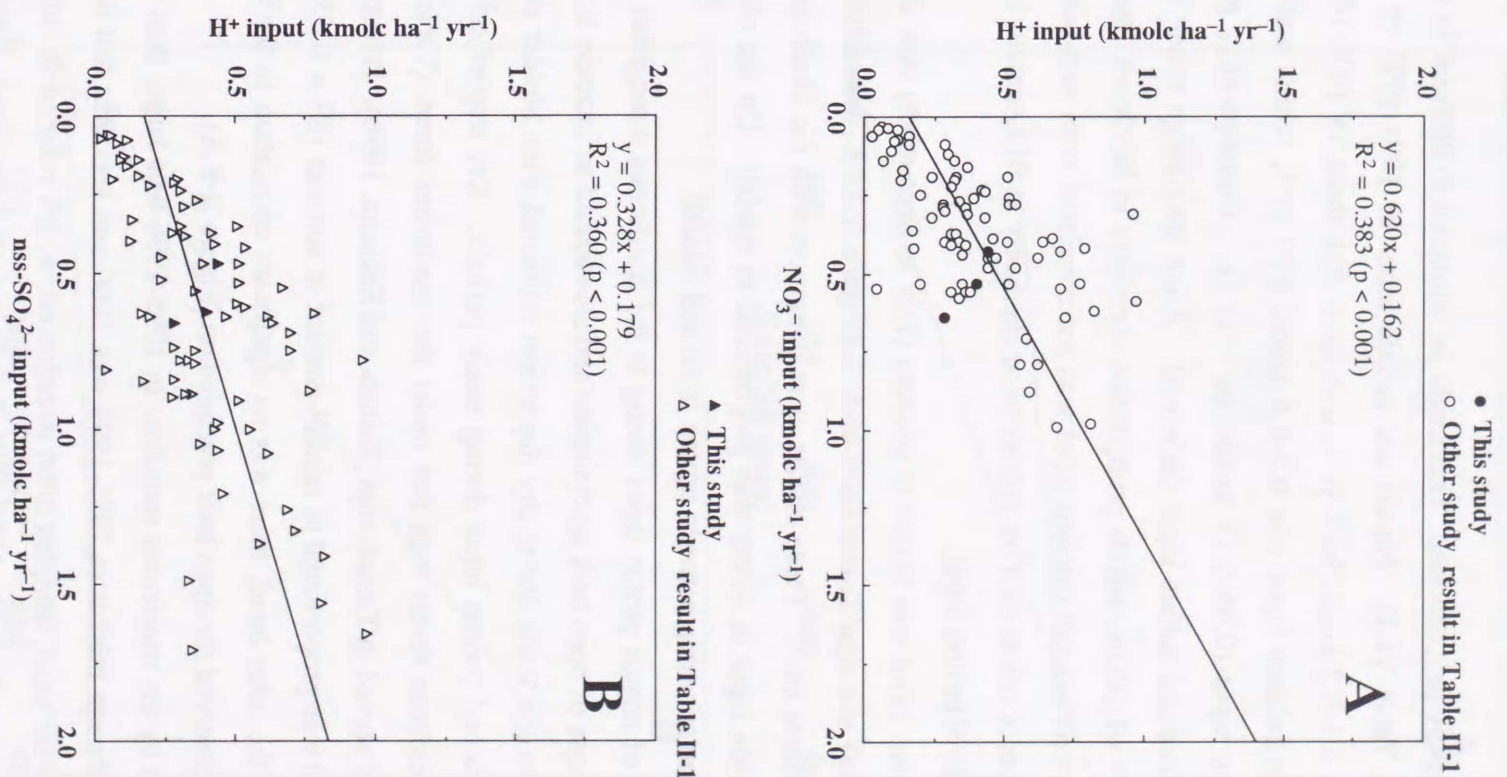
Figure II-7: Relationship between proton input and nitrate input (A) and proton input and non-sea salt sulfate input (B).

input at RLL was inversely proportional. This might be attributed to decrease in calcium and magnesium input (see Table VI-1). Nitrate and sulfate input in 1991-1992 or 1995-1996 decreased respectively 0.1-0.2 kmolc ha^{-1} yr^{-1}, compared with those in 1990-1991 On the other hand, decrease in calcium input was 0.3-0.6 kmolc ha^{-1} yr^{-1}, which was larger than increase in ammonium input (0.05-0.15 kmolc ha^{-1} yr^{-1}). Consequently, proton input increased although nitrate and sulfate input decreased. Asian long-range eolian dust, which contain 100-200 g kg^{-1} of calcite, affects precipitation chemistry in Northeast Japan (Inoue et al., 1998). Although non-sea salt calcium input was not correlated with non-sea salt sulfate input at RLL, the effects of eolian dust on precipitation chemistry at RLL should be studied to elucidate factors to control proton input.

Monthly proton input was higher in summer (July to September) than that in winter (December to February) at a significance level of 5 % (Figure II-8A). Monthly inputs were almost less than 0.1 kmolc ha^{-1}. These results were congruent with the observation by Hara (1997). Monthly proton input in winter was proportional to rainfall. On the other hand, in summer there was no relationship between proton input and rainfall.

The amount of annual proton input owing to the coniferous throughfall at the distal point was similar to those of open bulk precipitation and also tended to increase throughout the study (Table II-2). Proton loads due to dry deposition estimated after Mulder et al. (1987a) were larger than measured proton input during study periods. Dry deposition acidity was smaller under the deciduous forest than that under the coniferous forest (Table II-2, II-3). Similar results were observed in Tomakomai (Shibata and Sakuma, 1996). Proton input due to coniferous throughfall was proportional to rainfall amount in summer ($R^2 = 0.535$, $p < 0.05$) (Figure II-8 B). On the other hand, there was no significant correlation in the winter. The opposite result was observed for open bulk precipitation (Figure II-8 A).

Proton input by the coniferous stemflow in 1995-1996 was larger than that in 1991-1992 (Table II-4), although rainfall in 1995-1996 was 1000 mm less than that in 1991-1992. When 20 L vessels were used, samples often overflowed, which resulted in underestimating input associated with stemflow. In 1995-1996 200 L vessels were used, which performed successfully (to collect whole amount of stemflow). Deciduous throughfall and stemflow were less important than coniferous, especially for stemflow. Proton input due to the deciduous stemflow was less than the coniferous stemflow by factors of 7.5 to 22. The difference in
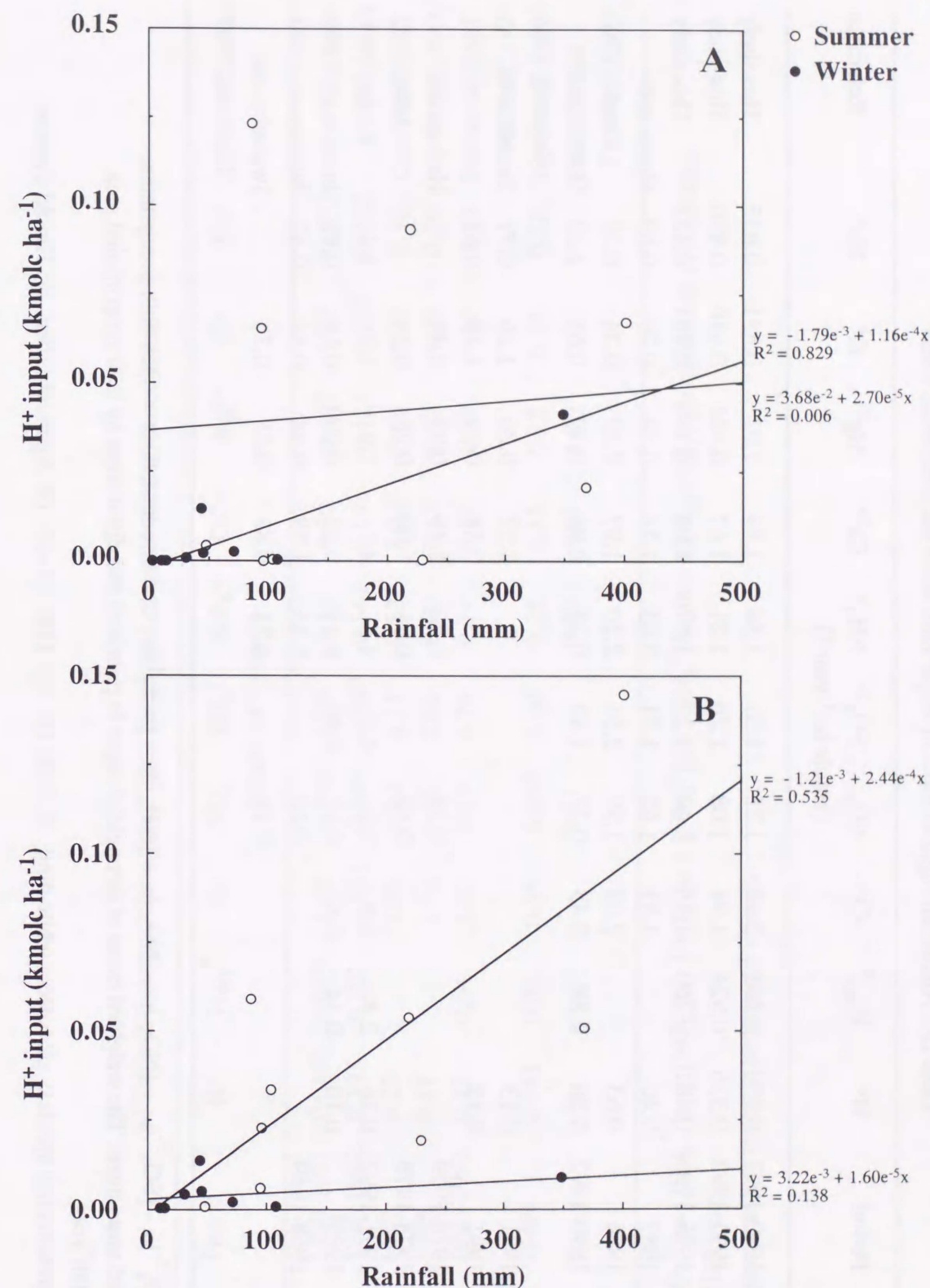

Figure II-8: Seasonal difference in proton input due to open bulk precipitation (A) and coniferous throughfall (B).

Table II-2 Annual throughfall input of major ions under the coniferous forest

Study site	Period	H^+	H_{dry}[*]	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Reference
					(kmolc ha^{-1} year^{-1})							
RLL	1990-1991	0.230	0.401	2.13	1.25	1.61	1.54	1.84	1.02	0.851	0.835	This study
RLL	1991-1992	0.336	0.924	1.94	1.08	1.76	1.21	1.67	0.935	0.940	0.550	This study
RLL	1995-1996$	0.481	0.760	1.56	1.40	1.22	1.57	1.08	0.448	0.484	0.433	This study
RLL	1987	0.40		1.81	1.62	1.71	2.03	1.25	0.52	0.20	0.67	Ogura and
RLL	1988	0.63		2.02	1.59	2.51	2.20	1.97	0.50	0.34	0.59	Sasaki, 1990
Tomakomai(pi)	1990-1992	0.36	0.88	2.43	0.27	1.42	0.23	0.94	0.70	0.61	2.22	Shibata and Sakuma, 1996
Sapporo(fi)	1991	0.13						0.52	0.26	1.26	0.71	Sanada et al.,
Sapporo(sp)	1991	0.12						0.58	0.19	1.18	0.61	1991
Seta, Gunma(ce)	1978-1979				0.39		0.60	1.49	0.35	0.49		Haibara and
Seta, Gunma(cy)	1978-1979				0.62		0.71	1.00	0.28	0.24		Aiba, 1982
Isogo^{cy}	1991-1992	0.16	2.4	7.6	3.1	4.7	4.6	4.7	1.9	1.2	4.4	Katou, 1996
Fujinomiya(cy)	1989§	0.10	-0.14	0.51	0.12	0.38	0.17	0.23	0.077	0.15	0.41	Inoue et al., 1993
Ohtsu, Shiga	1968-1969				0.16		0.16	1.28	0.48	0.54	0.42	Nishimura, 1973
Kyoto^{cy}					0.14		0.31	0.83	0.35	0.34		Iwatsubo and Tsutsumi, 1967

[*]: $[H^+]_{dry} = [SO_4^{2-}]_{th} - [SO_4^{2-}]_{pr} + [NO_3^-]_{th} - [NO_3^-]_{pr} + [NH_4^+]_{pr} - [NH_4^+]_{th}$; th = throughfall, pr = open bulk precipitation

$: Area weighted mean input: The weighted mean of throughfall input in proximal and distal areas by their proportional area.

§: May-Nov; Half year

Parenthesis represents tree species; pi: eastern white pine, fi: Todo fir, sp: Yezo spruce, ce: Japanese ceder, cy: Hinoki cypress

Table II-3 Annual throughfall input of major ions under the deciduous forest

Study site	Period	H^+	H_{dry}[*]	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	Reference
					(kmolc ha^{-1} year^{-1})							
RLL	1990-1991	0.0433	0.049	1.40	0.818	1.29	1.14	1.39	0.602	1.22	0.673	This study
RLL	1991-1992	0.195	0.207	0.851	0.486	0.969	0.542	0.876	0.424	0.762	0.432	This study
RLL	1987	0.23		1.01	0.62	1.35	0.52	2.02	0.56	1.00	0.30	Ogura and
RLL	1988	0.11		1.22	0.56	1.86	0.60	1.43	0.72	1.09	0.29	Sasaki, 1990
Tomakomai	1990-1992	0.13	0.04	1.22	0.15	0.76	0.19	0.73	0.39	0.53	1.10	Shibata and Sakuma, 1996
Fujinomiya(be)	1989§	0.041	0.01	0.58	0.088	0.60	0.21	0.33	0.12	0.76	0.38	Inoue et al., 1993
Kyoto					0.11		0.29	0.65	1.00	0.30		Iwatsubo and Tsutsumi, 1967

[*]: $[H^+]_{dry} = [SO_4^{2-}]_{th} - [SO_4^{2-}]_{pr} + [NO_3^-]_{th} - [NO_3^-]_{pr} + [NH_4^+]_{pr} - [NH_4^+]_{th}$; th = throughfall, pr = open bulk precipitation

§: May-Nov; Half year

Parenthesis represents tree species; be:Siebold's beech

Table II-4 Annual input of elements due to stemflow at the Rolling Land Laboratory

	H	Cl	NO_3	SO_4	nss-SO_4	NH_4	Ca	Mg	K	Na
					(mmolc tree^{-1} year^{-1})					
Coniferous stemflow										
1990-1991*	47.0	68.5	45.0	84.0	81.8	83.0	35.8	12.0	5.40	18.4
1991-1992	110	90.5	73.9	132	130	102	53.7	21.9	12.4	22.0
1995-1996	165	130	124	147	143	149	49.1	22.2	20.5	33.7
Deciduous stemflow										
1990-1991*	2.12	14.4	16.4	19.0	18.5	8.65	16.2	7.97	12.0	3.76
1991-1992#	14.7	109	70.1	136	131	41.0	112	84.4	158	33.3

*: The total input from July, 1990 to March, 1991

#: Calculated as ratio annual rainfall (2397.9 mm) to total rainfall (2145.3 mm) from March, 1991 to November, 1991 by input in this period.

proton input would be very important for the difference in soil (solution) acidity as discussed in Chapter IV and V.

II-3-3. Annual input of major ions

Annual input of NO_3^-, SO_4^{2-}, Cl^-, Na^+, and NH_4^+ gradually decreased. Sodium and chloride input remarkably decreased in 1995-1996, compared to nitrate and sulfate input (Table II-5, II-1). Concerning throughfall, chloride and sodium input also decreased in 1995-1996 (Table II-2). The decrease in Cl^- and Na^+ input was attributed to a decrease in rainfall in 1995-1996, which was the most notable in thee autumn (Figure II-9). The annual rainfall in 1987 was also less than that in 1995-1996. However, sodium and chloride input in 1987 (Ogura and Sasaki, 1990) were larger than those in 1995-1996. Typhoons brought sea salt in the autumn (Baba et al., 1995: Arrows in Figure II-9, 10 show typhoons). Typhoons (No. 13, 16 and 19) affected rainfall in autumn of 1987, which gave larger amounts of rainfall than the average. By contrast, rainfall from September to October in 1995 was 240 mm (Figure II-9), only half of the average. Sparse rainfall in the autumn resulted in a small input of sodium and chloride in 1995-1996 and resulted in a small sea salt contribution to the chloride input that was less than 50 % of the total chloride input in 1995-1996 (Table II-5). The sea salt contributions were estimated by a equivalence ratio of chloride to sodium in sea water (Methodological committee for acid rain survey, 1993). In 1990-1991 and in 1991-1992, sea salt contributed nearly 100 % of chloride input. The weighted mean concentrations of Cl^- and Na^+ in 1995 were remarkably lower than those in 1990-1991 and in 1991-1992 (Table II-6). This also contributed to the small Cl^- and Na^+ input. In addition, sodium and chloride input at RLL were less than 50 % of the Japanese average in 1986-1988 (Japan Environment Agency, 1989).

Hara (1997) showed that there were no distinct seasonal differences in sodium input on the side facing Pacific Ocean. Sodium inputs at RLL were higher in summer than those in winter (at a significance level of 5 %) although significant correlation with rainfall amount was not confirmed in summer (Figure II-11). By contrast, inputs in winter were correlated with rainfall ($R^2 = 0.97$, $p < 0.001$). This relationship was also observed for Cl^- input.

The sea salt contribution to the coniferous throughfall input was a third of the total chloride input (Table II-5). This value in 1995-1996 was not different from those in 1990-

Table II-5 Contribution of sea salt to chloride and sulfate inputs at the Rolling Land Laboratory

Period	Sodium	Chloride Total	Seasalt		Sulfate Total	Seasalt	
	$kmolc\ ha^{-1}\ yr^{-1}$	$kmolc\ ha^{-1}\ yr^{-1}$	$kmolc\ ha^{-1}\ yr^{-1}$	(%)	$kmolc\ ha^{-1}\ yr^{-1}$	$kmolc\ ha^{-1}\ yr^{-1}$	(%)
Open-bulk							
1990-1991	0.881	0.927	1.04	(112)	0.766	0.107	(13.9)
1991-1992	0.714	0.823	0.839	(102)	0.710	0.0866	(12.2)
1995-1996	0.152	0.376	0.178	(47.4)	0.490	0.0184	(3.75)
Coniferous throughfall							
1990-1991	0.835	2.13	0.752	(33.9)	1.61	0.0388	(4.58)
1991-1992	0.550	1.94	0.645	(33.3)	1.76	0.0333	(3.78)
1995-1996	0.425	1.52	0.500	(32.8)	1.16	0.0516	(4.46)
1995-1996P	0.472	1.75	0.555	(31.7)	1.53	0.0572	(3.75)
Deciduous throughfall							
1990-1991	0.610	1.26	0.792	(56.6)	1.19	0.0817	(6.34)
1991-1992#	0.432	0.851	0.455	(59.7)	0.969	0.0469	(5.41)
	$mmolc\ tree^{-1}\ yr^{-1}$	$mmolc\ tree^{-1}\ yr^{-1}$	$mmolc\ tree^{-1}\ yr^{-1}$	(%)	$mmolc\ tree^{-1}\ yr^{-1}$	$mmolc\ tree^{-1}\ yr^{-1}$	(%)
Coniferous stemflow							
1990-1991*	18.4	68.5	21.7	(31.7)	84.0	2.24	(2.66)
1991-1992	22.0	90.5	25.9	(28.6)	132	2.67	(2.02)
1995-1996	33.7	130	39.7	(30.5)	147	4.09	(2.79)
Deciduous stemflow							
1990-1991*	3.76	14.4	4.43	(30.6)	19.0	0.457	(2.40)
1991-1992#	33.3	109	35.0	(36.1)	136	3.62	(2.98)

P: Throughfall at the proximal point. No entry represents throughfall at the distal point.
*: Weighted mean from July, 1990 to March, 1991
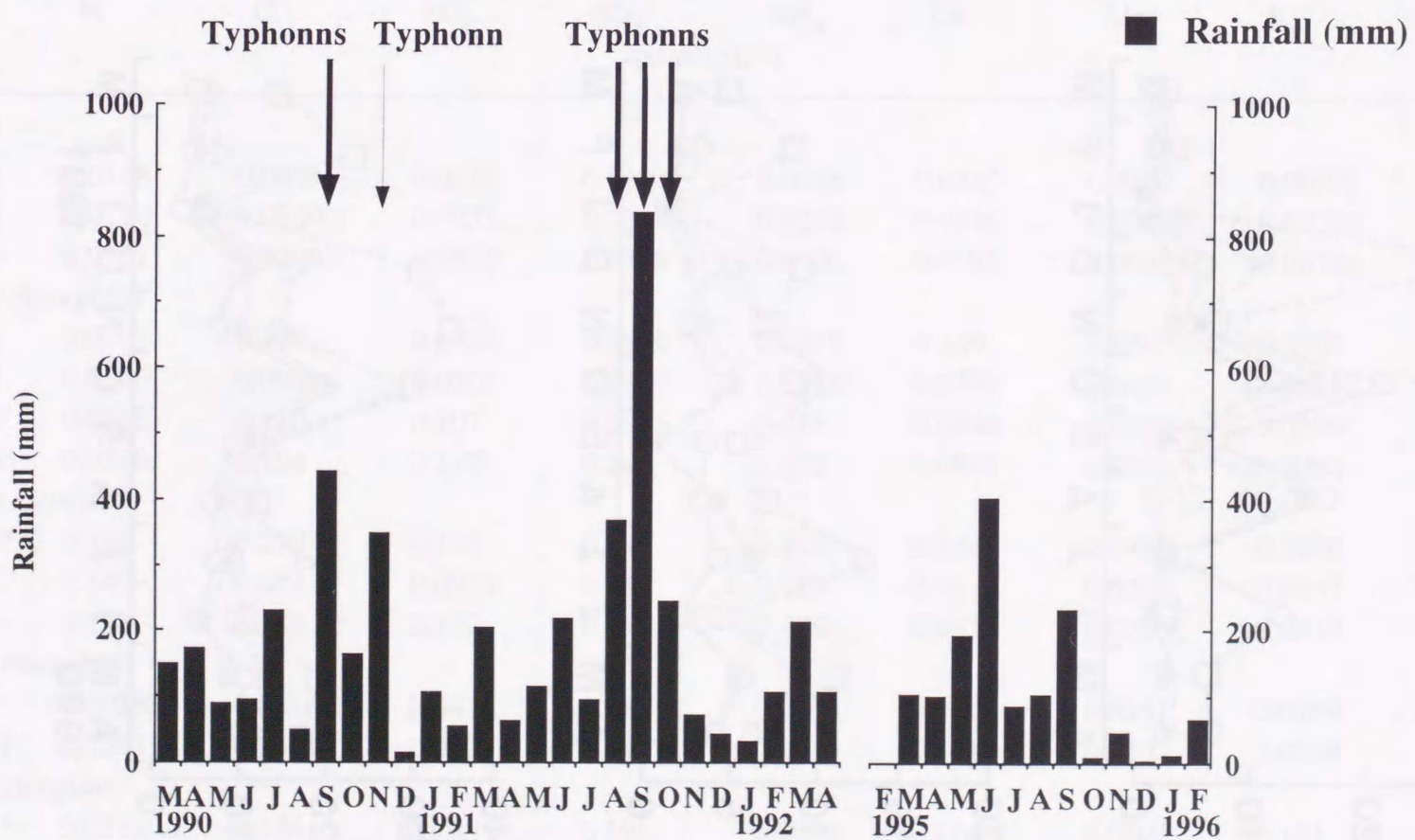#: Weighted mean from March, 1991 to November, 1991

Figure II-9: Rainfall at RLL during study periods.

Cl
10^{-2} kmol ha^{-1}

SO$_4$–S
10^{-2} kmol ha^{-1}

Na
10^{-2} kmol ha^{-1}

○ : Open bulk precipitation, □ : throughfall in mixed coniferous trees,
△ : throughfall in mixed deciduous trees, ▲ : throughfall in mixed deciduous trees
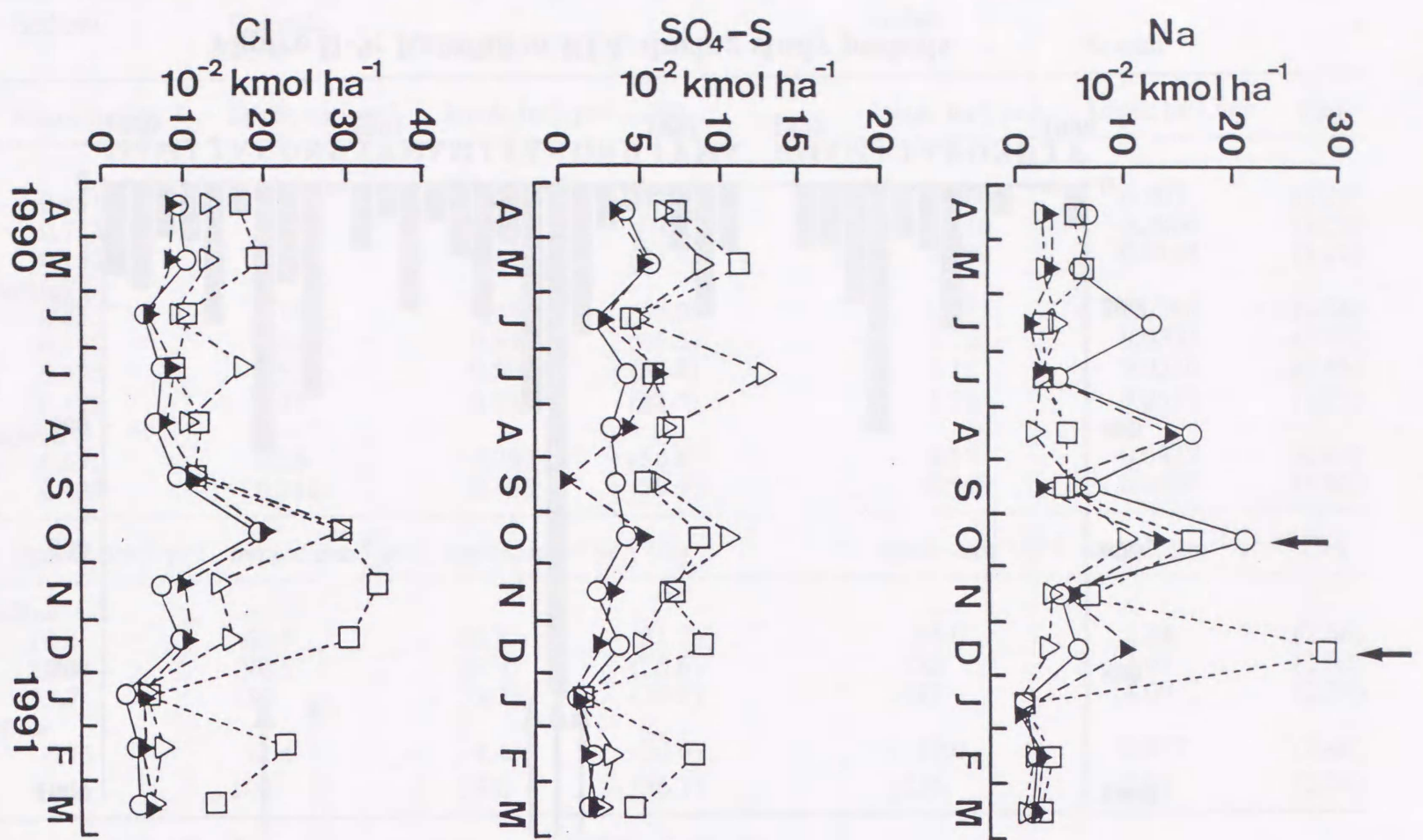Figure II-10: Monthly inputs of sodium, sulfate and chloride.

Table II-6 Weighted mean concentrations of precipitations at the Rolling Land Laboratory

Period	H	Cl	NO$_3$	SO$_4$	NH$_4$ (mmolc L^{-1})	Ca	Mg	K	Na
Open-bulk									
1990-1991	0.0145	0.0473	0.0324	0.0391	0.0246	0.0425	0.0102	0.00391	0.0448
1991-1992	0.0174	0.0360	0.0233	0.0311	0.0235	0.0219	0.00670	0.00274	0.0312
1995-1996	0.0351	0.0298	0.0342	0.0388	0.0500	0.0181	0.00575	0.00728	0.0120
Coniferous throughfall									
1990-1991	0.0107	0.118	0.0728	0.0899	0.0875	0.109	0.0447	0.0502	0.0340
1991-1992	0.0156	0.0901	0.0500	0.0817	0.0560	0.0774	0.0434	0.04337	0.0256
1995-1996	0.0326	0.120	0.107	0.0915	0.113	0.0844	0.0355	0.0396	0.0336
1995-1996^P	0.0576	0.124	0.117	0.108	0.142	0.0807	0.0312	0.0284	0.0334
Coniferous stemflow									
1990-1991*	0.191	0.279	0.183	0.342	0.338	0.146	0.0490	0.0220	0.0752
1991-1992	0.140	0.114	0.0935	0.167	0.129	0.0679	0.0276	0.0157	0.0278
1995-1996	0.175	0.138	0.132	0.155	0.158	0.0522	0.0238	0.0219	0.0.344
Deciduous throughfall									
1990-1991	0.00252	0.0816	0.0477	0.0751	0.0666	0.0812	0.0351	0.0709	0.0392
1991-1992#	0.00921	0.0401	0.0229	0.0457	0.0256	0.0413	0.0200	0.0359	0.0204
Deciduous stemflow									
1990-1991*	0.0214	0.146	0.165	0.191	0.0872	0.164	0.0804	0.121	0.0380
1991-1992#	0.00997	0.0720	0.0465	0.0898	0.0272	0.0739	0.0559	0.105	0.0221

P: Throughfall at the proximal point. No signature represents throughfall at the distal point.
*: Weighted mean from July, 1990 to March, 1991   #: Weighted mean from March, 1991 to November, 1991
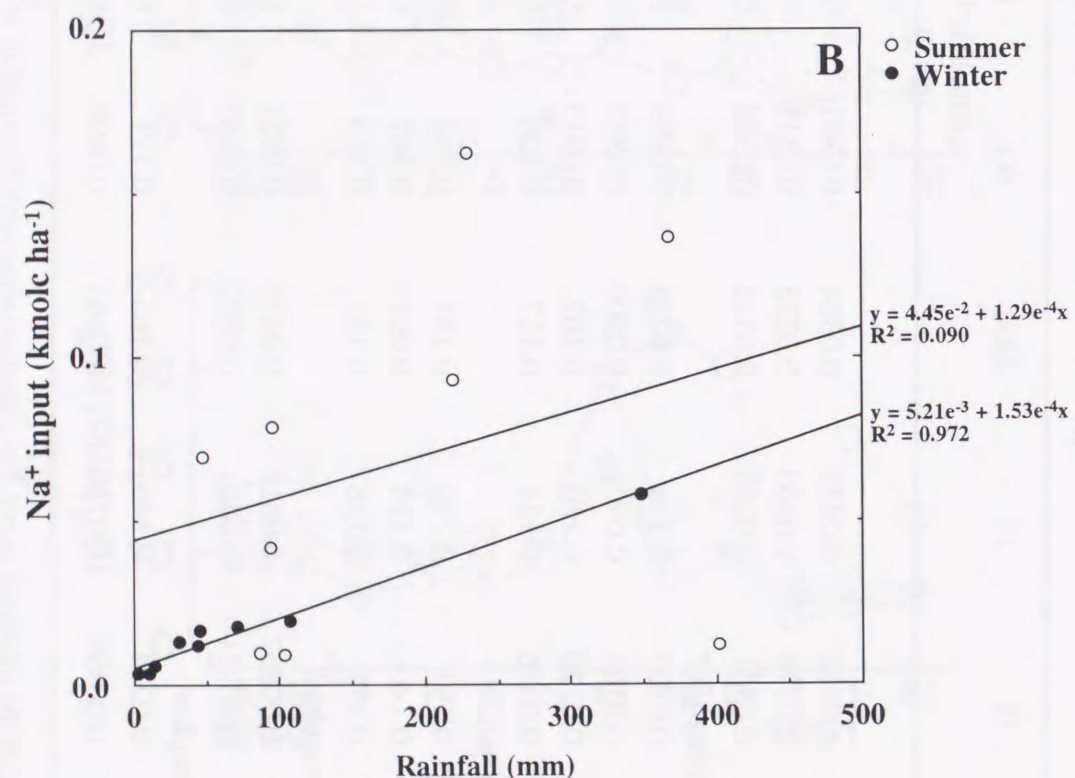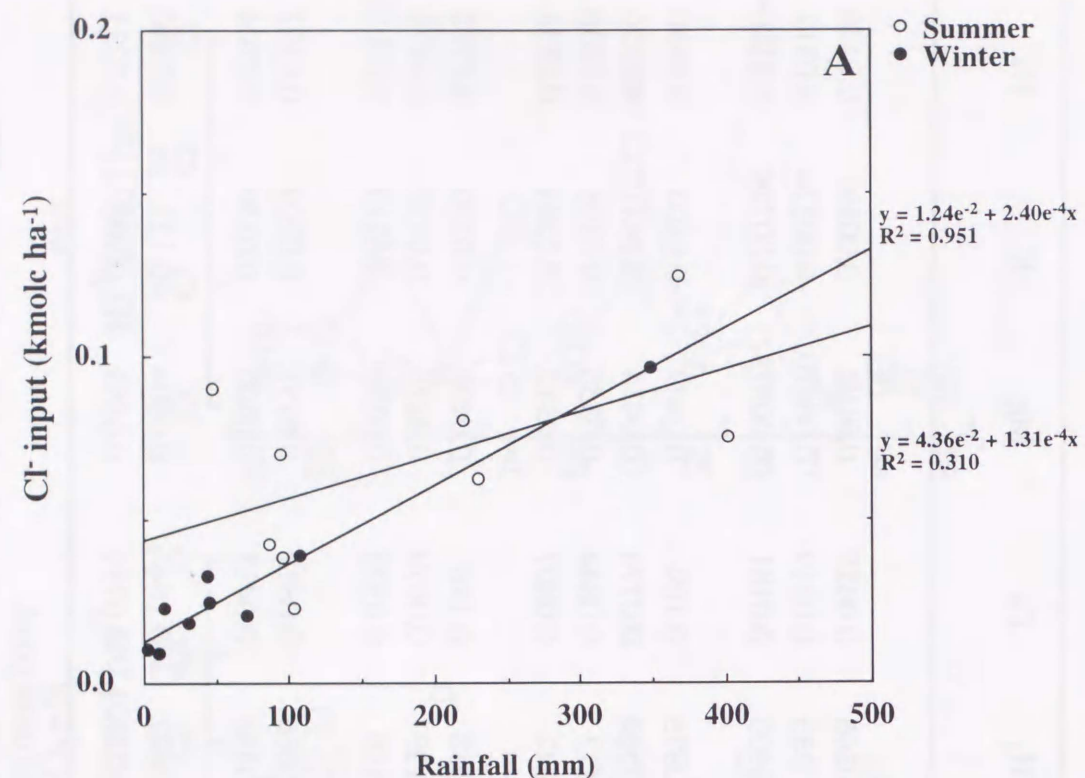
A

○ Summer
● Winter

$y = 1.24e^{-2} + 2.40e^{-4}x$
$R^2 = 0.951$

$y = 4.36e^{-2} + 1.31e^{-4}x$
$R^2 = 0.310$

Cl⁻ input (kmolc ha⁻¹)

Rainfall (mm)

B

○ Summer
● Winter

$y = 4.45e^{-2} + 1.29e^{-4}x$
$R^2 = 0.090$

$y = 5.21e^{-3} + 1.53e^{-4}x$
$R^2 = 0.972$

Na⁺ input (kmolc ha⁻¹)

Rainfall (mm)

**Figure II-11: Seasonal difference in chloride (A) and
sodium (B) input due to open bulk precipitation.**

1991 and in 1991-1992 in contrast with open bulk precipitation. Sodium inputs owing to the coniferous throughfall in 1990-1991 and in 1991-1992 were less than those owing to open bulk precipitation. This resulted in the small sea salt contribution, because the sea salt contribution was estimated by sodium input. Sea salt contribution was higher for the deciduous throughfall than for the coniferous throughfall. Excretion and uptake of chloride and sodium at the canopy was neglected. The differences in dry deposition, therefore, reflected the percentage of the sea salt contribution in both coniferous and deciduous throughfall. Leaf areas of the coniferous trees are relatively wider, compared to the deciduous trees. Coniferous canopies, therefore, can intercept larger amounts of aerosols, dust and gaseous particles than the deciduous canopy. Sea salt contribution to both coniferous and deciduous stemflow were smaller than the corresponding throughfall. Sea salt contribution was 30 % of chloride input in case of the stemflow.

When compared with the results in Tomakomai, Hokkaido Prefecture (Shibata and Sakuma, 1996), sodium input was notably lower (Table II-6), because RLL is located in Hachioji which is 35 km from Tokyo Bay and 36 km from the Pacific Ocean. As Tomakomai is only 6 km from the Pacific Ocean, sea salt contribution to throughfall input was relatively high. Tsunogai and Shinagawa (1977) revealed relationship between the distance from sea and the sea salt input.

Sea salt contribution to sulfate input was less than that of chloride. It was the largest for open bulk precipitation and smaller for throughfall and stemflow (Table II-5). Sulfate input by open bulk precipitation tended to decrease (Table II-1). Nitrate input by open bulk precipitation also gradually decreased from 0.64 kmolc ha⁻¹ yr⁻¹ in 1990-1991 to 0.43 kmolc ha⁻¹ yr⁻¹ in 1995-1996. Consequently, the equivalent ratio of non-sea salt sulfate to nitrate (nss-SO_4^{2-} / NO_3^-: S/N ratio) was stable. Using data in Table II-1 except data in Chongqing, China, relationship between nss-SO_4^{2-} and NO_3^- is shown in Figure II-12. Dots of this study result are close to the line of 1:1. The S/N ratio at RLL was 1.1 during the study periods, which was markedly lower than the Japanese average of 2.9 in 1983-1987, 2.7 in 1988-1992, and 2.0 in 1995 (Japan Environment Agency, 1989, 1994, 1997). Nitrate input at RLL were twice as much as the Japanese average and sulfate input was slightly smaller than the Japanese average, which resulted in the low ratio. The S/N ratio at RLL was lower than those in Europe (3.1 in Erzgebirge (Paces, 1985); 2.3 in Solling (Hauhs, 1989)) and in North
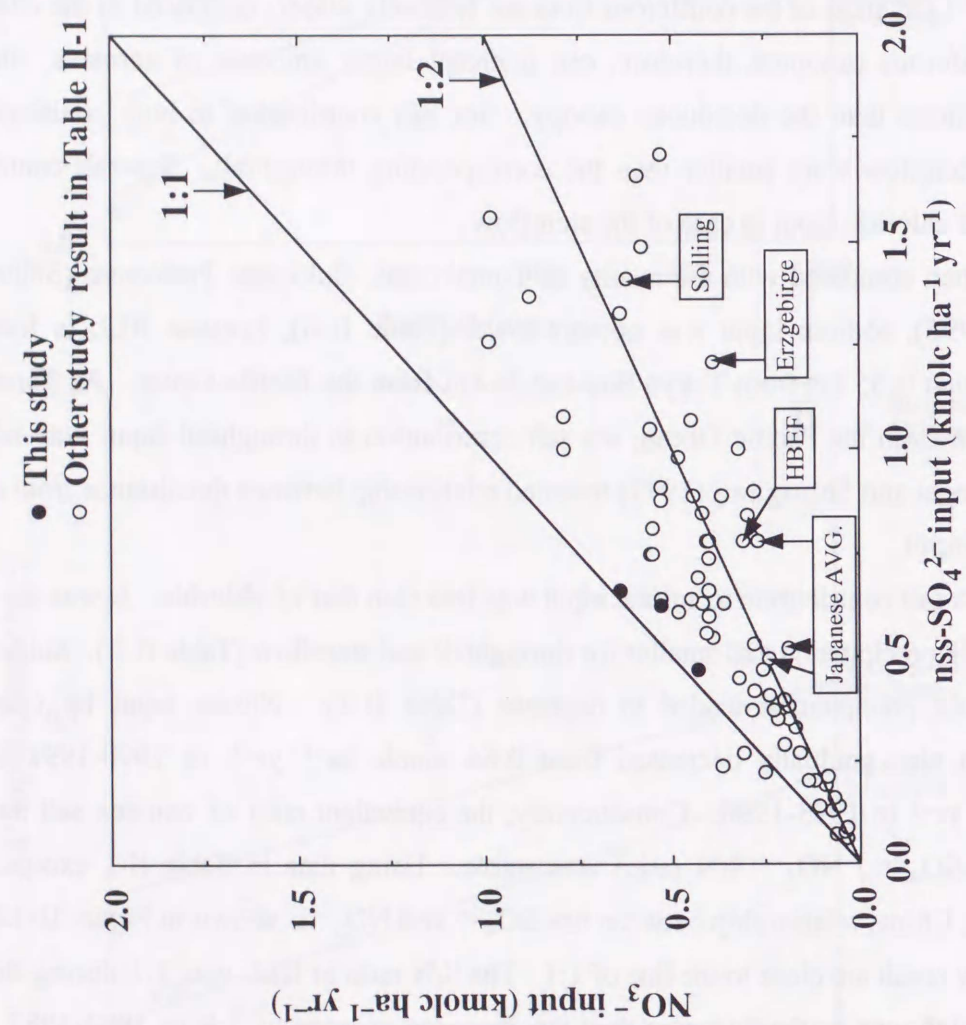
Figure II-12: Relationship between nss-SO$_4^{2-}$ and NO$_3^-$

nss-SO$_4^{2-}$ input (kmolc ha^{-1} yr^{-1})

NO$_3^-$ input (kmolc ha^{-1} yr^{-1})

● This study
○ Other study result in Table II-1

1:1 1:2 Solling Erzgebirge HBEF Japanese AVG.

America (2.6 in Hubbard Brook Experimental Forest (HBEF) (Likens, et al., 1977)). Nitrate inputs at RLL were larger than those in HBEF and Erzgebirge. On the other hand, sulfate inputs were smaller than those in Erzgebirge and Solling. High nitrate input was attributed to the non-point source emissions of nitrogen oxides, mainly from cars in Tokyo (Japan Environment Agency, 1991, 1995). According to the annual report of the Air Quality Bureau, Japan Environment Agency (1996), the mean sulfur dioxide concentration in the air in 1995 was 0.21 μmol m^{-3} at Katakura, Hachioji, the closest measurement station to RLL. Whereas, nitrogen dioxide was 1.13 μmol m^{-3}. The sum of average concentration of nitrogen oxide and nitrogen dioxide concentration was 2.25 μmol m^{-3}. The air quality affected the deposition chemistry at RLL.

Ammonium input associated with open bulk precipitation was proportional to nitrate input or sulfate input (Figure II-13 which was made as Figure II-7). However, ammonium input at RLL was inversely proportional to nitrate input or sulfate input. From October to March ammonium input was correlated with nitrate input or sulfate input (Figure II-14). On the other hand, from April to September there was no relationship. Factors, which control ammonium input from April to September, were not elucidated. Ammonium input from April to September tended to be higher than that from October to March.

Annual ammonium input increased from 0.48 kmolc ha^{-1} yr^{-1} in 1990-1991 to 0.63 kmolc ha^{-1} yr^{-1} in 1995-1996. As a result, the total inorganic nitrogen input exceeded 1 kmolc ha^{-1} yr^{-1}. Nitrogen input exceeded the minimum threshold for nitrogen saturation proposed by Wright *et al.* (1995). Nitrate and ammonium input in 1995-1996 in central Tokyo was 0.61 kmolc ha^{-1} yr^{-1} and 0.64 kmolc ha^{-1} yr^{-1}, respectively (Japan Environment Agency, 1997). These were the highest values in Japan. Deposition chemistry in Tokyo is characterized by the high nitrogen input. Nitrogen saturation status at RLL and its effects were examined in Chapter VI.

The coniferous throughfall fluxes of nitrate and ammonium were enriched by factors of 2 to 3 compared with those by open bulk precipitation. On the other hand, fluxes by the deciduous throughfall were increased by factors 0.9 to 2. Both ammonium and nitrate input due to the coniferous throughfall always exceeded those by open bulk precipitation and by the deciduous throughfall (Figure II-15). Nitrogen input due to the deciduous throughfall were occasionally lower than those by open bulk precipitation. In particular, inputs were almost the
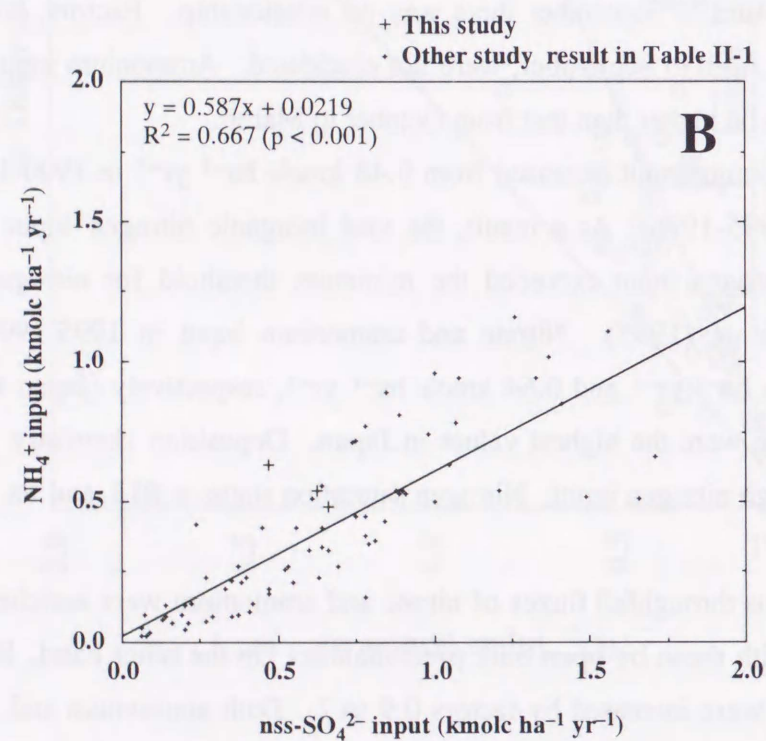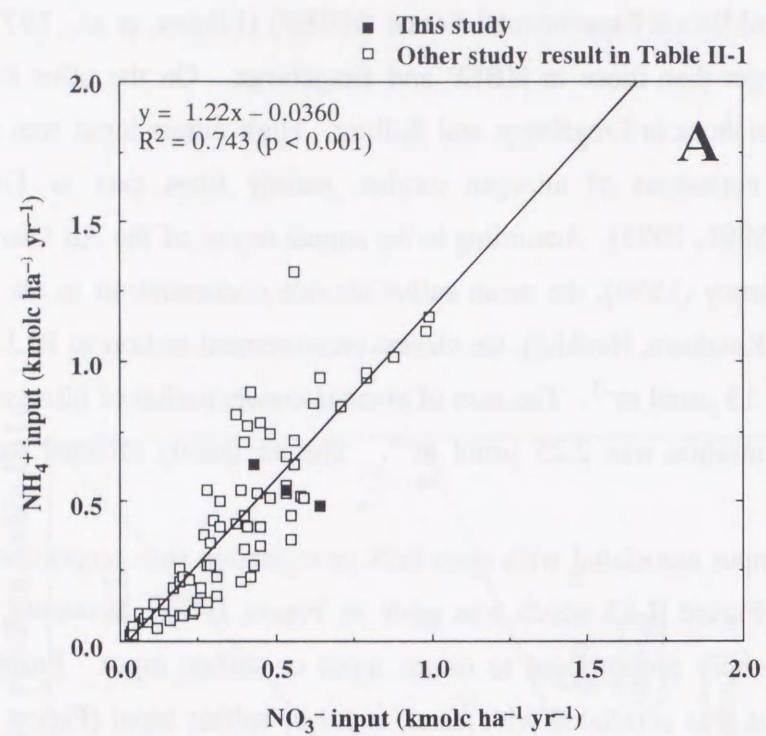
A

■ This study
□ Other study result in Table II-1

$y = 1.22x - 0.0360$
$R^2 = 0.743$ ($p < 0.001$)

NH$_4^+$ input (kmolc ha^{-1} yr^{-1})

NO$_3^-$ input (kmolc ha^{-1} yr^{-1})

B

+ This study
· Other study result in Table II-1

$y = 0.587x + 0.0219$
$R^2 = 0.667$ ($p < 0.001$)

NH$_4^+$ input (kmolc ha^{-1} yr^{-1})

nss-SO$_4^{2-}$ input (kmolc ha^{-1} yr^{-1})

Figure II-13: Relationship between ammonium input and nitrate input (A)
and ammonium input and non-sea salt sulfate input (B).

A

○ Oct-Mar
● Apr-Sep

$y = 0.950x - 0.00141$
$R^2 = 0.946$

$y = 0.169x + 0.0521$
$R^2 = 0.012$

NH$_4^+$ input (kmolc ha^{-1} month^{-1})

NO$_3^-$ input (kmolc ha^{-1} month^{-1})

B

□ Oct-Mar
■ Apr-Sep

$y = 0.802x - 0.00160$
$R^2 = 0.936$

$y = 0.713x + 0.0167$
$R^2 = 0.165$

NH$_4^+$ input (kmolc ha^{-1} month^{-1})
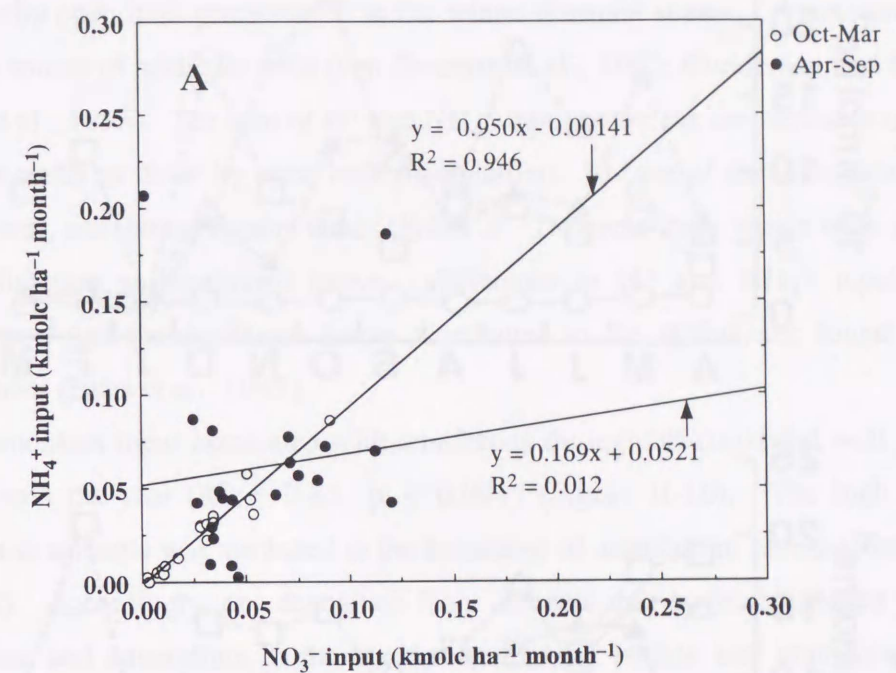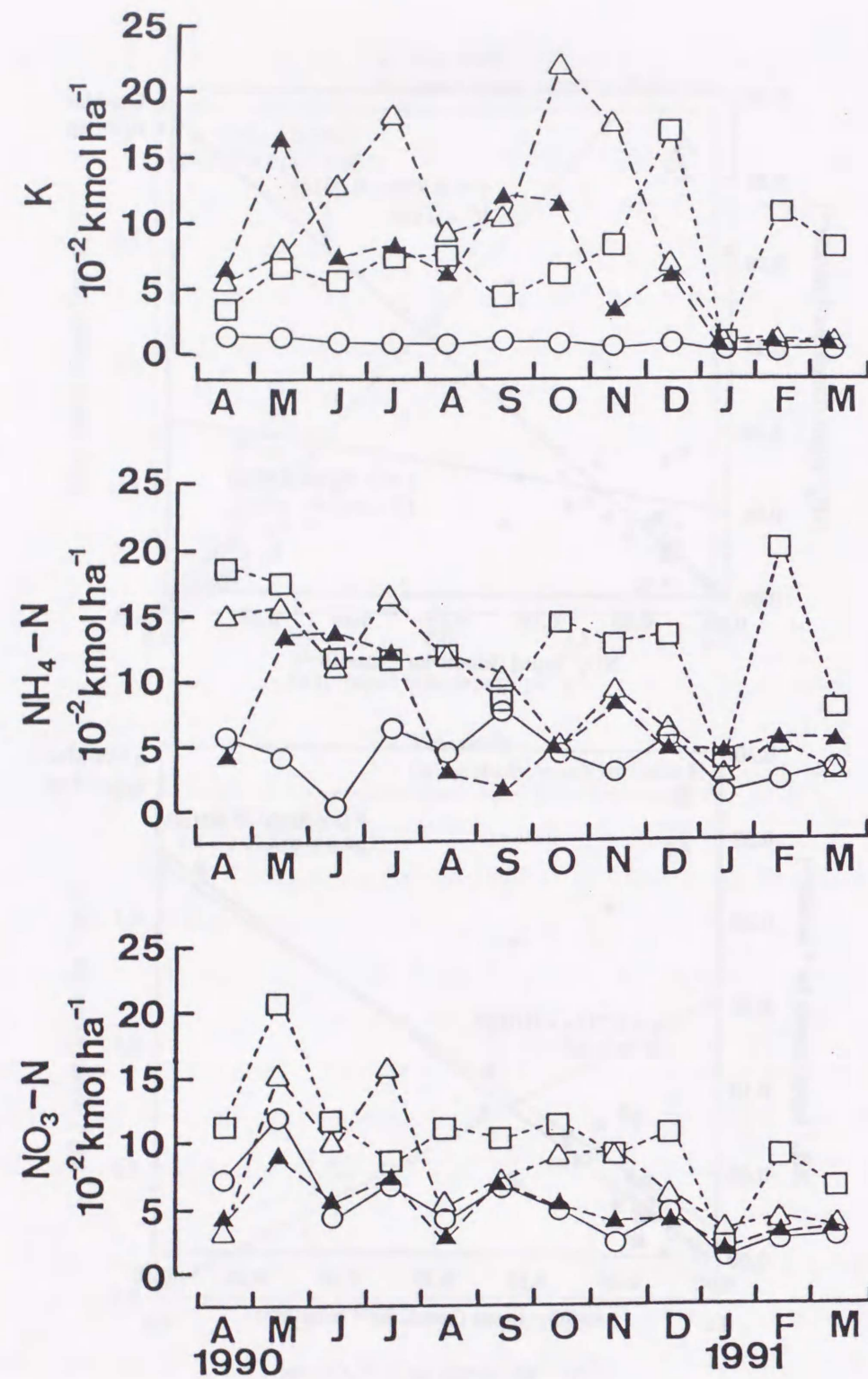
nss-SO$_4$ input (kmolc ha^{-1} month^{-1})
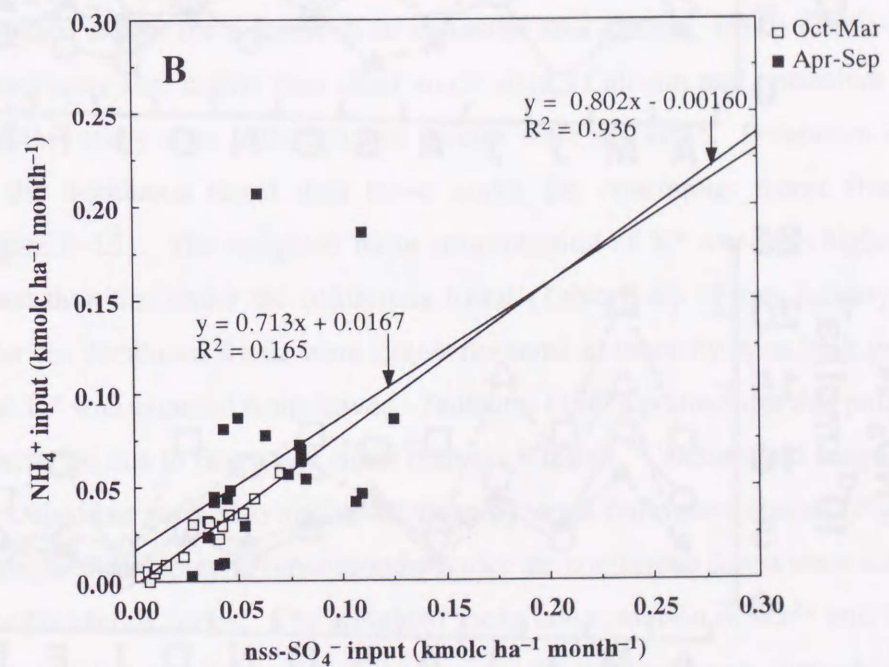
Figure II-14: Relationship between ammonium input and nitrate input (A)
and ammonium input and non-sea salt sulfate input (B) using
monthly input associated with open bulk precipitation at RLL.

○ : Open bulk precipitation, □ : throughfall in mixed coniferous trees,
△ : throughfall in mixed deciduous trees, ▲ : throughfall in mixed deciduous trees

Figure II-15: Monthly inputs of potassium, ammonium and nitrate.

same as those by open bulk precipitation in the winter dormant season. Ammonium could be regarded as a source of acidity in soils (van Breemen et al., 1982; Gundersen and Rasmussen, 1990; Baba et al., 1995). The sum of H^+ and NH_4^+ input under the coniferous forest was 1.6 - 2.3 times as much as those by open bulk precipitation. In case of the throughfall under the deciduous forest, enrichment factors were 0.8 to 1.4. Different ionic inputs were attributed to the canopy function as mentioned above. Difference in H^+ and NH_4^+ input under the coniferous forest and the deciduous forest contributed to the differences found in the soil (solution) acidity (Baba et al., 1995).

Ammonium input associated with coniferous throughfall correlated well with nitrate input throughout the year ($R^2 = 0.81$, $p < 0.001$) (Figure II-16). The high ammonium concentration in aerosols was attributed to the formation of ammonium nitrate (Matsumoto and Ogura, 1992). Accordingly, dry deposition from aerosols may have contributed to the large input of nitrate and ammonium in the coniferous forest. Nitrate and ammonium input by throughfall at RLL were larger than those in other study sites (Haibara and Aiba, 1982; Shibata and Sakuma, 1996) except for a forest in an industrial area (Katou, 1996) (Table II-2, II-3). Magnesium input were also higher than other study sites. Calcium and potassium input were comparable to other study sites, although tree species were not same. Potassium inputs were higher under the deciduous forest than those under the coniferous forest from April to December (Figure II-15). The weighted mean concentration of K^+ was also higher under the deciduous forest than that under the coniferous forest (Table II-6). From January to March, K^+ inputs under the deciduous forest were almost the same as those by open bulk precipitation. It indicated that K^+ was excreted from leaves. Tsutsumi (1987) pointed out that potassium was recycled via excretion due to rain water rather than via litterfall. Calcium and magnesium input from April to December were also similar to those by open bulk precipitation (Figure II-17). Calcium and magnesium inputs in other months under the coniferous forest were comparable to those under the deciduous forest. The weighted mean concentration of Ca^{2+} and Mg^{2+} in the coniferous throughfall were also comparable to those in the deciduous throughfall in 1990-1992. The equivalent $(Ca^{2+} + Mg^{2+} + K^+)/(H^+ + NH_4^+)$ ratio of the coniferous throughfall was relatively lower than that of the deciduous throughfall. This low ratio would contribute to the difference in the soil (solution) acidity.

$y = 0.918x + 0.0161$
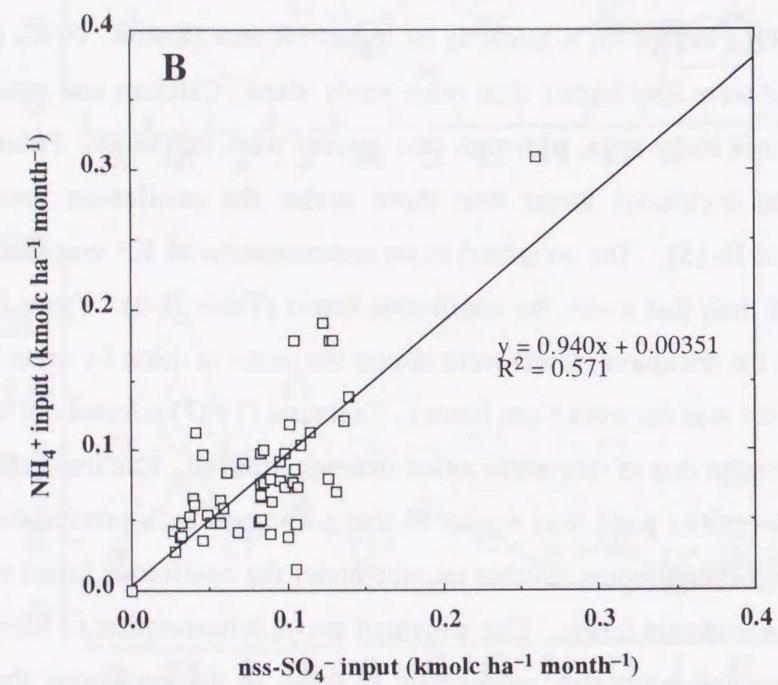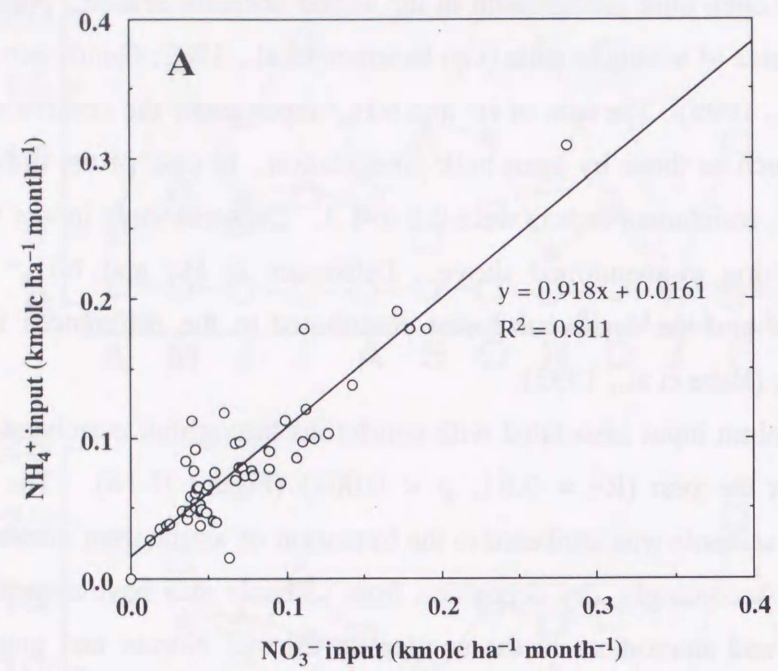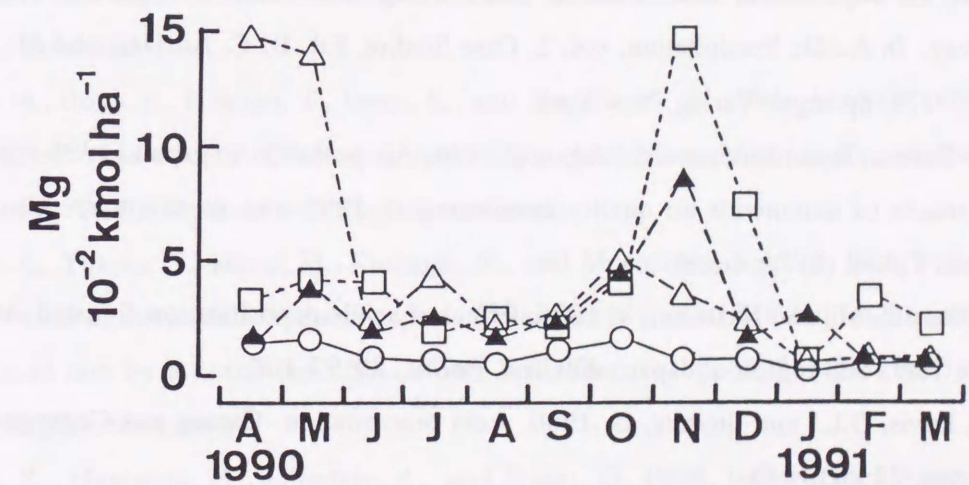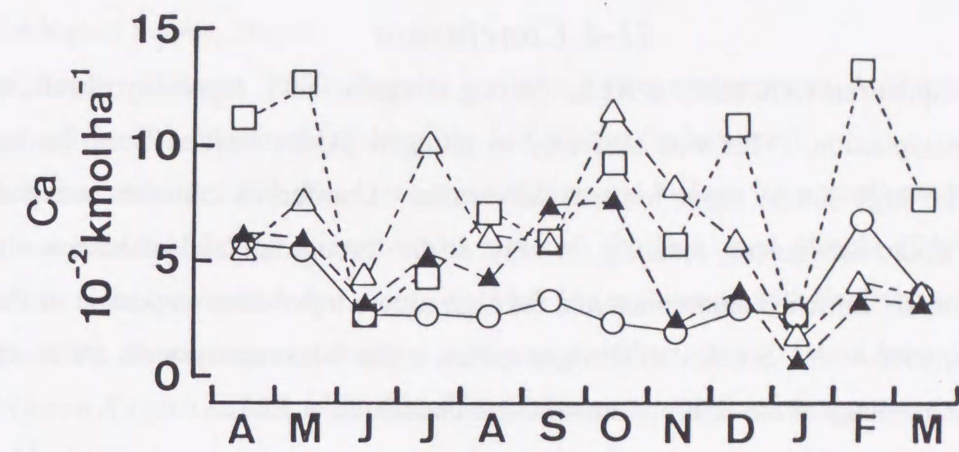$R^2 = 0.811$

$y = 0.940x + 0.00351$
$R^2 = 0.571$

**Figure II-16: Relationship between ammonium input and nitrate input (A)
and ammonium input and non-sea salt sulfate input (B) using
monthly input associated with coniferous throughfall at RLL.**

○ : Open bulk precipitation, □ : throughfall in mixed coniferous trees,
△ : throughfall in mixed deciduous trees, ▲ : throughfall in mixed deciduous trees

Figure II-17: Monthly inputs of calcium and magnesium.

II-4 Conclusion

Precipitations were acidic at RLL. Strong inorganic acid, especially nitrate, acidified open bulk precipitation. This was attributed to nitrogen oxides emitted from the non-point sources. The high nitrate input lowered S/N ratio. Coniferous canopies trapped larger amounts of acidic substances, resulting in very acidic throughfall and stemflow under the coniferous forest. Enriched ammonium and the high nitrate input were important in this study site in combination with . Studies on nitrogen cycles in the forest ecosystems are essential for further understandings of the effect of atmospheric deposition at RLL.

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Chapter III

Sulfate Concentration in Soil Solution of Sulfate Sorptive Soils

III-1 Introduction

Abstract

Sulfur dioxides are one of the main sources of acidic deposition. Estimates of sulfate dynamics in forest ecosystems are very important. The objective of this section is to study the effect of sulfate adsorptive properties of Andisols on anion components in soil solutions. Sulfate concentration in soil solution was governed by the sulfate adsorption capacity of Andisols. The sulfate adsorption capacity was influenced by various factors. Protons and nitrate ions were produced by nitrification, resulting in a seasonal decrease in soil and soil solution pH. Sulfate adsorption capacity increased with a decrease in pH levels. Sulfate concentration in soil solution consequently decreased with an increase in nitrate concentration. Typhoons which had relatively high pH and low sulfate concentration resulted in a decrease in sulfate adsorption capacity. Sulfate concentration in soil solutions increased in the autumn when typhoons came across. Soil and soil solution pH increased with soil depth. Therefore, sulfate adsorption capacities were smaller in the deeper horizons, resulting in higher sulfate concentration.

III-1 *Introduction*

Sulfuric acid is one of the main components of acidic deposition (See Table II-1). Sulfuric acids are occasionally neutralized by ammonia and deposited as ammonium sulfate (van Breemen *et al.* 1982). Forest decline in the Czech Republic was attributed to dry sulfur dioxide (SO_2) gaseous deposition (Paces, 1985; Materna, 1989). Sulfuric acids were transformed from sulfur dioxides, which were emitted from the combustion of lignite in the Czech Republic (Moldan, and Schnoor, 1992). Asthma, which was attributed to tremendous air pollution, had risen in Yokkaichi, Mie Prefecture, Japan since 1961. Desulfurizing equipment has been installed as the counter measure. Sulfur dioxide emission has decreased since the late 1960s (Japan Environment Agency, 1992). Sulfur dioxide emission in China is still high (Ogura, 1994). Kitada (1994) estimated that 73 % of deposited sulfate in Japan was derived from China and Korea. Sulfate is an important component of atmospheric deposition in Japan (Table II-1). The estimation of sulfate dynamics in the forest ecosystems would contribute to the understanding of forest response to acid deposition.

Several soils can retain sulfate ions (Table III-1). Evaluation of sulfate adsorption capacity is essential for estimation of sulfate dynamics. Okazaki (1989) revealed that sulfates were adsorbed by Andisols, even though their surface charges were negative (Figure III-1, 2). That is, sulfate ions were specifically adsorbed by Andisols. The objective of this section is to
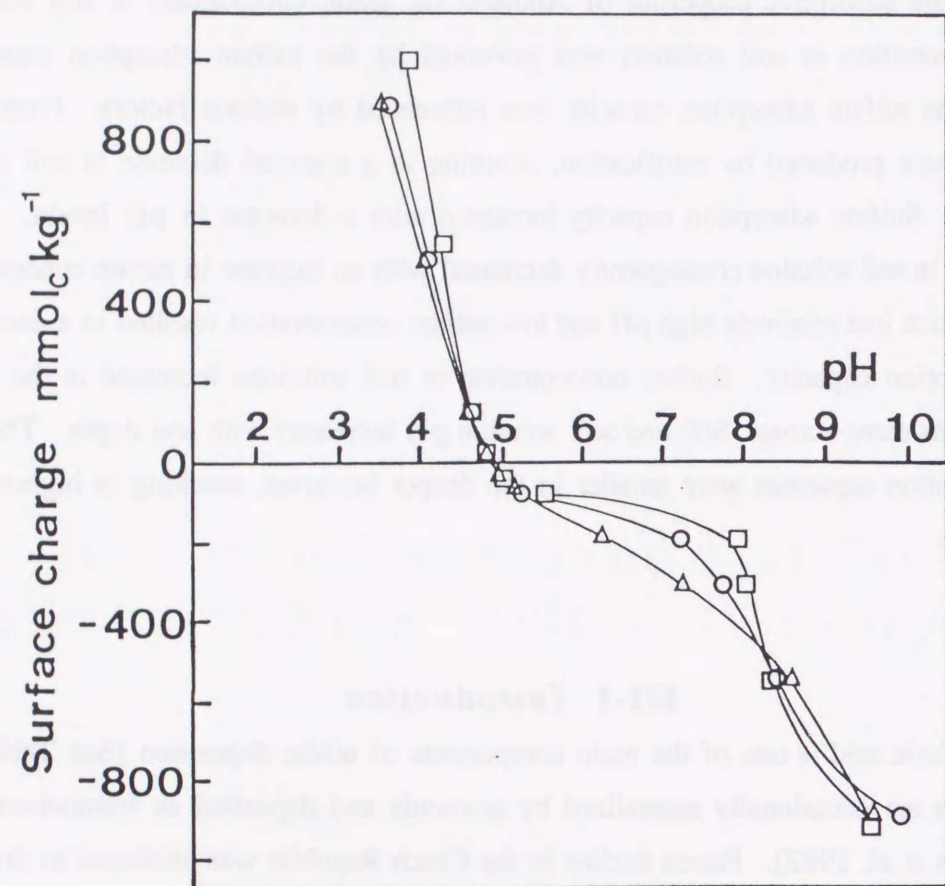
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Figure III-1: Surface charges on the Andisols in the Rolling
Land Laboratory (Cited from Okazaki, 1989).
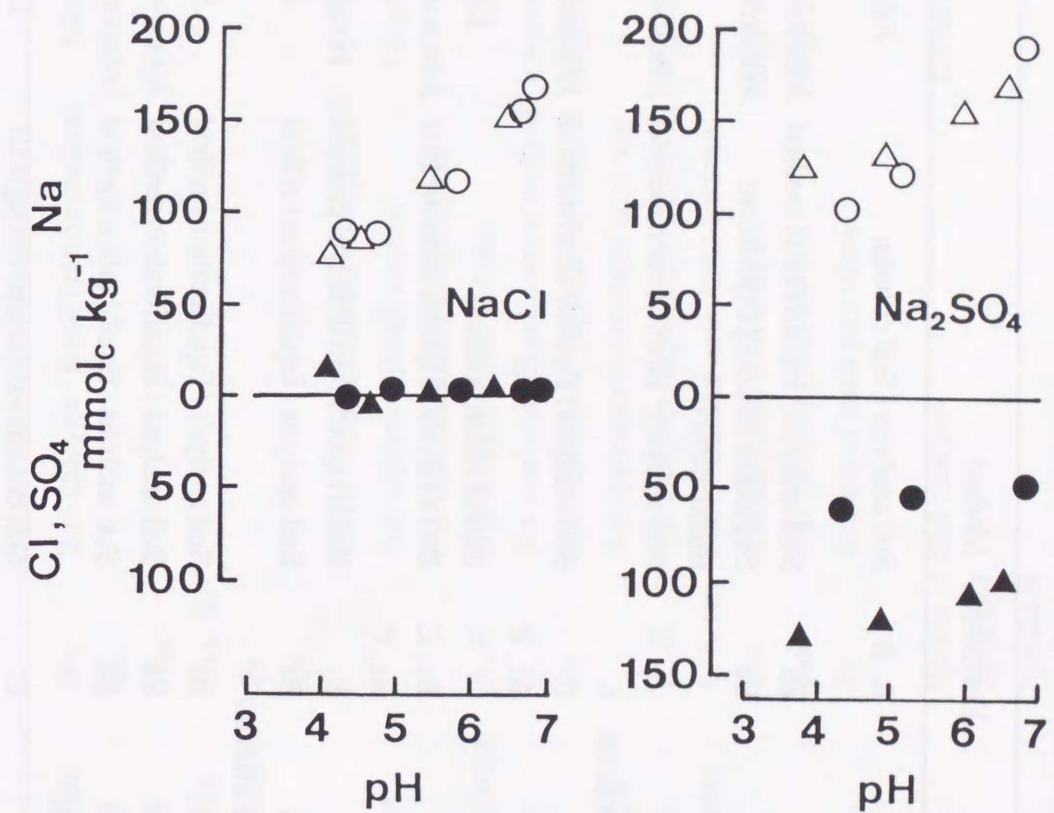□: 0.01 M NaNO3 solution
△: 0.1 M NaNO3 solution
○: 1 M NaNO3 solution

Figure III-2: Sulfate adsorption on the Andisols in the Rolling
Land Laboratory (Cited from Okazaki, 1989).
○ ● : 0.02 M NaCl or Na$_2$SO$_4$ solution
△ ▲ : 0.1 M NaCl or Na$_2$SO$_4$ solution

Table III-1: Estimate of sulfate retention in soils.

Study sites	Soil types	Horizons$	Method	Reference
Walker Branch, Oak Ridge, TN, U.S.[#]	Typic Paleudult Typic Fragiudult	A, B	Soil analysis / Soil column	Johnson et al., 1986
Walker Branch, Oak Ridge, TN, U.S.	Typic Paleudult	B2	Soil analysis / Equilibration method	Johnson and Todd, 1983
Walker Branch, Oak Ridge, TN, U.S.[#]	Typic Paleudult	B2	Sequential leaching experiment Batch method	Johnson and Henderson, 1979
Camp Branch, TN, U.S.	Typic Paleudult Fluvaquetic Dystrochrept	C	Soil analysis / Equilibration method	Johnson and Todd, 1983
Cross Creek, TN, U.S.	Typic Hapludult Aquic Hapludult	C B2, C	Soil analysis / Equilibration method	Johnson and Todd, 1983
Melton Branch, Oak Ridge, TN, U.S.[#]			Equilibration method	Kooner et al., 1995
Coweeta, NC, U.S.	Humic Hapludult Typic Hapludult	B2, C B2, C	Soil analysis / Equilibration method	Johnson and Todd, 1983
Anderson Country, SC, U.S.[#]	Typic Hapludult	Bt	Batch equilibrium isotherm procedure	Hodges and Johnson, 1987
Huntington, Adirondack Mountains, NY, U.S.	Typic Haplorthods	Bs	Soil analysis / Equilibration method	Fuller et al., 1985
Hubbard Brook Experimental Forest, NH, U.S.	Typic / Lithic Haplorthods / Aquic Fragiorthods	Bs	Soil analysis / Equilibration method	Fuller et al., 1985
Hubbard Brook Experimental Forest, NH, U.S.	Typic Fragiorthods	B2	Soil analysis / Equilibration method	Johnson and Todd, 1983
Chesuncock, MA, U.S.	Typic Fragiorthods Aquic Fragiorthods	B2	Soil analysis / Equilibration method	Johnson and Todd, 1983
Maine, U.S.	Spodosols	B	Soil column+simulated throughfall	David, et al., 1991

Table III-1 (*Continued*)

Study sites	Soil types	Horizons$	Method	Reference
Michigan, U.S.	Typic Udipsamments Entic Haplorthods Typic Haplorthods Eutric Glossoboralfs Psammentic Hapludalfs Typic Hapludalfs	Bw Bs Bhs Bhs, Bs Bt Bt	Soil analysis / Equilibration method	MacDonald and Hart, 1990
Illinois, U.S.	Alfisols		Soil column+simulated throughfall	David, et al., 1991
Wind River Mountains, WY, U.S.[#]	Dystric Cryochrept Humic Cryaquept		Soil analysis / Batch method Soil column leaching experiment	Clayton et al., 1991a, b
Thompson, WA, U.S.[#]	Dystic Entic Durochrept	A, B	Soil analysis / Soil column	Johnson et al., 1986
Thompson, WA, U.S.	Dystic Xerochrept	A, B	Soil analysis / Equilibration method	Johnson and Todd, 1983
Findley Lake, WA, U.S.	Cryandept	B2	Soil analysis / Equilibration method	Johnson and Todd, 1983
U.S.	Typic Halpumbrepts		Soil lysimeters+simulated acid rain	Lee, 1985
La Selva, Costa Rica	Typic Hydrandept	A, B	Soil analysis / Equilibration method	Johnson and Todd, 1983
Southern Norway[#]	Typic Udipsamments	0-40 cm	Soil lysimeters+simulated acid rain	Singh et al., 1980
Birkenes, southern Norway	Spodosols	Bsh	Soil analysis / Soil column	Singh and Johnson, 1986
Storgama, southern Norway	podzol	Bsh	Soil analysis / Soil column	Singh and Johnson, 1986
Metta-Dokkas, Sweden[#] - Kvalneset, Norway	Haplocryods	Bs	Sequential leach procedure	Gustafsson, 1995
Sweden	Typic Cryorthods Humic Cryorthod Typic Cryorthents	Spodic B Spodic B Spodic B	Soil analysis	Karltun and Gustafsson, 1993

Table III-1 (*Continued*)

Sweden	Orthic Podsols Dystrc Cambisols	Spodic B	Soil analysis / Equilibration method	Nommik et al., 1988
Solling, Germany	Dystric Cambisol	0-40 cm	Soil lysimeters+simulated rain	Alewell and Matzner, 1993
Harz Mountains, Germany	Cambisols / Spodozols	30-60 cm	Soil analysis	Lukewille et al., 1995
Glen Dye, northeastern Scotland	Iron podzol (275 m*1) Peaty podzol (325 m*1) Peaty ranker (390 m*1)		Soil lysimeters+simulated rain	Sanger et al., 1994
Galicia, northwestern Spain	Typic Haplorthod	Bh, Bs	Equilibration with H_2SO_4 solution (pH 3)	Merino et al., 1994
	Umbric Dystrochrept	A, Bw		
	Typic Haplumbrept	A, Bw		
	Andic Haplumbrept	A, BC		
	Lithic Dystrandept	A2		
	Aeric-humic Haplaquept	Ag, Bg		
	Typic Humaquept	A		
	Typic Dystrandept	A, AB		
	Oxic Dystrandept	A, Bw		
Hachioji, Tokyo, Japan	Andisols		Based on Wada and Okamura (1980, 1983)	Okazaki, 1989
Geihoku-cho, Hiroshima, Japan	Ultisols		Based on Wada and Okamura (1980, 1983)	Okazaki, 1989
Seto, Aichi, Japan	Inceptisols		Based on Wada and Okamura (1980, 1983)	Okazaki, 1989
Eastern part of Japan	Andisols		Soil analysis / Batch equilibrium procedure	Fumoto et al., 1996

$: Horizons which retained the largest amount sulfate in soil profiles.

*1: Altitude

#: Sulfate adsorption isotherms were described.

study the effect of sulfate adsorptive properties of Andisols on anion components in soil solutions.

III-2 Materials and Methods

III-2-1 Site description and field monitoring

The detailed site description is given in II-2-1. Sulfate inputs due to open bulk precipitation ranged from 0.49 kmol$_c$ ha^{-1} yr^{-1} to 1.07 kmol$_c$ ha^{-1} yr^{-1}. Sulfate inputs increased by factors of 2.1-3.5 under the coniferous forest and of 1.4-2.6 under the deciduous forest. Soil solutions were taken at the different depths (10, 20, 30 and 50 cm) at Plot II, III, IV and V using soil solution extractors (Figure III-3). Extractors using porous ceramic cups were always connected to glass bottles at a potential vacuum (85-95 kPa). Glass bottles were depressurized again using a Handy Aspirator (Nalgene, 6130-0020; 36 mL with gauge) at least 2 days before the bottle exchange. Bottles were exchanged every two weeks in 1990-1992. In 1995-1996 bottles were removed 2 weeks after connecting and the tubes were wrapped with several bags to keep them clean until again connecting the bottles, 2 weeks later.

III-2-2 Column experiment

Two soil columns were prepared (Figure III-4). Soil sample was taken from the uppermost layer at a depth of 10 cm under the coniferous forest and at least 1 m away from any trunks of Hinoki cypress (*Chamaecyparis obtusa*) at RLL on November 1st in 1993. The diameter at the breast height (DBH) of the closest trunk was 10.5 cm. A hundred grams of fresh soil (69.1 g as oven-dried soil) was packed in each column. The diameter of each column was 6 cm. A plastic sponge, 1 cm in thickness, was placed on the surface of the packed soil to spread drops of the artificial acid rain or distilled water. First, 1 L of distilled water was added. The rate of addition was 200 mL per 20-25 hrs (1 L per week). The leachate was collected in 1 L glass flasks. Distilled water was allowed to continue percolating in one column (Column 1). The other was subjected to artificial acid rain with a pH of 3.6 (Column 2). The artificial rain was comprised of 0.137 mmol$_c$ L^{-1} of sulfate and 0.132 mmol$_c$ L^{-1} of nitrate. The addition amounted total of 2.42 kmol$_c$ ha^{-1} of sulfate and 2.34 kmol$_c$ ha^{-1} of nitrate. This represents 1.5 times as much sulfate and twice as much nitrate as those brought by the coniferous throughfall in 1991. Atmospheric nitrogen deposition consisted of equal amounts of ammonium and nitrate. In this experiment, all ammonium ions were assumed to be nitrified. Nitrate and protons were produced in the soil horizon.
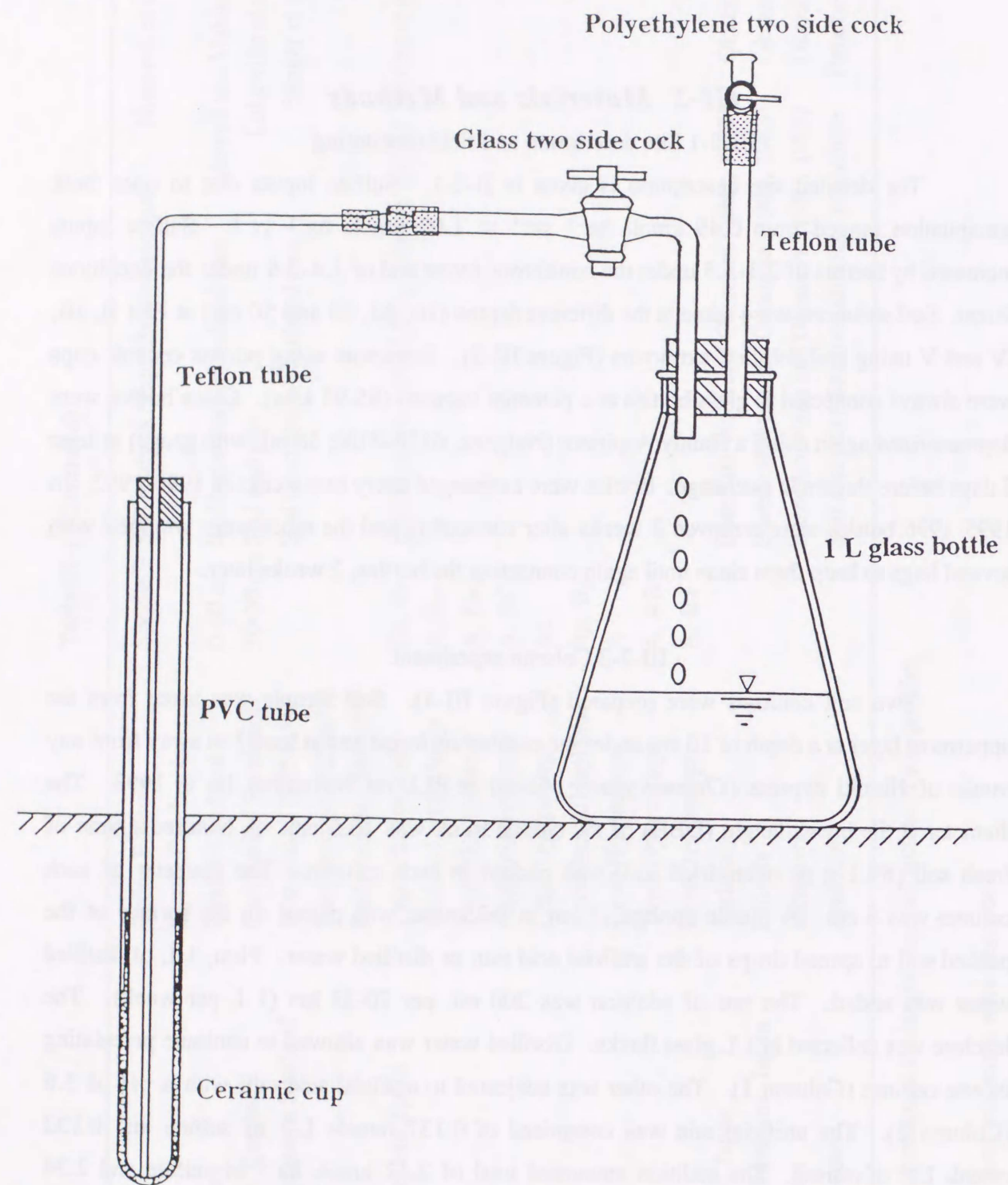
Polyethylene two side cock

Glass two side cock

Teflon tube

Teflon tube

1 L glass bottle

PVC tube

Ceramic cup

Figure III-3: Collecting equipment for the soil solution.

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Artificial acid rain
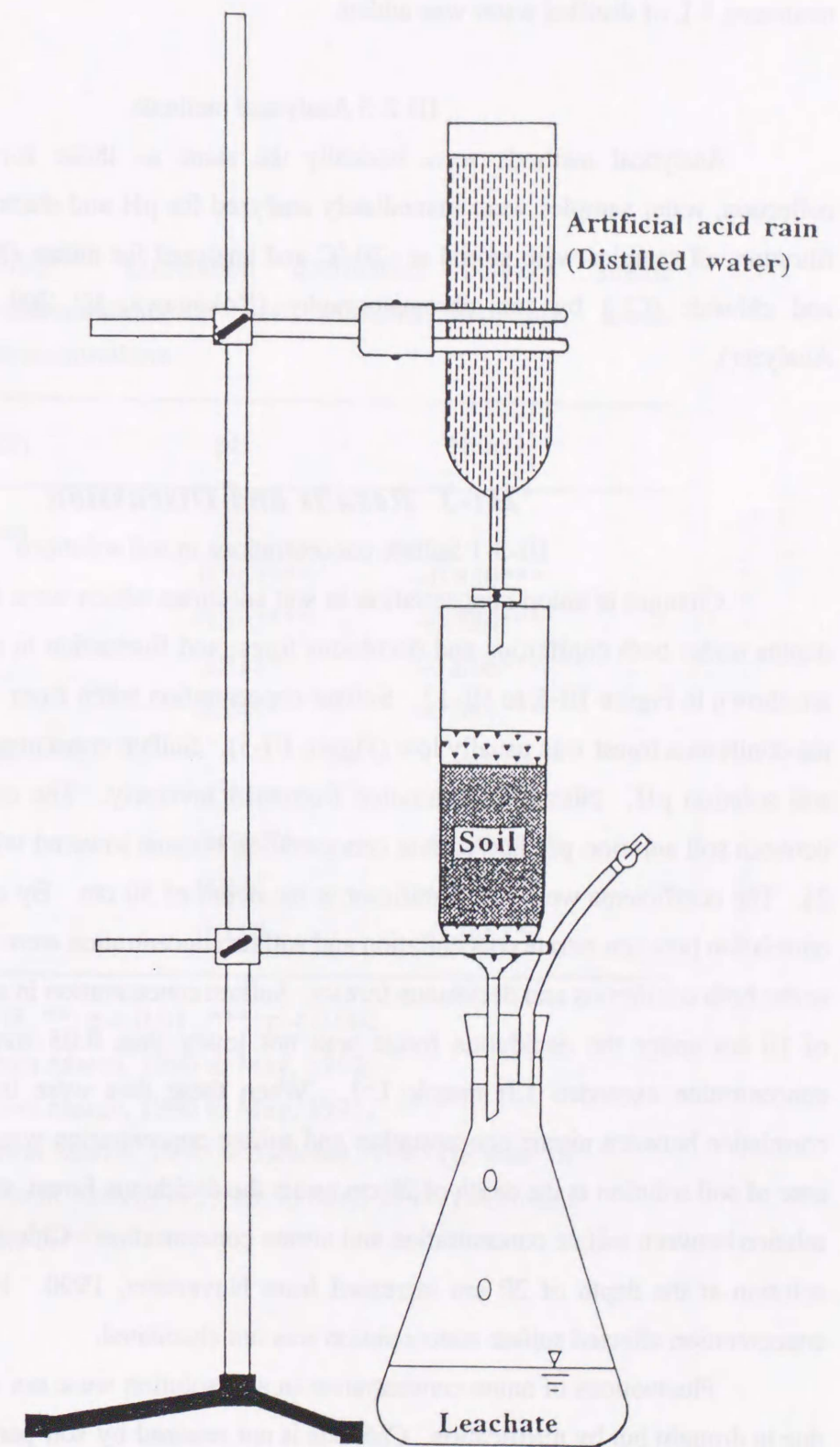(Distilled water)

Soil

Leachate

Figure III-4: Equipment for the column experiment.

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Accordingly, twice the amount of nitrate input was added to the soil. At the of 5 weeks of acid treatment, 1 L of distilled water was added.

III-2-3 Analytical methods

Analytical methods were basically the same as those for precipitation. After collection, water samples were immediately analyzed for pH and electric conductivity. After filtration, all samples were stored at $-20\ ^\circ C$ and analyzed for nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-) by ion chromatography (Yokogawa, IC 200 Ion Chromatographic Analyzer).

III-3 Results and Discussion

III-3-1 Sulfate concentrations in soil solutions

Changes in anion concentration in soil solutions which were taken from various soil depths under both coniferous and deciduous forest and fluctuation in soil solution pH values are shown in Figure III-5 to III-12. Sulfate concentration taken from 10 cm soil depth under the coniferous forest was usually low (Figure III-5). Sulfate concentration fluctuated with the soil solution pH. Nitrate concentration fluctuated inversely. The coefficient of correlation between soil solution pH and sulfate concentration became lowered with soil depth (Table II-2). The coefficients were not significant at the depth of 50 cm. By contrast, coefficients of correlation between nitrate concentration and sulfate concentration were significant at all depths under both coniferous and deciduous forests. Sulfate concentration in soil solution at the depth of 10 cm under the deciduous forest was not lower than 0.05 mmolc L^{-1}, when nitrate concentration exceeded 1.0 mmolc L^{-1}. When these data were included, coefficients of correlation between nitrate concentration and sulfate concentration was not significant. In the case of soil solution at the depth of 20 cm under the deciduous forest, there was a difference in relation between sulfate concentration and nitrate concentration. Chloride concentration in soil solution at the depth of 20 cm increased from November, 1990. However, how chloride concentration affected sulfate concentration was not elucidated.

Fluctuations of anion concentration in soil solution were not caused by concentration due to drought but by nitrification. Chloride is not retained by soil particles and/or assimilated by plant and microorganisms. Therefore, chloride concentration in soil solution was governed by its concentration in rainfall or degree of drought. Except during summer, chloride concentration in soil solution, at least in the upper layers, changed directly with nitrate

Table III-2 Correlation coefficients between sulfate concentrations in soil solutions and pH, nitrate concentrations.

Depth (cm)	pH	Nitrate
Coniferous		
10[1]	0.767***	−0.850***
20[1]	0.545***	−0.784***
30[1]	0.311*	−0.866***
50[1]	0.249	−0.681***
Deciduous		
10[1]	0.791***	−0.612***
20[2]	0.539**	−0.882***[3]
30[2]	0.032	−0.844***
50[2]	0.118	−0.765**

*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$

1: Data from March, 1990 to May, 1992.

2: Data from March, 1990 to May, 1991.

3: Data from March, 1990 to October, 1990 (In case of period from November, 1990 to May, 1991, coefficient was −0.811***).
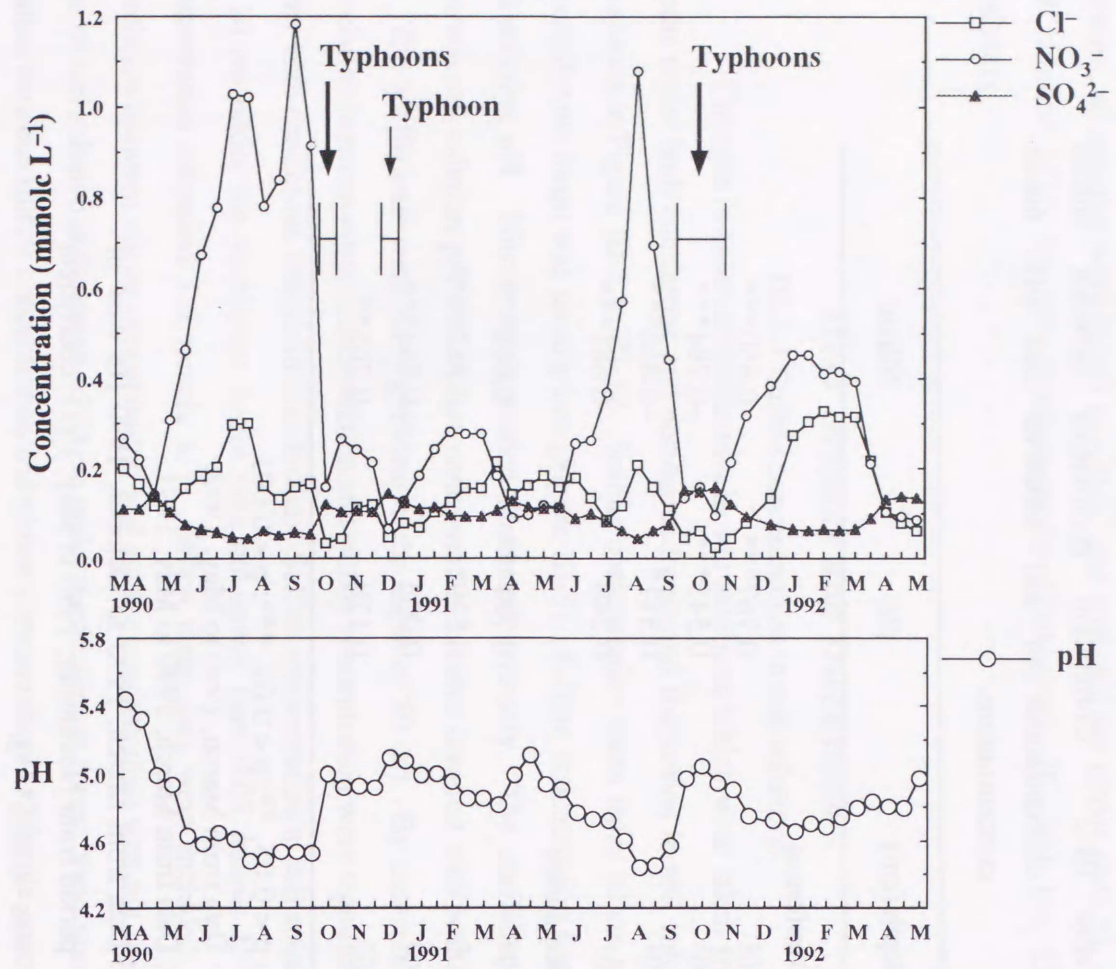
Figure III-5: Changes in anion concentrations and pH values of soil solutions which were taken from 10 cm soil depth under the coniferous forest.
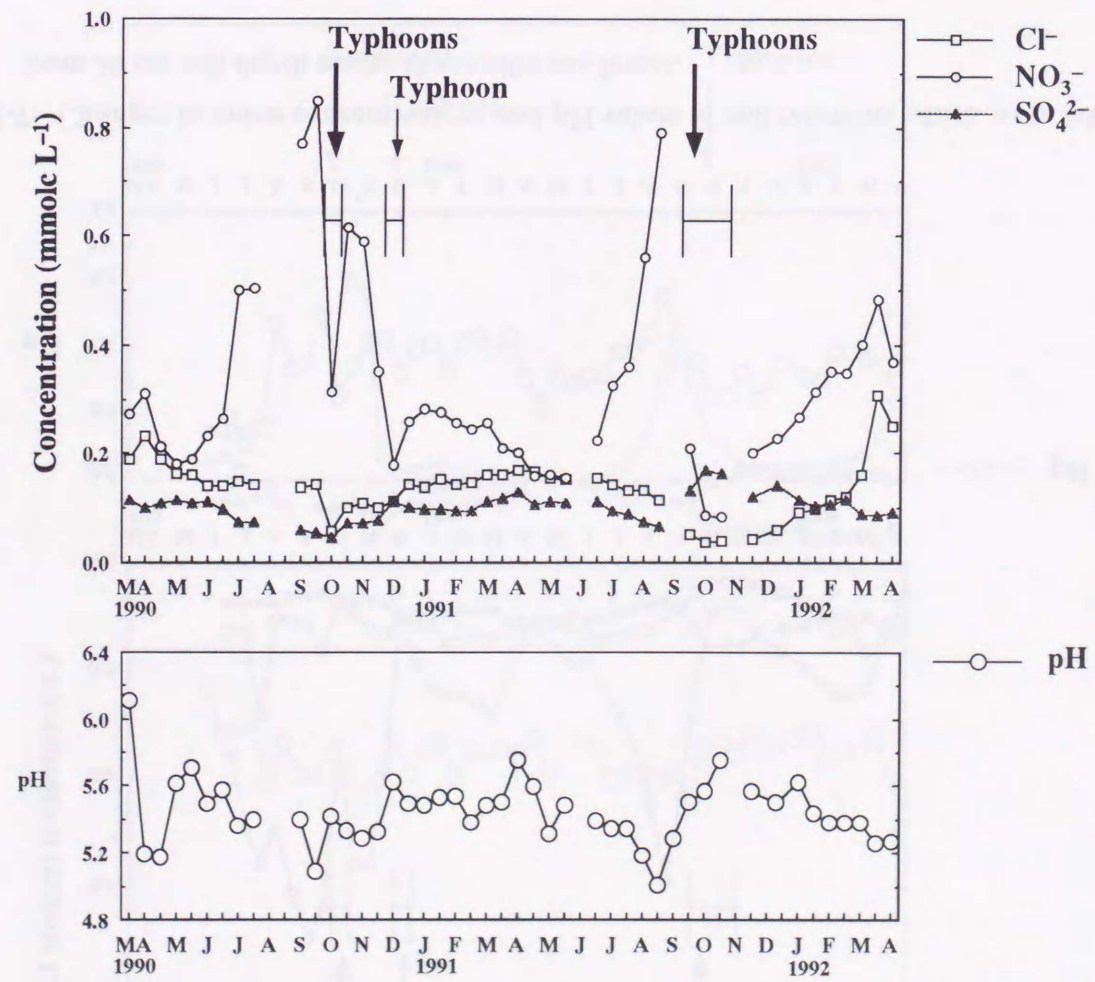
Figure III-6: Changes in anion concentrations and pH values of soil solutions which were taken from 20 cm soil depth under the coniferous forest.
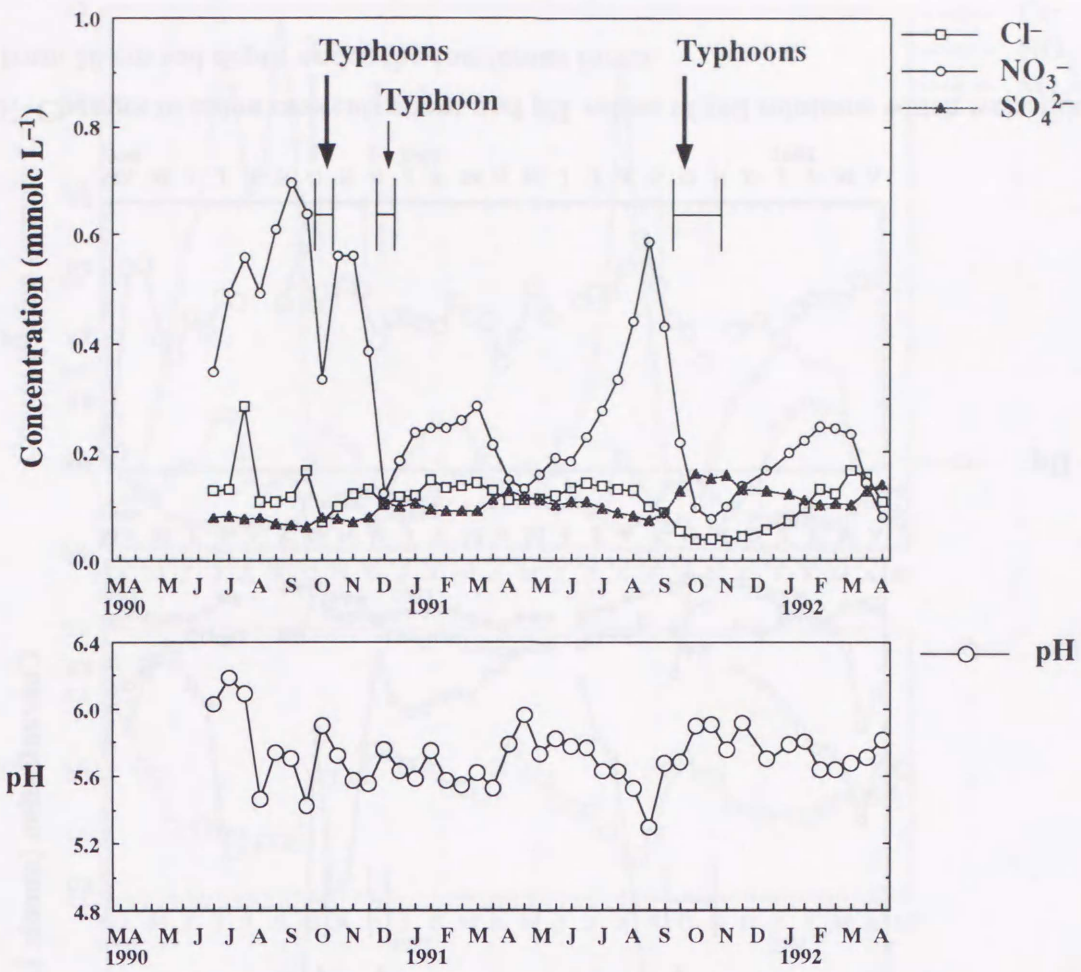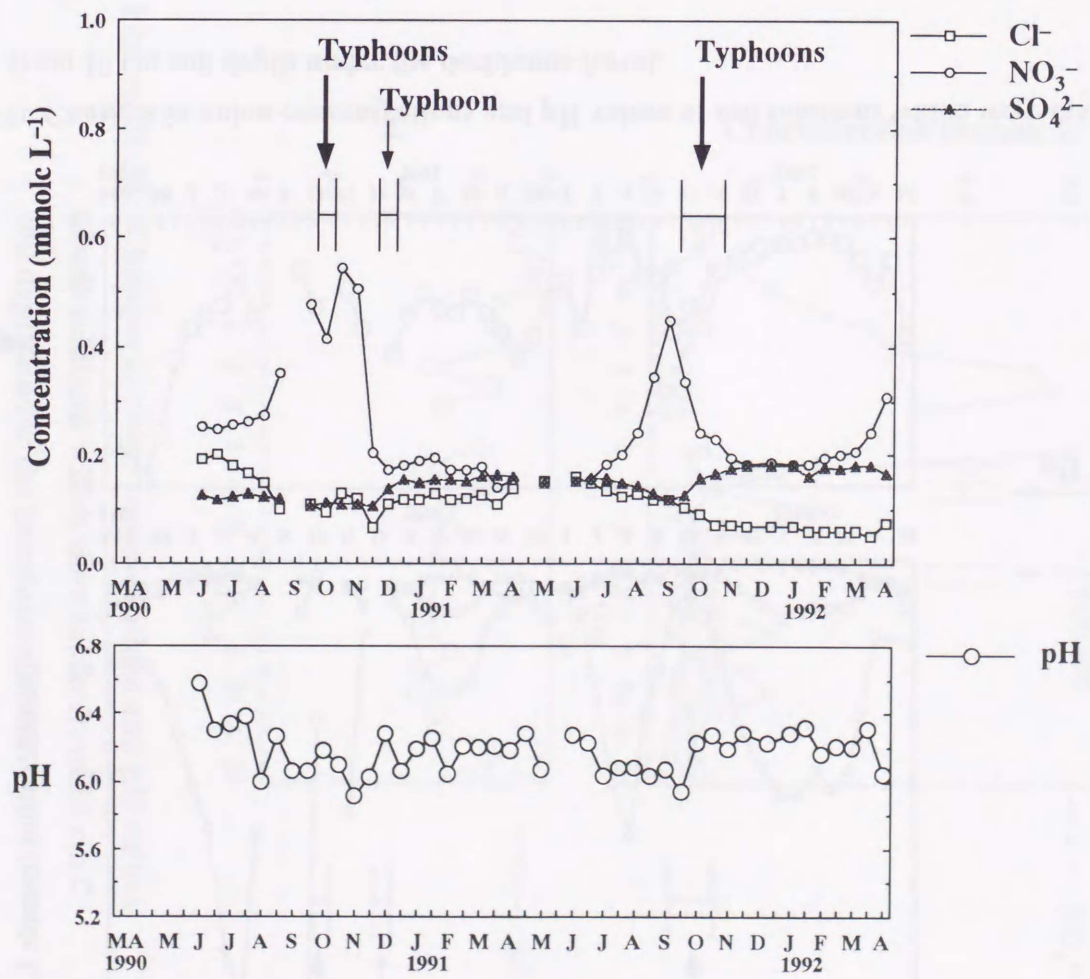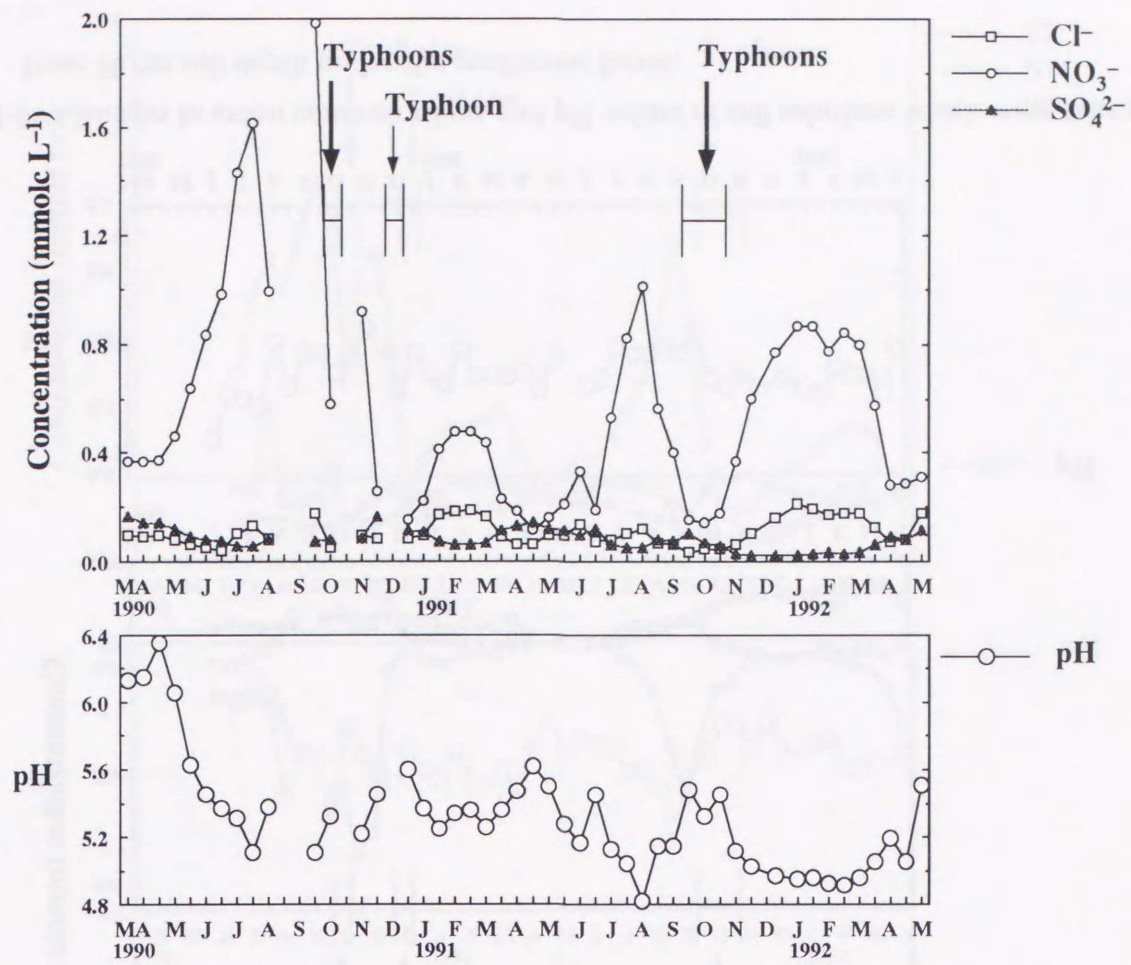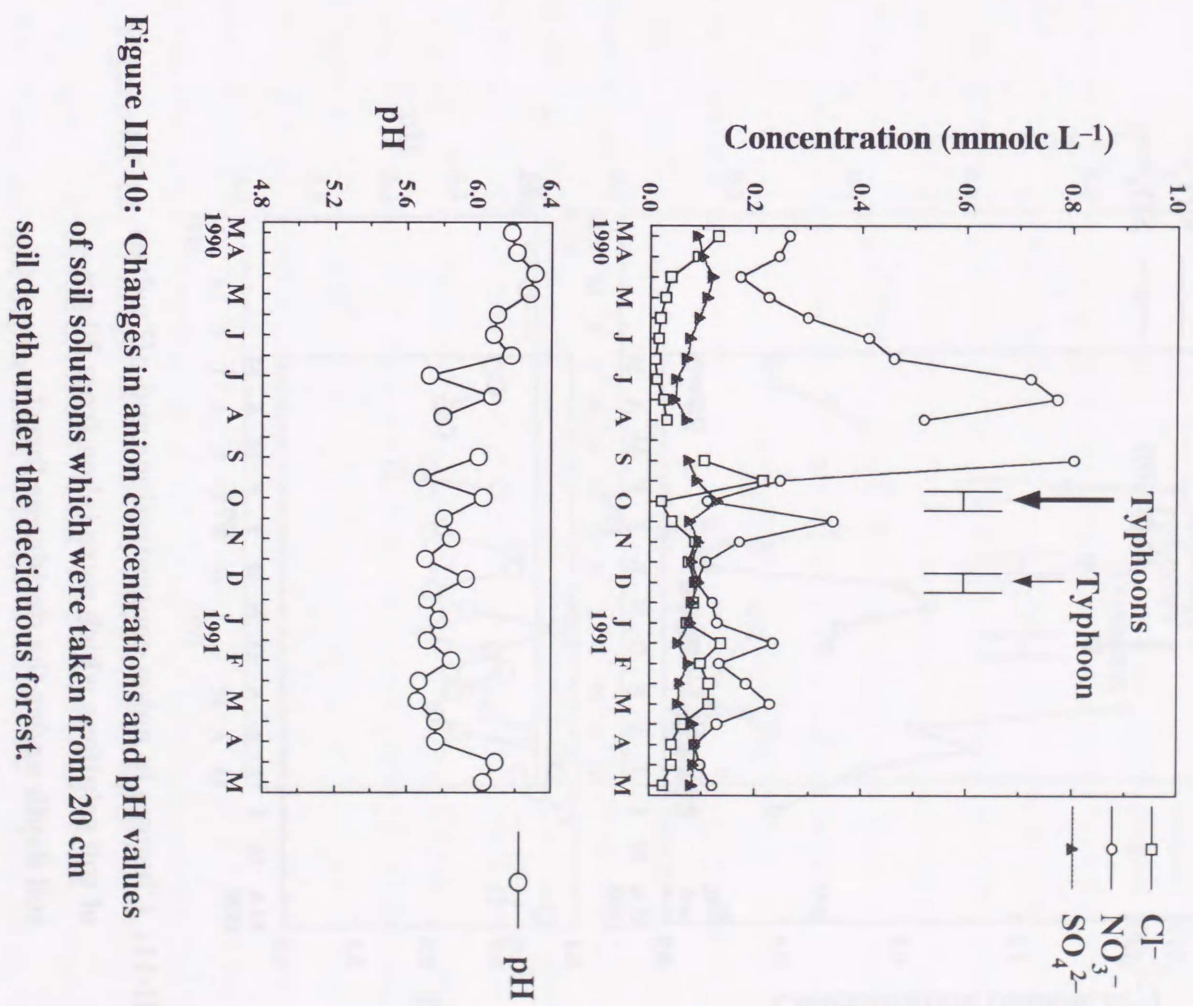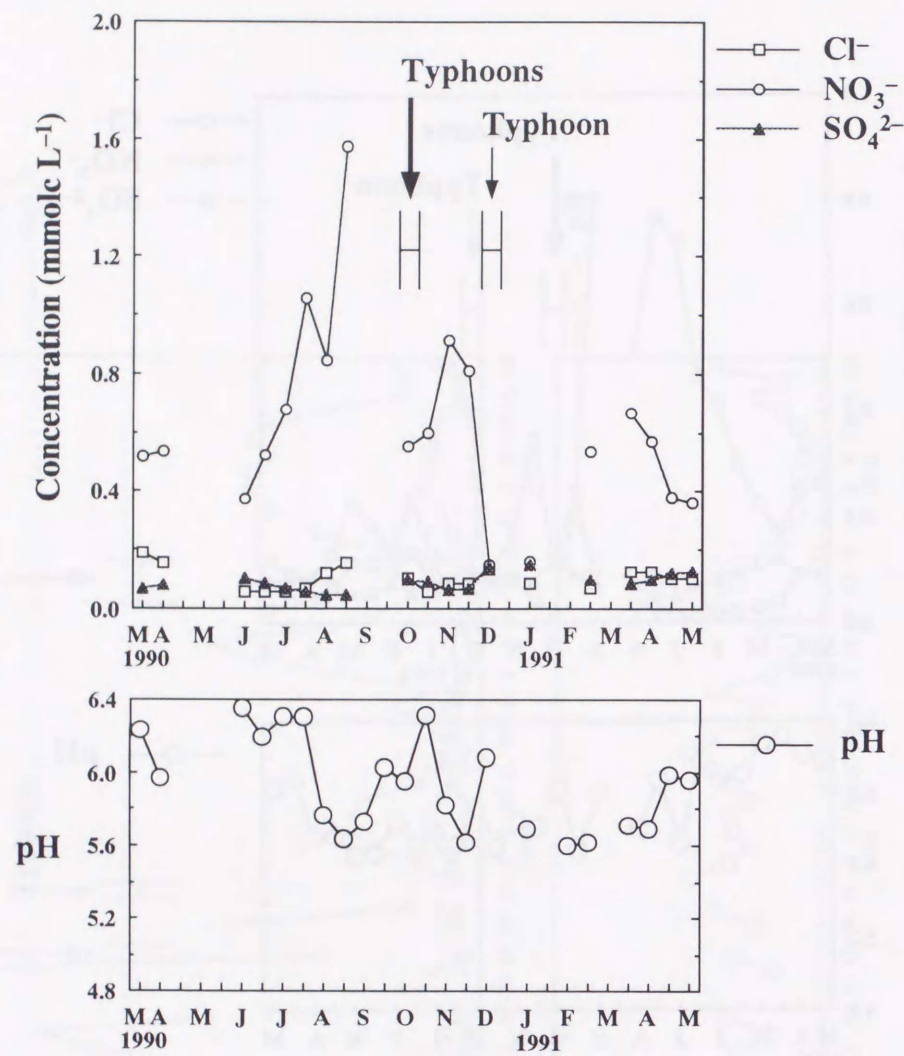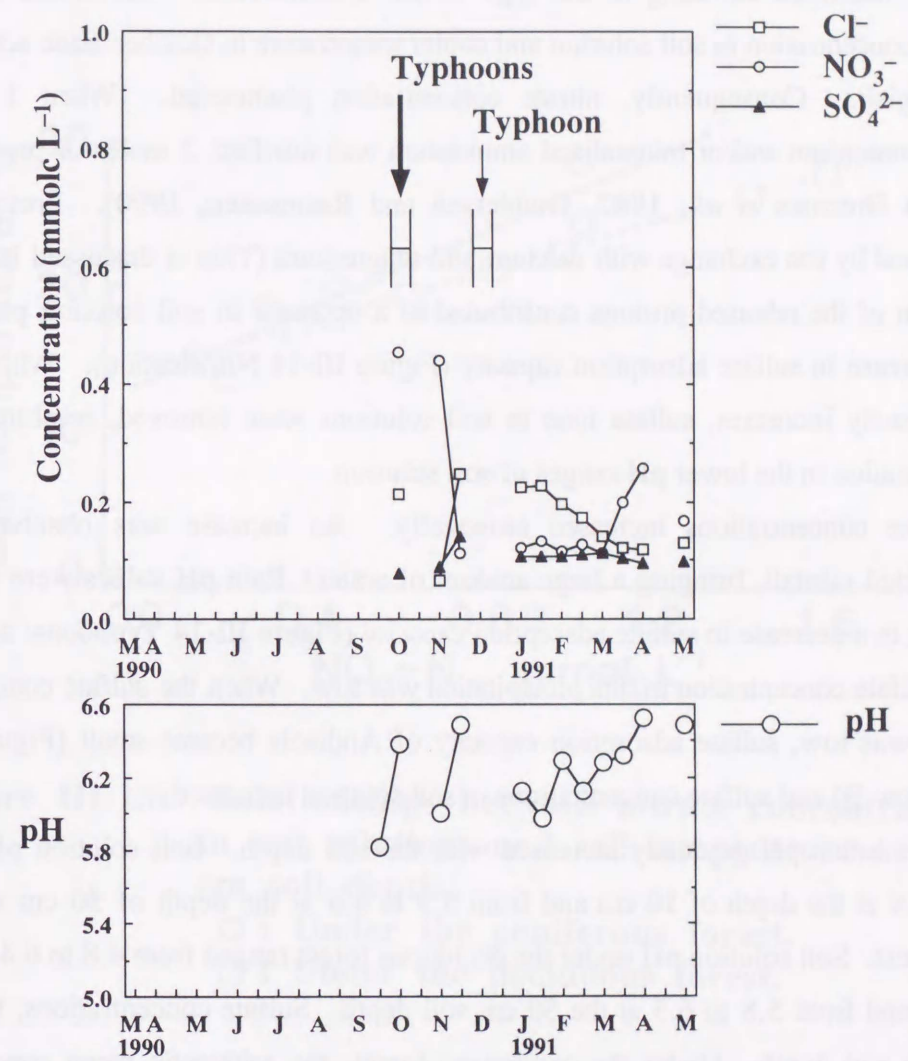
Figure III-7: Changes in anion concentrations and pH values of soil solutions which were taken from 30 cm soil depth under the coniferous forest.

Figure III-8: Changes in anion concentrations and pH values of soil solutions which were taken from 50 cm soil depth under the coniferous forest.

Figure III-9: Changes in anion concentrations and pH values of soil solutions which were taken from 10 cm soil depth under the deciduous forest.

Figure III-10: Changes in anion concentrations and pH values of soil solutions which were taken from 20 cm soil depth under the deciduous forest.

Figure III-11: Changes in anion concentrations and pH values of soil solutions which were taken from 30 cm soil depth under the deciduous forest.

Figure III-12: Changes in anion concentrations and pH values of soil solutions which were taken from 50 cm soil depth under the deciduous forest.

concentration. However, during summer, only nitrate concentration increased sharply which implies that nitrate is produced in the soil by microorganisms. Nitrate concentration was correlated with soil temperature from spring to summer (Figure III-13). The activities of nitrifiers were facilitated resulting in the high nitrate concentration. Occasional typhoons diluted nitrate concentration in soil solution and cooler temperature in October made activities of nitrifiers sluggish. Consequently, nitrate concentration plummeted. When 1 mol of atmospheric ammonium and/or mineralized ammonium was nitrified, 2 moles of proton were produced (van Breemen *et al.*, 1982, Gundersen and Rasmussen, 1990). Protons were almost consumed by ion exchange with calcium and magnesium (This is discussed in Chapter IV). A portion of the released protons contributed to a decrease in soil solution pH, which resulted in increase in sulfate adsorption capacity (Figure III-14 Nitrification). When sulfate adsorption capacity increases, sulfate ions in soil solutions were removed, resulting in low sulfate concentration in the lower pH ranges of soil solution.

Sulfate concentrations increased seasonally. An increase was observed when typhoons affected rainfall, bringing a large amount of water. Rain pH values were relatively high, resulting in a decrease in sulfate adsorption capacity (Figure III-14 Typhoons: arrow A). In addition, sulfate concentration in this precipitation was low. When the sulfate concentration in the rainfall was low, sulfate adsorption capacity of Andisols became small (Figure III-14 Typhoons: arrow B) and sulfate concentrations in soil solution increased.

Soil solution pH gradually increased with the soil depth. Soil solution pH ranged from 4.5 to 5.4 at the depth of 10 cm and from 5.9 to 6.6 at the depth of 50 cm under the coniferous forest. Soil solution pH under the deciduous forest ranged from 4.8 to 6.4 at the 10 cm soil depth and from 5.8 to 6.5 at the 50 cm soil depth. Sulfate concentrations, therefore, increased with soil depth. Under the coniferous forest, the arithmetic mean concentration increased from 0.0953 mmol$_c$ L^{-1} at the depth of 10 cm to 0.148 mmol$_c$ L^{-1} at the depth of 50 cm. The arithmetic mean concentration under the deciduous forest was 0.0831 mmol$_c$ L^{-1} at the depth of 10 cm and 0.105 mmol$_c$ L^{-1} at the depth of 50 cm. The increase in soil solution pH induced the decrease of sulfate adsorption capacity as mentioned above (Figure III-14 Soil depth). Stable high pH at the depth of 50 cm was responsible for the high sulfate concentration compared to a depth of 10 cm.

III-3-2 Column experiment

Sulfate output initially amounted to 2.10 mmol$_c$ kg^{-1} soil, on average, due to the addition of distilled water (Figure III-15). During second week, 1.43 mmol$_c$ kg^{-1} of sulfate
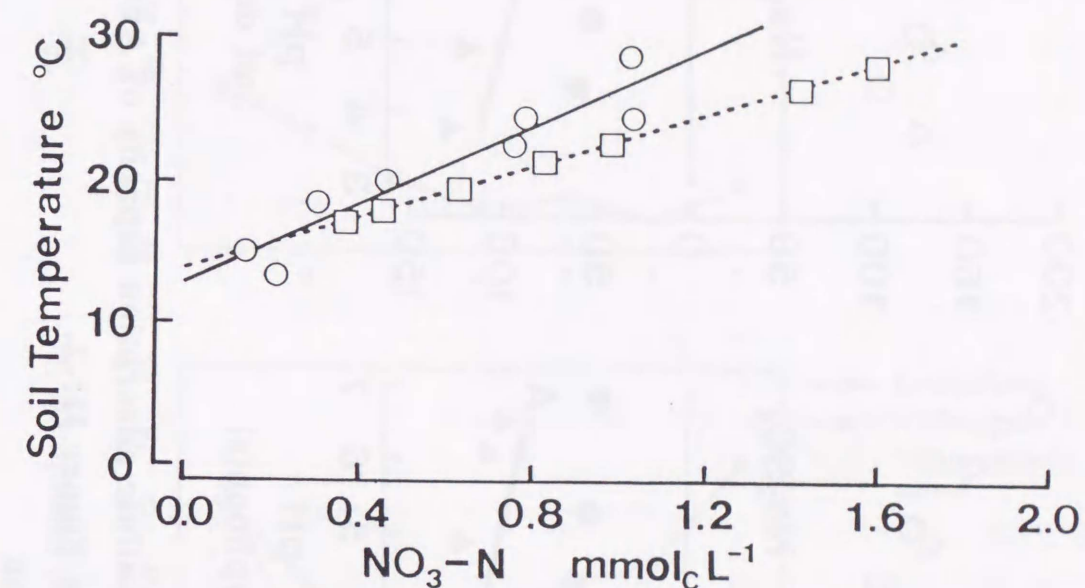

Figure III-13: Relationships between nitrate concentrations in soil solutions and soil temperature at the 10 cm soil depth.
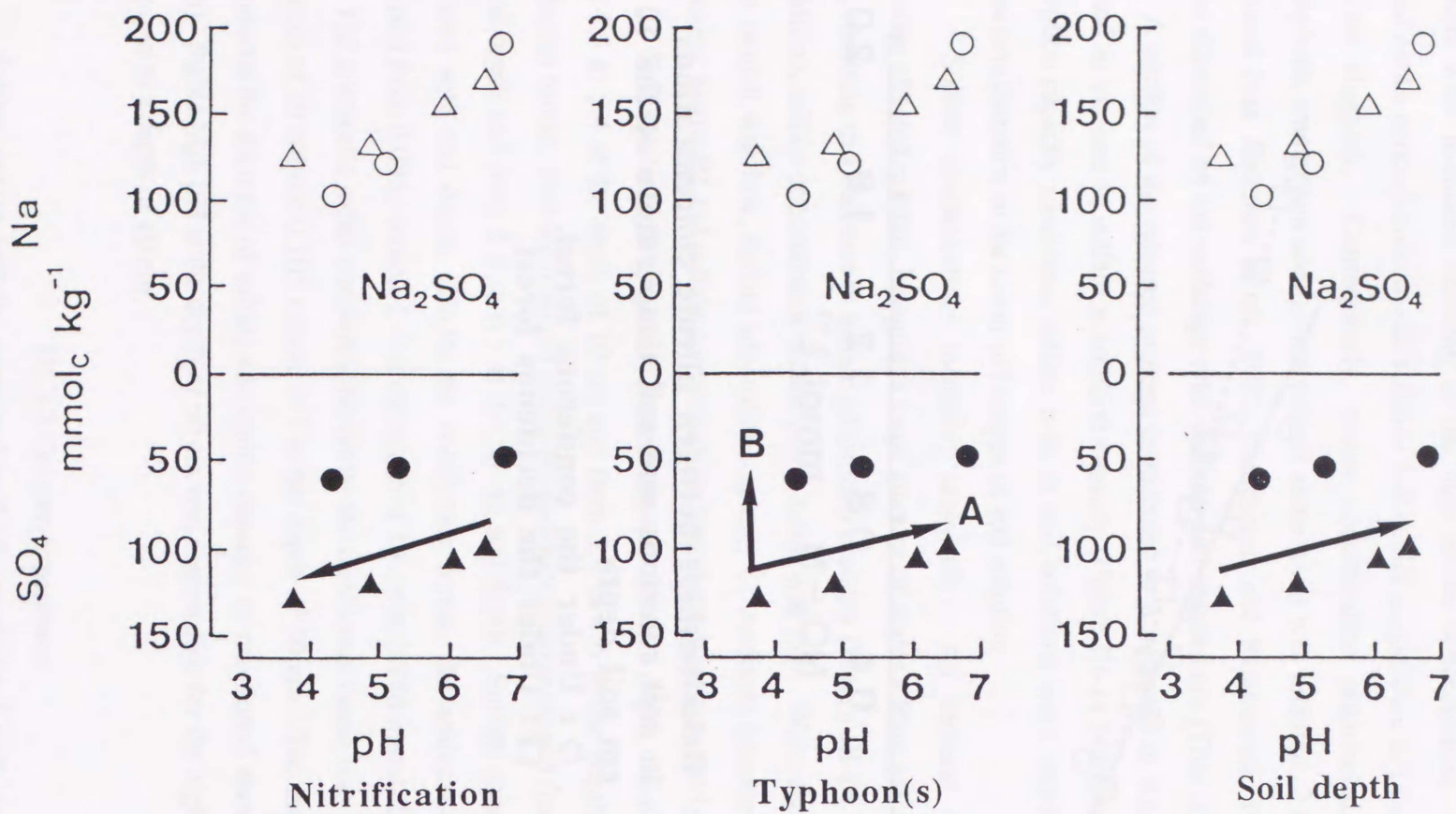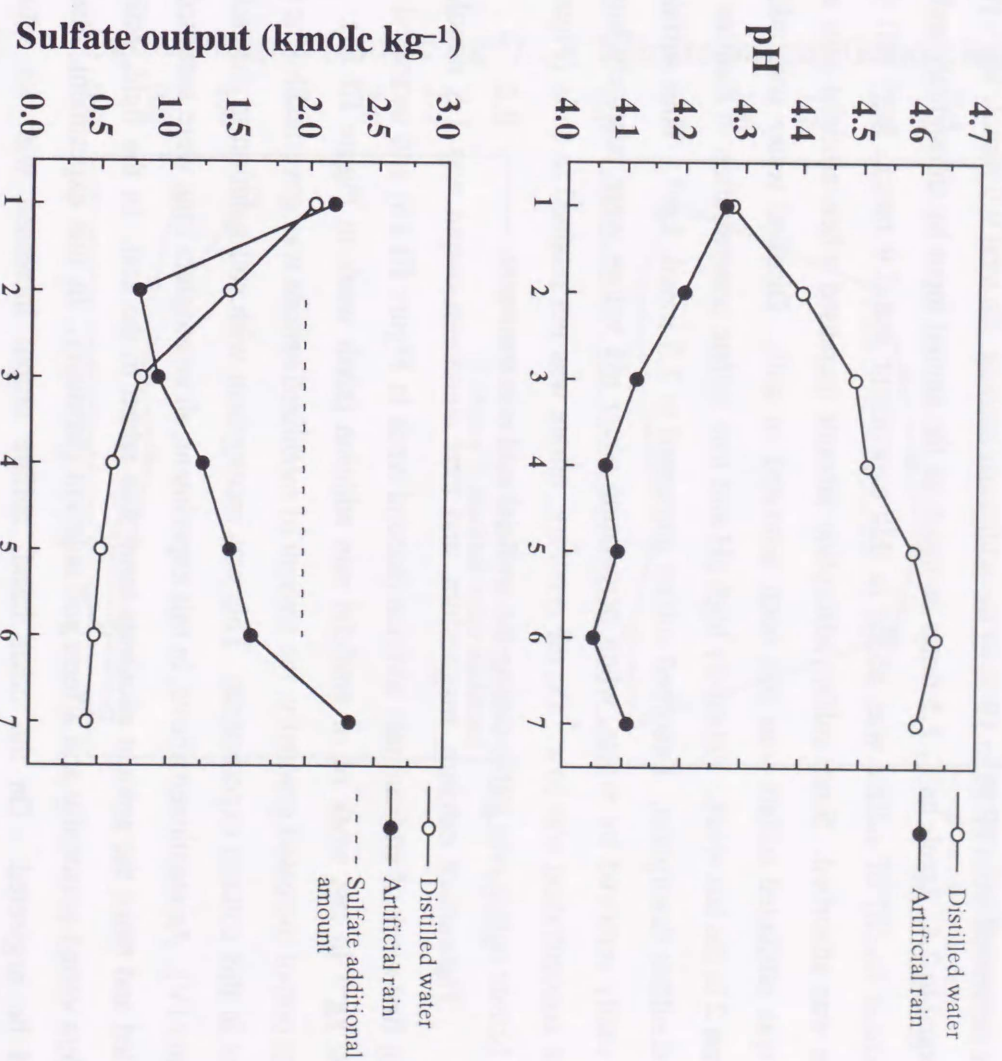○ : Under the coniferous forest.
□ : Under the deciduous forest.

Figure III-14: Various factors to change sulfate adsorption capacity of Andisols.
This figure is arranged from Figure III-2.

○ ● : 0.02 M Na₂SO₄ solution

△ ▲ : 0.1 M Na₂SO₄ solution

Figure III-15: Changes in sulfate outputs from columns and pH values of leachates.

leached from column 1. The total sulfate output from column 1 reached 6.24 mmolc kg^{-1}. When the artificial acid rain was added to Andisols taken from RLL, adsorbed amounts of sulfate decreased from 60 % to 19 % of the additional amount. In total 9.9 mmolc kg^{-1} (which was equal to 2.42 kmolc ha^{-1}, 1.5 times as much as the annual input by throughfall under the coniferous forest) of sulfate was added in this experiment and 3.9 mmolc kg^{-1} (40 %) of sulfate was adsorbed. Since sulfate adsorption amount increased when artificial rain added. This was attributed sulfate ions has been saturated in soil. Distilled water was added to Column 2 in the last week. Relatively high pH and low sulfate concentration in distilled water caused sulfate desorption. Desorbed sulfate amounted to 2.3 mmolc kg^{-1}. Thus sulfate ions were easily removed by water, when percolating water pH values were relatively high and sulfate concentration was low. On the contrary, nitrate was not retained in soils (Figure III-16). Nitrate output was stable during the artificial acid rain treatment.

The sum of calcium, magnesium, and total aluminum output was 1.8 mmolc kg^{-1} during first week of artificial rain addition (second week in Figure III-16) and increased to 2.4 mmolc kg^{-1} in last week of of artificial rain addition (sixth week in Figure III-16). Since sulfate output increased gradually, the amount of mobilized cations was governed by the sulfate output in this column experiments. This was incongruent with soil solution in the field (see Chapter IV). As mentioned above, in this experiment, all ammonium ions were assumed to be nitrified and twice the amount of nitrate input was added to the soil. In the field, activity of nitrifers varied seasonally and affects soil solution chemistry. In this experiment, this effect could be neglected. On the other hand, sulfate output increased with its saturation. Consequently, cation output increased with increase in sulfate output.

Johnson *et al.* (1986) revealed that Inceptisols adsorbed more sulfate than Ultisols because of greater amorphous (oxalate extractable) iron (Fe) and aluminum (Al). Karltun and Gustafsson (1993) also showed high correlation between sulfate adsorption amounts and amorphous (oxalate extractable – pyrophosphate extractable) Fe and Al. They also found that as the proportion of organically complexed Fe and Al increases, the sulfate adsorption ability of soils decreased. Johnson and Todd (1983) pointed out that organic matter had a decidedly negative influence upon sulfate adsorption. In addition, Johnson and Todd (1983) and Merino *et al.* (1994) exhibited the correlation between crystalline Fe and sulfate adsorption amounts.

Fumoto *et al.* (1996) revealed correlation between adsorbed sulfate amounts and amorphous (oxalate extractable – pyrophosphate extractable) Al in several Andisols in Japan. As discussed in Chapter V, Andisols at RLL contained large amounts of amorphous Al. However, this fraction depleted at most acidified points. Depletion of amorphous Al decreases
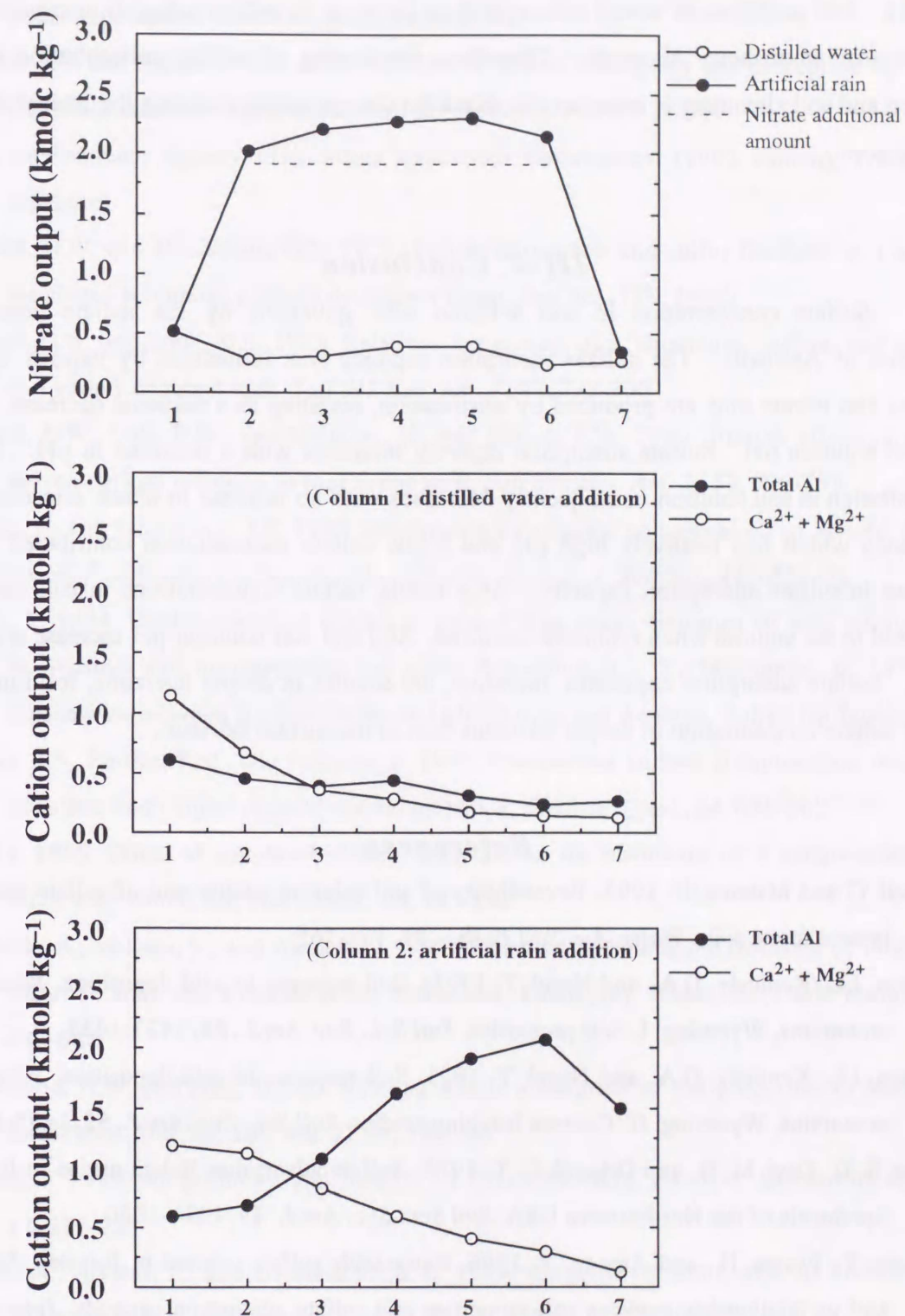

Figure III-16:
Changes in nitrate and cation outputs from columns .

in sulfate retention ability. On the other hand, sulfate adsorption capacity increases at relatively low pH. Soil acidification would induce both an increase in sulfate adsorption capacity and depletion of amorphous Al pools. Therefore, monitoring of sulfate concentration in soil solution and soil chemistry is necessary to detect the change and to elucidate the interrelation of both factors.

III-4 Conclusion

Sulfate concentration in soil solution was governed by the sulfate adsorption capacities of Andisols. The sulfate adsorption capacity was influenced by various factors. Protons and nitrate ions are produced by nitrification, resulting in a seasonal decrease in soil and soil solution pH. Sulfate adsorption capacity increases with a decrease in pH. Sulfate concentration in soil solution consequently decreases with an increase in nitrate concentration. Typhoons which had relatively high pH and a low sulfate concentration contributed to the decrease in sulfate adsorption capacity. As a result, sulfate concentrations in soil solutions increased in the autumn when typhoons occurred. Soil and soil solution pH increase with soil depth. Sulfate adsorption capacities, therefore, are smaller in deeper horizons, resulting in a higher sulfate concentration in deeper horizons than in the surface horizon.

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Chapter IV

Spatial Variability of Soil Acidification

Abstract

A monitoring study on precipitation and soil solution was conducted to analyse soil acidification processes at the Rolling Land Laboratory (RLL), Hachioji, Tokyo based on the spatial variability of the soil solution chemistry around the Hinoki cypress (*Chamaecyparis obtusa*) trunk. Soil solution samples were taken at various distances from the tree trunks and at various depths. Soil solution pH at the depth of 10 cm decreased to 4.1-4.2 on the downslope side of large tree trunks, presumably due to heterogeneity of throughfall input and infiltration of acidic stemflow. Ammonium ions brought by throughfall and stemflow were nitrified and provided large amounts of H^+. Protons were replaced with exchangeable cations. When base cations were depleted, aluminum ion became the dominant cation species. On the average, Ca^{2+} concentration in the soil solutions at the depth of 10 cm decreased from 0.28 mmolc L^{-1} at the reference site to 0.18 mmolc L^{-1} on the downslope side and Mg^{2+} concentration decreased from 0.30 mmolc L^{-1} to 0.15 mmolc L^{-1}. Arithmetic mean aluminum concentration at the depth of 10 cm on the downslope side was 0.35 mmolc L^{-1}. Here aluminum dissolution was the main acid sink. Based on the spatial variability of the soil solution chemistry, soil solution acidification processes were divided into four stages.

IV-1 Introduction

The soils in areas where forest ecosystems have been affected by acidic deposition have developed on alluvial sediments, glacial till, sandstone and granite (Krahl-Urban et al., 1988; Cerny and Paces, 1995: See Table I-1). These soils are poor in base cations and display a limited acid neutralizing capacity (ANC) (van Breemen et al., 1983). Soil acidification (decrease in ANC) is considered to be an indirect cause of forest decline (e.g. Krahl-Urban et al., 1988; Heij et al., 1991; Matzner and Murach, 1995). For example, yellowing of spruce needles was attributed to magnesium deficiency due to the depletion of magnesium in the soil profiles. Acidic deposition promotes soil acidification and induces aluminum dissolution. Aluminum would adversely affects biota (Foy *et al.*, 1978; Cleveland *et al.*, 1989; Parker *et al.*, 1989; Godbold, 1994). The decline in freshwater organisms has been related to increased water acidity in combination with increased concentrations of toxic aluminum species in the water (Abrahamsen *et al.*, 1989). It has been suggested that the uptake of aluminum from drinking water may cause dementia as a result of accumulation of aluminum in the brain (McLachlan, 1989; Kuroda, 1992; Kuroda, 1998).

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Based on laboratory experiments, Andisols exhibit a larger acid neutralizing capacity than Dystrochrepts and Hapludults (Okazaki, 1990; Oba, 1990) and show a relatively high tolerance to acid substances (Japan Environment Agency and Japanese Society of Soil Science and Plant Nutrition, 1983), due to the presence of allophane and a high organic matter content (Ishizuka et al., 1990). However, a larger amount of aluminum can be dissolved from Andisols, rich in allophane and imogolite, than from soils consisting of crystalline clay minerals at low pH (Shioiri, 1952; Oba, 1990). Based on an equilibrium study in the pH range of 3.5-4.5, Takahashi et al. (1995) estimated that the dissolved aluminum was derived from both organically bound aluminum fractions (ca. 20 % of total dissolved aluminum) and amorphous aluminum fractions (80%) of allophanic Andisols.

Kato and Shirai (1995) studied the acidification of Andisols around the tree trunk base of Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) in Tochigi Prefecture, northern Kanto. Soil acidification around the tree trunks had been reported in various other study areas (Table IV-1). Wolfe et al. (1987) investigated soils around tree trunks in which different amounts of atmospheric sulfur has been deposited and showed that soils around the trunk base which were exposed to a higher sulfur input were more acidified than those with less exposure. These studies indicate that the estimation of soil acidification around the trunk base is a suitable method for evaluating the effects of atmospheric deposition and estimating acidification processes based on field conditions.

Baba et al. (1995a) observed acidified soil around the Hinoki cypress trunk at the Rolling Land Laboratory (RLL), Tokyo University of Agriculture and Technology, Hachioji, Tokyo, southern Kanto. The soil solution, rather than soil itself, was a more suitable indicator for predicting subtle changes in soil acidification, especially when the soils displayed a high tolerance to acids like Andisols (Baba et al., 1995a). In fact, nitrate was the dominant anion in soil solution at all the depths and affected cation concentration (Baba et al., 1995a: Figure IV-1). Calcium and magnesium were usually codominant cations. When nitrate concentration markedly increased, aluminum was dissolved into soil solutions in surface layers under a mixed coniferous forest at RLL (Figure IV-2).

In this study, the spatial variability of soil solution chemistry was emphasized for interpreting the stages of acidification. The causes of variability were examined based on a long-term monitoring study with simultaneous analysis of throughfall, stemflow and soil solutions.

Table IV-1: Studies on spatial variability of soils and soil solutions.

Site	Soil type	Vegetation	Characteristics which were spatially varied	Reference
Yaroslavl' Oblast, Russia	Strongly podzolic	Spruce	litter and soil at the distal point was acidified	1
	Weakly podzolic	Birch	litter and soil at the distal point was acidified	1
	Podzol	Pine	litter and soil at the proximal point was acidified	1
Moscow Oblast, Russia	Weakly podzolic	Pine	litter and soil at the proximal point was acidified	1
	Strongly podzolic	Birch	litter and soil at the proximal point was acidified	1
	Weakly podzolic	Mountain ash	litter and soil at the proximal point was acidified	1
	Weakly podzolic	Basswood	litter at the proximal point was acidified	1
Skåne, Sweden	Podzolic soils	Beech	Soils at the proximal point were acidified	2
		-Grey-brown forest soils	organic matter content, Al, Ca, Mg, Mn, Base saturation	
Solling, Germany	Dystric Cambisols	Beech	Soils at the proximal point were acidified, Ca, Mg, K, Al	3
		Spruce	Ca, K, NH_4, NO_3 concentration in soil solutions	3
Fichtelgebirge, Germany	Cambisols - Cambic Podzols	Norway spruce	NH_4 and SO_4 content in forest floor	4
Gottinger Wald, Germany	Terrafusca	Beech	pH (H_2O) and pH (KCl)	5
Klosterhede, Denmark	Typic Haplorthod	Norway spruce	Sulfate concentration in soil solutions	6
Northwestern Yugoslavia	Terrafusca - Rendzina		Soils at the proximal point were acidified	7
	Brown forest soils		Ca, Mg, K, Base saturation, Al, saturation of (H+Fe)	
Camp branch, TN	Typic Hapludults	Scarlet oak	Soil at the distal point was acidified	8
		Red maple	Soil at the distal point was acidified	8
			No distance-related effect on SO_4-S	8

Table IV-1 (*Continued*)

Cross Creek, TN	Typic Hapludults	Scarlet oak	Soils at the <u>proximal</u> point were acidified	8
		Red maple	Soils at the <u>proximal</u> point were acidified	8
Tuscarawas Country, OH		Beech	[137]Cs	9
Blacklick Woods, OH		American beech	Radioisotopes	10
Krantz Woods, OH		American beech	Radioisotopes	10
Blacklick Woods, OH		American beech	Soils at the <u>proximal</u> point were acidified, organic carbon,	11
		Sugar maple	Ca, Mg, K, [137]Cs	
		Red oak		
Krantz Woods, OH		American beech	Soils at the <u>proximal</u> point were acidified, organic carbon,	11
			Ca, Mg, K, [137]Cs	
		Pignut hickory	Ca, [137]Cs	11
		White oak	Organic carbon, Ca	11
Recknagel Memorial	Lithic Dystrochrept	Red pine	Soils at the <u>proximal</u> point were acidified	12
	Management Forest			
Kanto district, Japan		Japanese ceder	Soils at the <u>proximal</u> point were acidified	13
Shioya, Tochigi, Japan	Andisols	Japanese ceder	Soils at the <u>proximal</u> point were acidified, Mg, Al	14
		Hinoki cypress	Soils at the <u>proximal</u> point were slightly acidified	14
Leimigrain, Germany		Beech	Distribution of acid indicator plant at forest floor	15

1: Mina, 1967, 2: Falkengren-Grerup, 1989, 3: Koch and Matzner, 1993, 4: Seiler and Matzner, 1995, 5: Ulrich, 1983, 6, Beier et al., 1992, 7: Jochheim and Schafer, 1988, 8: Wolfe et al., 1987, 9: Franklin et al., 1967, 10: Gersper, 1970, 11: Gersper and Holowaychuk, 1971, 12: Pallant and Riha, 1990, 13: Matsuura, 1992, 14: Kato and Shirai, 1995, 15: Wittig and Neite, 1985
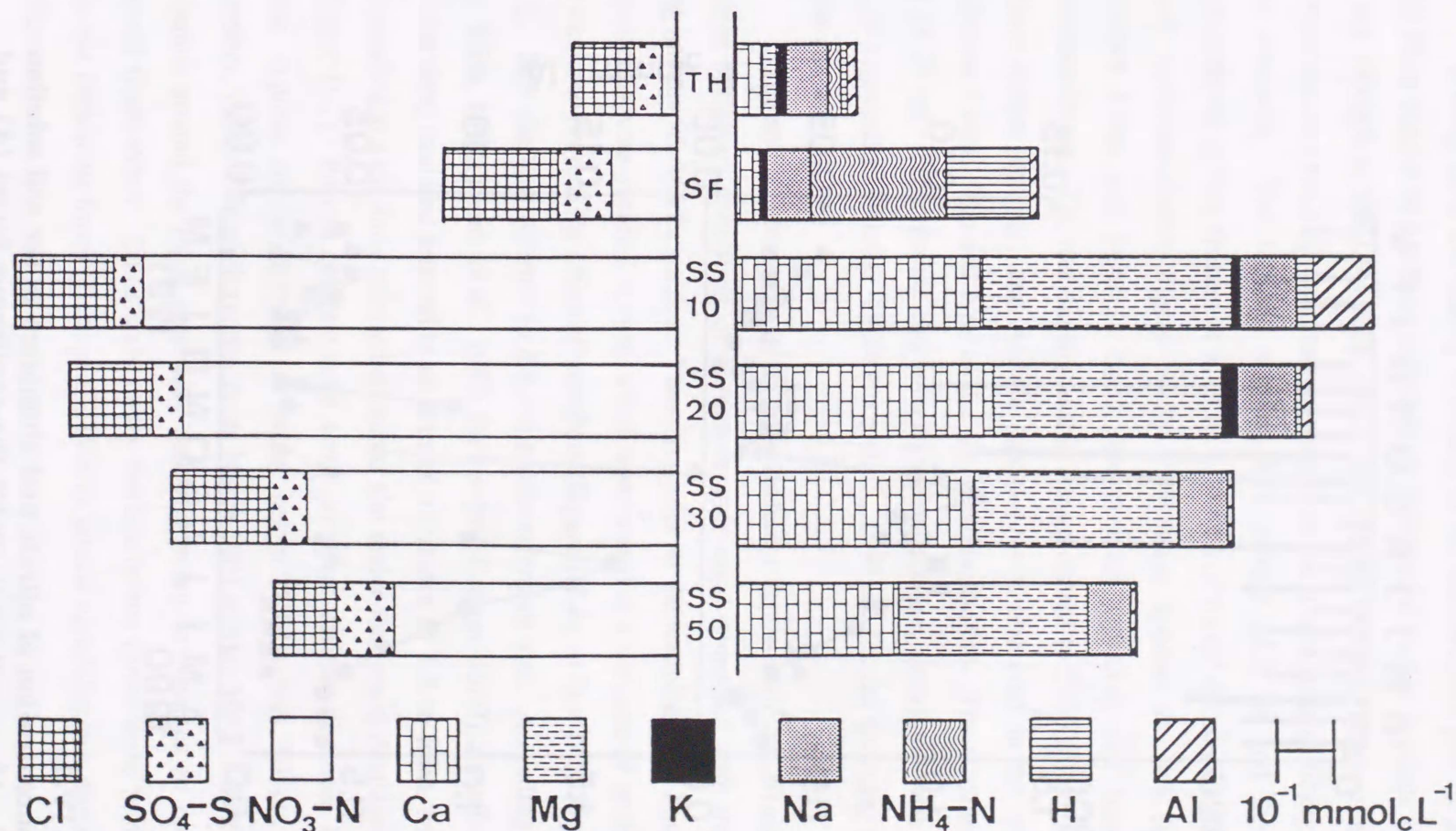
Figure IV-1: Elemental composition of throughfall, stemflow and soil solutions during 17-29 September 1990. TH: Throughfall; SF: Stemflow; SS10: Soil solution at the 10 cm soil depth; SS20: Soil solution at the 20 cm soil depth; SS30: Soil solution at the 30 cm soil depth; SS50: Soil solution at the 50 cm soil depth.
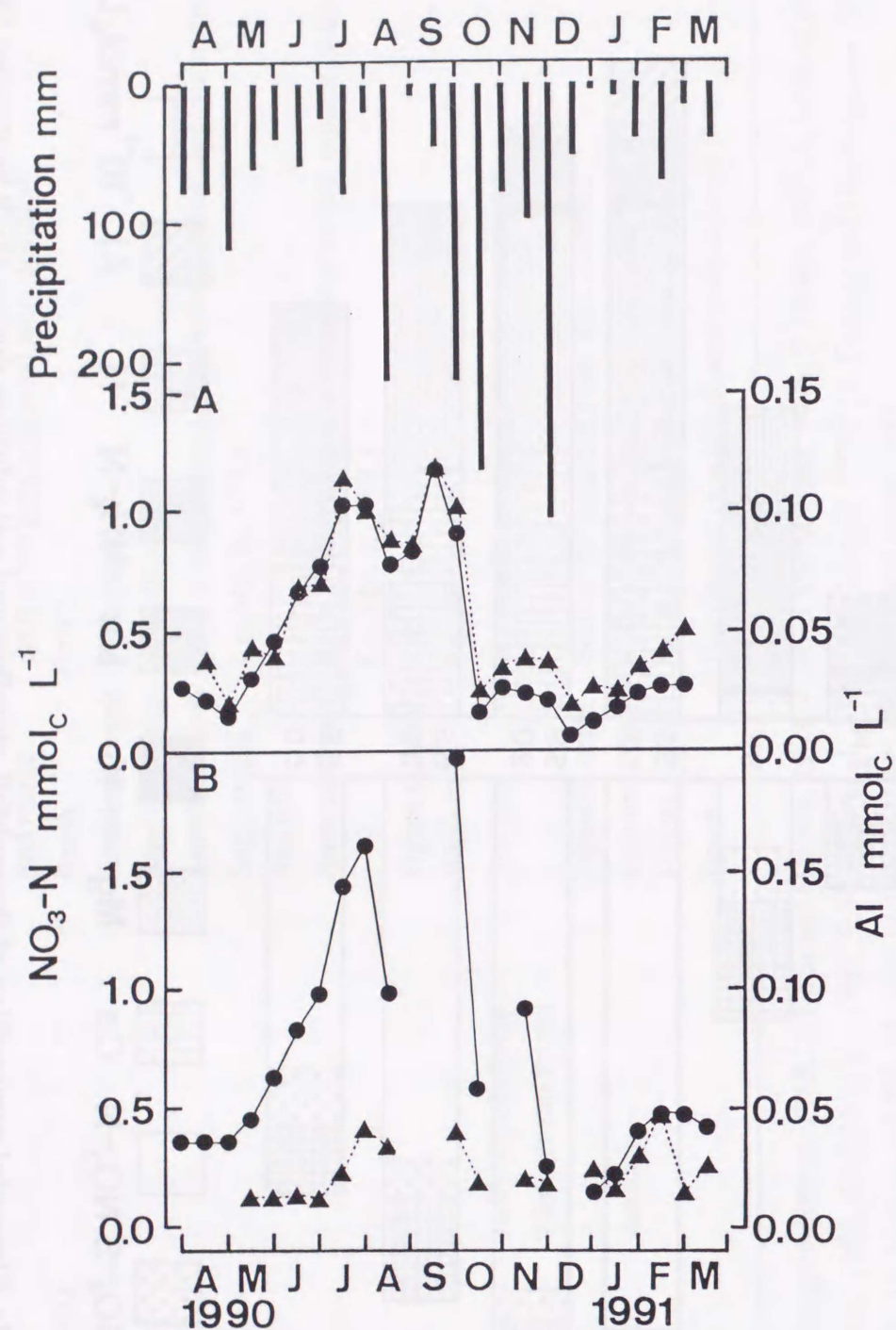
Figure IV-2:
The concentration of nitrate and aluminum in the soil solution from the 10 cm soil depth under the coniferous forest (A) and the deciduous forest (B). ▲: Aluminum; ●:Nitrate.

IV-2 Materials and Methods

Rolling Land Laboratory is located in the northwestern part of the Tama Hills. The Tama Hills consist of a terrace underlain by interglacial marine deposits which emerged from the sea 300,000 to 500,000 years ago. The aeolian volcanic ashes from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji had been deposited on the Tama Hills resulting in the formation of thick Andisols. The forested area of RLL covers 11.3 ha and the studied catchment (Nishinosawa) covers an area of 2.15 ha (1.55 ha of mixed deciduous forest and 0.60 ha of mixed coniferous forest: Figure IV-3). The major species are oak (*Quercus serrata*) in deciduous forest and Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress in the coniferous forest. The tree density at this site amounted to 2500 trunks ha^{-1}. *Dendropanax trifidus*, *Eurya japonica*, and *Ardisia japonica* were observed in the same area under the coniferous forest. The soil type of the site was Hapludand. The thickness of the A horizon was 15-25 cm. Predominant clay mineral was allophane, associated with halloysite (0.7 nm) and Al-vermiculite (Okazaki, 1989; Baba et al., 1995a). On the average, the slope inclination of this site was 20°.

The soil solution was taken from different depths (10, 20, 30 and 50 cm) with soil solution extractors consisting of porous ceramic cups connected with vacuum glass bottles using initially 85-95 kPa suction. Two days prior to the sampling, the bottles were deaerated. Porous cups were installed at a site which was located at a distance of at least 1.5 m from any tree trunks to prevent the effect of stemflow (Figure IV-4a, at Plot II in Figure IV-3 [or Figure II-1]). This site was referred to the coniferous reference site. According to previous studies (e.g. Mina, 1967; Wolfe et al., 1987; Falkengren-Grerup, 1989), no effects of stemflow on soil chemistry could be detected in an area of a distance of 1.5 m from the trunk. Cups were also installed at a similarly selected reference site under the mixed deciduous forest (at Plot III in Figure II-1). Porous ceramic cups were set up at various distances from the trunk of a Hinoki cypress whose diameter at breast height (DBH) was 30 cm (Figure IV-4b) in December, 1990. During the period from March 1991 to May 1992, a single sample at each of the points around the trunk base was collected every two weeks in order to examine the seasonal fluctuations. Since soils under the coniferous forest were more acidic than those under the deciduous forest (Baba et al., 1995a), spatial variability was examined only under the coniferous forest.

During the period from March 15, 1995 to March 15, 1996, soil solutions were sampled in triplicate (Table IV-2). Three large trunks (30 cm in DBH) and three small trunks (20 cm in DBH) were selected for replication. One of the large trunks was the same as that

○ Open bulk precipitation
● Throughfall
■ Stemflow
▼ Weir
□ Soil Solution
▧ Spatial variability site

0   50 m

Figure IV-3: The topographical map of Nishinosawa catchment.
The broken line represents boundary of catchment.
The area enclosed by dotted line represents coniferous forests.

Figure IV-4 Sampling site for soil solutions. a: Reference site, b: Spatial variability site.

Table IV-2 Sampling reprication of soil solutions.

Soil depth	D*1-0.5 m L*5	S*6	D-1.0 m L	S	D-1.7 m L	S	L*2-0.5 m L	S	R*3-0.5 m L	S	R-0.0 m L	S	U*4-0.5 m L	S	Coni*7	Deci*8
1991-1992																
10 cm	1		1		1		1		1		1		1		1	1
20 cm	1		1												1	1
30 cm															1	1
50 cm															1	
1995-1996																
10 cm	3	3	3	3	3	3									3	
20 cm	3	3	3	3	3	3									3	
30 cm	3		3		3											
50 cm	3		3		3										3	

Figures in this table denote the number of sampling replications.
*1: D; Downslope side. *2: L; Left side. *3: R; Right side, *4: U; Upslope side, *5: L; Large tree trunk, *6: S; Small tree trunnk.
*7: Coni; Under the coniferous forest, *8: Deci; Under the deciduous forest,

around which soil solutions were taken in 1991-1992. Trees which were not suppressed by neighboring tree crowns were chosen. This criterion was also applied when throughfall or stemflow collectors were installed. Ceramic cups were set up on the downslope side of these trunks in January, 1995. Three reference sites were also selected and porous cups were installed. One of these sites was the same as that used as the coniferous reference site in 1991-1992. Soil solutions were sampled for two weeks once each month, so that the extractors were sufficiently depressurized to obtain adequate samples. The vacuum was then released for two weeks.

Sampling point codes were used for the soil solution around the tree trunks. The first letter of the soil solution sampling point code indicates the trunk size (L: Large, S: Small). The second letter indicates the direction (D: Downslope side of the trunk, U: Upslope side of the trunk, L: Left side of the trunk facing the upslope side, R: Right side of the trunk facing the upslope side, Figure IV-4b). The following two digits indicate the distances (in dm) from the trunk and the last two digits indicate the soil depth (in cm).

Throughfall or stemflow collectors were installed near the soil solution sampling site. Throughfall samples were collected using 200 cm^2 polyethylene funnels with 5 L glass bottles under both the coniferous and deciduous forests in 1991-1992. However, throughfall samples were collected only under the coniferous forest using 10 L polyethylene bottles in 1995-1996. Throughfall collectors were installed at a distance of 0.5 m (proximal point) and 1.5 m (distal point) from the tree trunks under the coniferous forest. Stemflow samples of Hinoki cypress and oak were collected through glued vinyl tubes (28 mm in diameter) forming a rolling spiral using 20 L polyethylene collection vessels in 1991-1992. Only the stemflow of Hinoki cypress was collected using 200 L vessels in 1995-1996. Samples were collected at least once every two weeks in 1991-1992 and once a month in 1995-1996. Throughfall and stemflow samples were collected singly in 1991-1992 and in duplicate in 1995-1996.

After collection, the samples were analyzed for the pH and electric conductivity. Subsequently, rain water samples (Open-bulk precipitation, throughfall, and stemflow) were filtered using membrane filters (Millipore mixed cellulose ester 0.45 μm in pore size), stored at −20 °C and analyzed for the concentration of nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-) by ion chromatography (Yokogawa, IC 200 Ion Chromatographic Analyzer); for the concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+) and total-aluminum by atomic absorption spectrophotometry (Shimadzu, 670/AA Atomic Absorption Spectrophotometer); and for the concentration of ammonium (NH_4^+) by colorimetry (Shimadzu, Spectrophotometer UV-140-01) using the indophenol-blue method. All the

samples were concentrated by heating under acidic conditions prior to aluminum analysis because of the low concentrations. Aluminum concentration was calculated as Al^{3+}.

The factors related to soil solution acidification such as tree size, distance from the tree trunks, and soil depth were analysed by t-test using data in 1995-1996. The differences between soil solutions around trunks and reference sites were also examined. The arithmetic mean concentration during March to October was used because it was not possible to collect a sufficient number of samples due to the occurrence of drought from November to March in the following year. The heterogeneity of the annual throughfall fluxes, however, was examined.

IV-3 Results

IV-3-1. Spatial variability of soil solution pH in relation to stemflow and throughfall chemistry

Soil solution pH values at the depths of 10 and 20 cm in the LD-plots (downslope side of large Hinoki cypress trunks) were about 0.2-0.9 pH units lower than those of the SD-plots (downslope side of small cypress trunks) (Table IV-3). It was assumed that larger amounts of stemflow had infiltrated around the trunk base of larger cypresses than that of smaller cypresses. In fact, the amount of stemflow of the larger trunk was on the average 1.2 times as much as that of the smaller trunk. The pH values at the depth of 10 cm of the LD-plots were similar to each other, regardless of the distance from the tree trunk. On the other hand, at the depth of 20 cm in the LD-plots, there was an obvious tendency for the pH to significantly decrease as one approached the trunk. In the case of the SD-plots, only samples taken at a depth of 10 cm and less than 1 m from the trunk showed a decrease in pH. Soil solution pH values at SD1710, SD0520, and SD1020 were similar to the pH values at the corresponding depth of the reference sites. The pH values increased with the soil depth and reached a neutral range at the depth of 50 cm. The values at the depth of 50 cm in the LD and SD plots except at LD0550 were higher than those at the corresponding depths of the reference sites.

Around the tree trunk bases, stemflow chemistry markedly affected the soil and soil solution chemistry. The pH values of the coniferous stemflow fluctuated between 3.1-4.3 (see Figure II-5). Weighted mean pH values of the stemflow which were 3.9 in 1991-1992 and 3.8 in 1995-1996, were 0.7-0.9 pH units lower than those of the coniferous throughfall at the distal point (4.8 in 1991-1992 and 4.5 in 1995-1996). Weighted mean proton concentration in Hinoki cypress stemflow was very high, 0.208 mmole L^{-1} (Figure IV-5). Since ammonium

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Table IV-3 Arithmetic mean pH of soil solution on the downslope side from March to October in 1995.

Depth	Distance from the trunk Large (LD-plots)			Small (SD-plots)			Reference site	
	0.5 m	1.0 m	1.7 m	0.5m	1.0m	1.7 m	1.7 m	
10 cm	4.09**S,***R,*2,*5	4.15**S,***R,*2,**5	4.15***S,**R,*2,**5	4.34*0,***7,**R,***2,***5	4.48*7,**2,***5	4.63*2,***5	4.60*2,***5	
20 cm	4.18***S,**0,***7,*R,*5	4.46*S,**R,**5	4.54*S,*R,**5	4.93***5	4.97***5	5.41*R,*5	4.89***5	
50 cm	5.52*0,*7	6.70*7,*R	6.42*R	6.60*R	6.77**R	6.59***R	5.96	

*: p < 0.05; **: p < 0.01, ***: p < 0.001.
S: Different from corresponding point around small tree trunk.   R: Different from the Reference site.
0: Different from soil solution at the same depth, 1.0 m distance from the same size trunk.
7: Different from soil solution at the same depth, 1.7 m distance from the same size trunk.
2: Different from soil solution at the depth of 20 cm, with the same distance from the same size trunk.
5: Different from soil solution at the depth of 50 cm, with the same distance from the same size trunk.
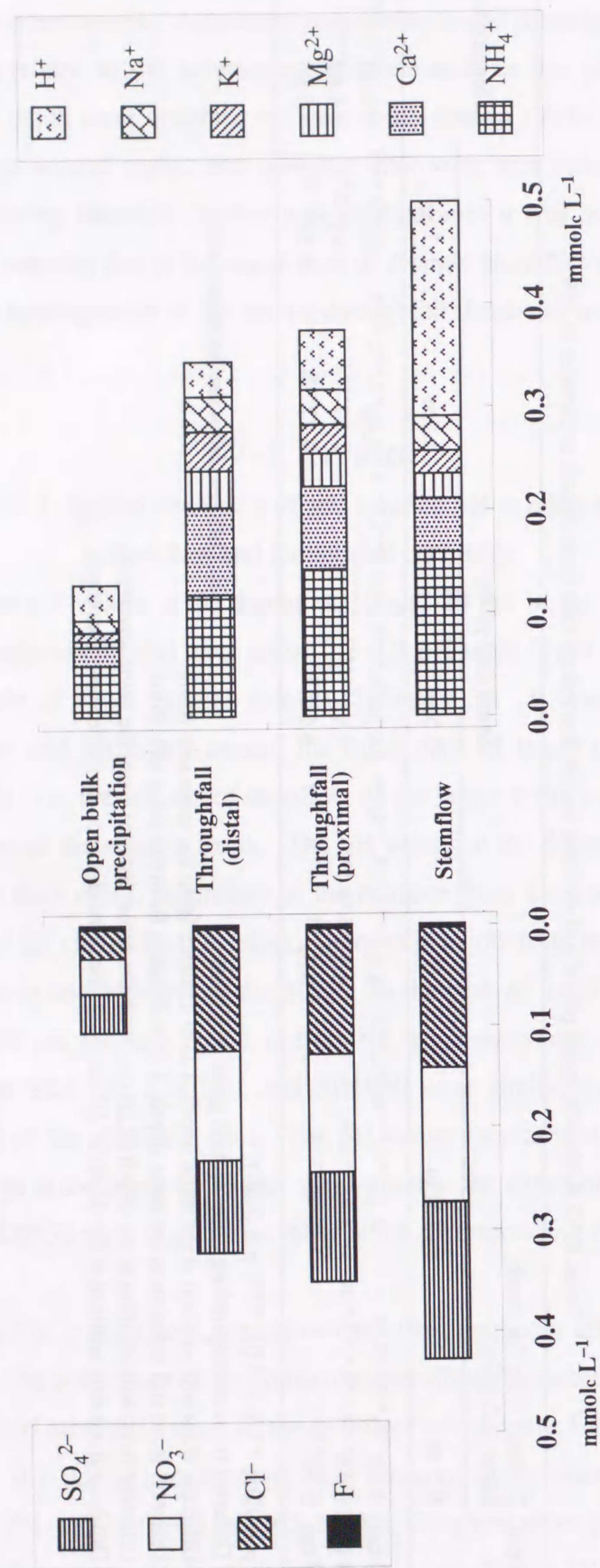
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Figure IV-5 Composition of open-bulk precipitation, throughfall, and stemflow at RLL.

ions act as an acid source in the soil profile, they could be considered to be acidic substances. Ammonium concentration showed the highest value in the stemflow, 0.158 mmolc L^{-1}. By contrast, base cation concentrations in the stemflow were lower than those in the coniferous throughfall. Proton and ammonium concentrations in the oak stemflow in 1991-1992 were 0.00977 mmolc L^{-1} and 0.0272 mmolc L^{-1}, respectively. These concentrations were slightly higher than those in the deciduous throughfall. Conversely, base cation concentration in the oak stemflow increased by factors of 1.1-2.9, compared with the deciduous throughfall. The sum of the percentage of proton and ammonium concentration in Hinoki cypress stemflow accounted for 73 % of the total cation concentration, while 16 % in the case of oak stemflow. Hinoki cypress stemflows were characterized by high proton and ammonium concentrations, which promoted acidification around the tree trunk base.

Proton and ammonium concentrations in the throughfall at the proximal points were higher than those in the throughfall at the distal points and open bulk precipitation (Figure IV-5). Heterogeneity of acidic substance input associated with coniferous throughfall (Table IV-4) was consistent with the spatial variability of the soil solution pH. Proton, nitrate, sulfate, and ammonium inputs at proximal points exceeded those at distal points. Proton input at proximal points was twice as high as that at distal points. Conversely, Ca^{2+} and Mg^{2+} inputs were similar to those at the distal points. Potassium input at proximal points was 80 % of that at the distal points.

IV-3-2. Changes in Soil Solution Composition

At all the sampling points, nitrate was the dominant anion in 1991-1992 (Figure IV-6), although soil solution data taken at deeper depths at the reference site are not shown. Nitrate concentration increased during the summer months (0.97 mmolc L^{-1} in maximum at LD-0510). Immediately after the decrease in autumn, the nitrate concentration in the soil solution at the depth of 10 cm increased again from winter to spring. On the other hand, at the depth of 20 cm, sulfate ion became the dominant anion from October to March. Both protons and nitrate ions were produced through nitrification. Soil solution pH values were inversely correlated with the nitrate concentration (r = −0.846 to −0.957; p < 0.001: Table IV-5), which implies that nitrification provided large amounts of H$^+$. Sulfate concentration was inversely proportional to the nitrate concentration (Table IV-5). Sulfate concentration in the soil solution increased when the nitrate concentration decreased (Figure IV-6). Sulfate concentration was positively correlated with the soil solution pH (Table IV-6). At LR0010, the sulfate concentration, however, was inversely proportional to the pH levels. Stemflow composition
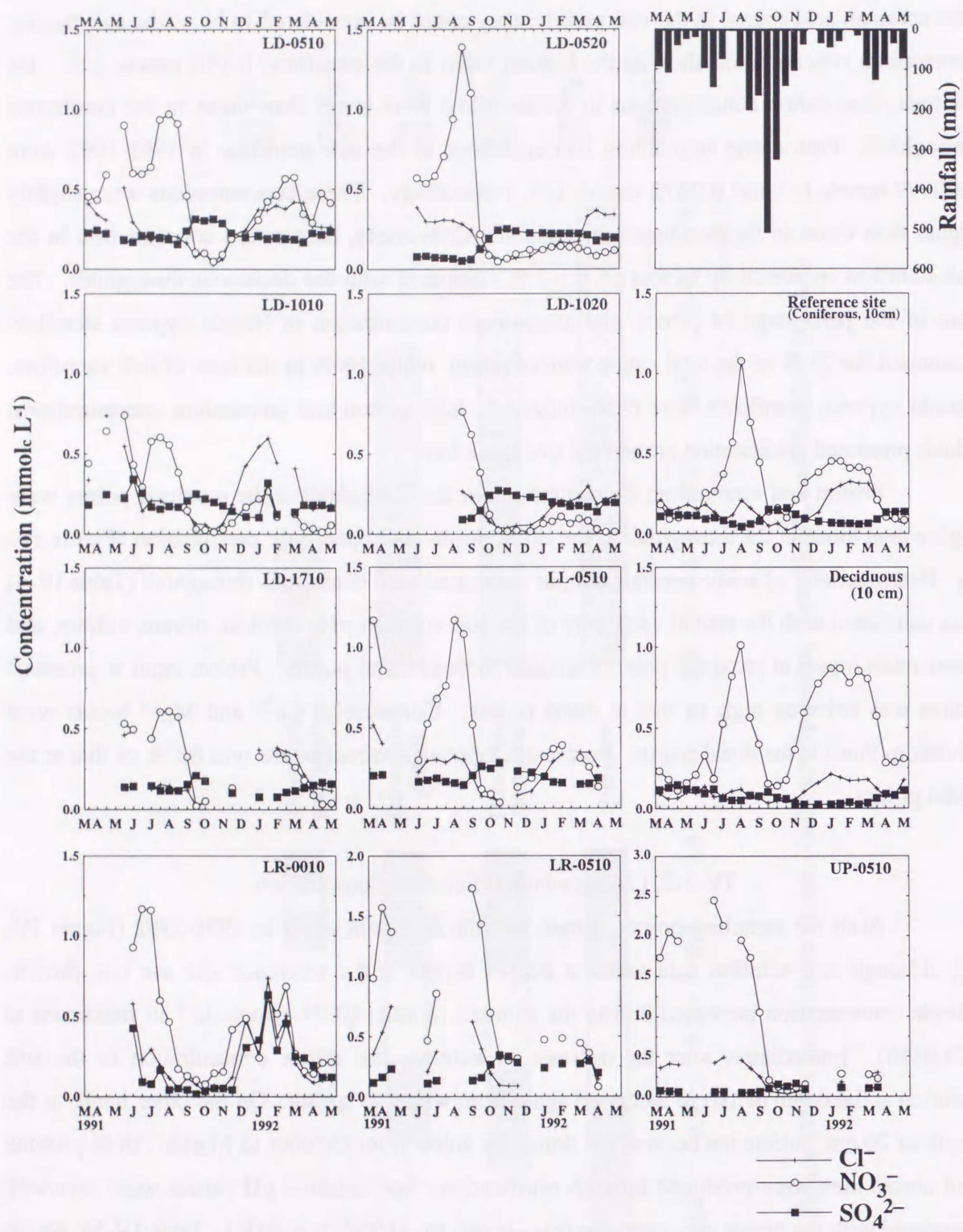
Figure IV-6:
Changes in chloride, sulfate, and nitrate concentrations in soil solutions.
Legend of points around the Hinoki cypress trunks was shown in Figure IV-4.
The first letter is the tree trunk size.
The second letter is the direction of transects.
The following two digits are distances from the trunk bases (dm).
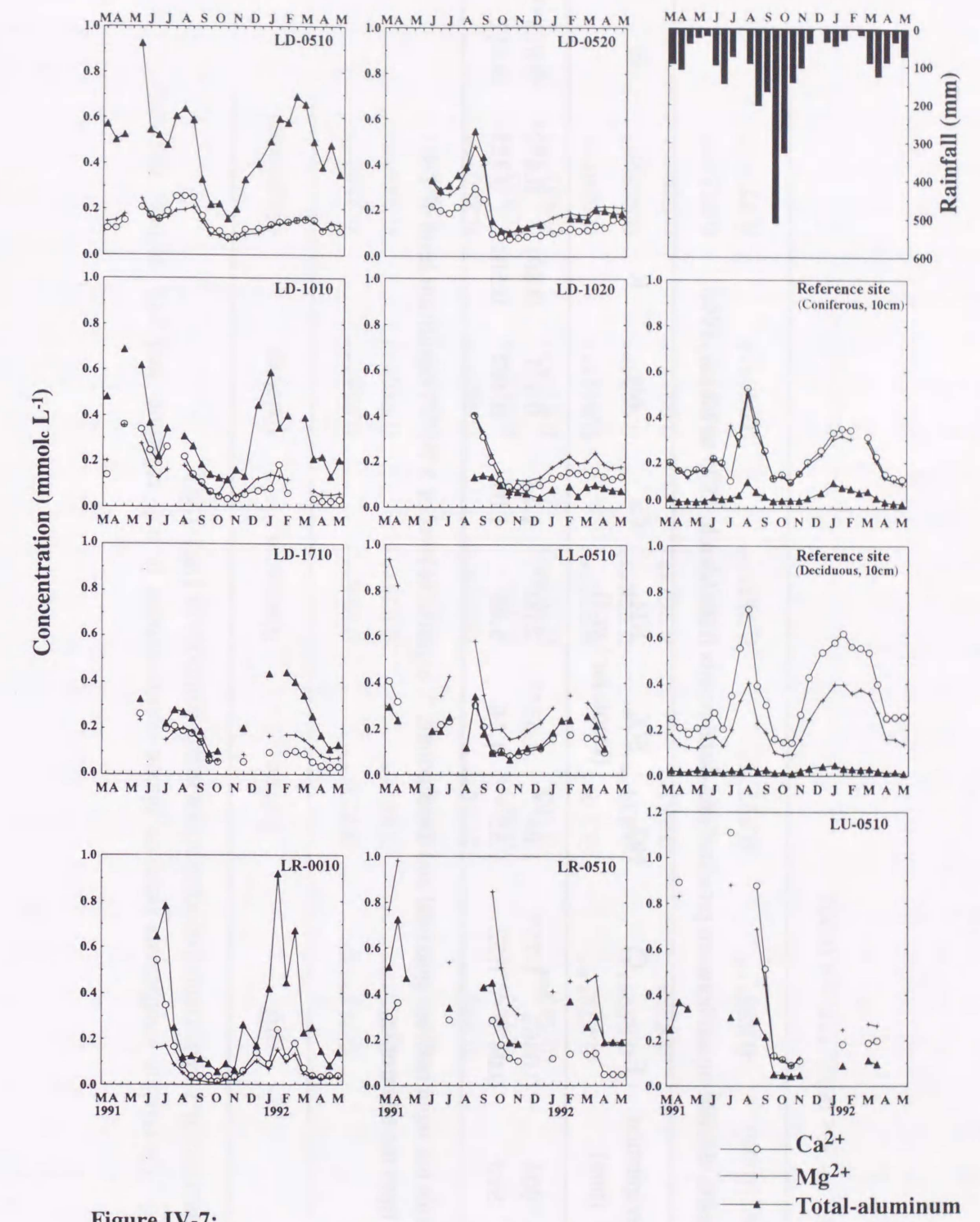The last two digits are soil depth (cm).

Figure IV-7:
Changes in calcium, magnesium, and aluminum concentrations in soil solutions.
Legend of points around the Hinoki cypress trunks was shown in Figure IV-4.
The first letter is the tree trunk size.
The second letter is the direction of transects.
The following two digits are distances from the trunk bases (dm).
The last two digits are soil depth (cm).

Table IV-4. Differences in element inputs between proximal and distal points from March, 1995 to March, 1996.

	Precipitation (mm)	F	Cl	NO_3	SO_4 (kmol$_c$ ha^{-1} yr^{-1})	NH_4	Ca	Mg	K	Na	H
Proximal (0.5 m)	904	0.0462	1.75*	1.65**	1.53**	2.00**	1.14	0.441	0.401	0.472*	0.813**
Distal (1.5 m)	810	0.0475	1.52	1.35	1.16	1.48	1.07	0.449	0.501	0.425	0.412

*,**: Difference in major ion input between proximal and distal points; *, significant level of 5 %; **, significant level of 1 %.
Parenthesis: Distance from the tree trunks.

Table IV-5 Correlation coefficients between nitrate concentrations in soil solutions and pH, sulfate, calcium, magnesium, and aluminum concentrations in soil solutions in 1991-1992.

	pH	Sulfate	Aluminum	Calcium	Magnesium
LD-0510	-0.911***	-0.723***	0.816***	0.936***	0.954***
LD-0520	-0.925***	-0.881***	0.975***	0.930***	0.944***
LD-1010	-0.879***	0.200	0.734***	0.949***	0.885***
LD-1020	-0.846***	-0.750***	0.831***	0.963***	0.860***
LD-1710	-0.957***	-0.487*	0.564*	0.918***	0.933***
LR-0010	-0.549**	0.304	0.793***	0.939***	0.933***
LR-0510	-0.872***	-0.578*	0.822***	0.944***	0.969***
LU-0510	-0.859***	-0.839***	0.978***	0.993***	0.988***
LL-0510	-0.535*	-0.462*	0.861***	0.981***	0.929***
Reference site (10 cm)	-0.868***	-0.823***	0.836***	0.917***	0.923***
Deciduous (10 cm)	-0.888***	-0.797***	0.785***	0.990***	0.977***

*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$

Table IV-6 Correlation coefficients between sulfate concentrations in soil solutions and pH or cations concentrations in soil solutions in 1991-1992.

	pH	Aluminum	Calcium	Magnesium
LD-0510	0.646***	-0.810***	-0.671***	-0.733***
LD-0520	0.923***	-0.886***	-0.886***	-0.853***
LD-1010	0.117	-0.140	0.439*	0.209
LD-1020	0.768***	-0.708**	-0.844***	-0.906***
LD-1710	0.328	-0.875***	-0.236	-0.626**
LR-0010	-0.605***	0.642**	0.214	0.541*
LR-0510	0.552*	0.672*	-0.727**	-0.623*
LU-0510	0.787***	-0.853***	-0.824**	-0.832**
LL-0510	0.497*	-0.780***	-0.412	-0.271
Reference site (10 cm)	0.803***	-0.829***	-0.860***	-0.877***
Deciduous (10 cm)	0.842***	-0.623***	-0.734***	-0.734***

*: $p < 0.05$, **: $p < 0.01$, ***: $p < 0.001$

affected the soil solution composition at LR0010. The coefficient of correlation between the soil solution pH and sulfate concentration at LD1010 was low, for unknown reasons. Cation concentration was inversely proportional to the sulfate concentration.

Calcium, magnesium and aluminum concentrations fluctuated simultaneously with the nitrate concentration (Table IV-5, Figure IV-7). The correlation coefficient between the nitrate concentration and both Ca^{2+} and Mg^{2+} concentrations was significant at all the points although at some points aluminum dominated. Mobilization of base cations was an important acid sink at RLL even in a relatively low pH range. The coefficient between nitrate and aluminum concentrations at LD1710 was small. Aluminum concentration at LD1710 was similar to the Ca^{2+} and Mg^{2+} concentrations until October (Figure IV-7). On the other hand, the aluminum concentration was higher than the Ca^{2+} concentration by factors of 2.6-4.9 from November to May. When the coefficients between nitrate and aluminum were calculated for the respective time period, correlation coefficients were 0.944 ($p < 0.001$) for the former period and 0.997 ($p < 0.001$) for the latter period. During the former period, only the nitrate concentration increased. On the other hand, the chloride concentration increased with the nitrate concentration during the latter period. Since chloride ions are not retained on soil or assimilated to plants and rainfall amounts were small during the latter period, the concentration associated with the drought affected the soil solution composition at LD1710. An increase in the chloride concentration during the latter period contributed to an increase in the aluminum concentration ($r = 0.980$, $p < 0.001$).

Arithmetic mean concentrations of Ca^{2+}, Mg^{2+}, and total-aluminum are shown in Table IV-7. Calcium concentration in the soil solution at a distance of 0.5 m from the large trunk was significantly lower than that of more distant samples. Around the small trunk, a significant decrease in the calcium concentration was observed only at SD0510. Calcium concentrations at the depth of 10 cm in the LD-plots ranged from 0.127 to 0.198 mmolc L^{-1}, values which were lower than that at the depth of 10 cm at the reference site (0.282 mmolc L^{-1} on average). Calcium concentration in soil solution at LD0520, LD0550, LD1010, LD1020, SD0510, and SD0550 was markedly lower than that at the corresponding depths at the coniferous reference site.

In the case of the magnesium concentration, values at a 0.5 m distance from the small trunk base decreased significantly, compared with more distant points regardless of the depth. The arithmetic mean at SD0510 was 0.199 mmolc L^{-1}, a value which was similar to that of the Ca^{2+} and total-aluminum concentrations (0.215 mmolc L^{-1}, 0.184 mmolc L^{-1}, respectively). Three cations (Ca^{2+}, Mg^{2+} and total-aluminum) were also codominant at LD0520. Around the

Table IV-7 Arithmetic mean calcium, magnesium, and total-aluminum concentrations in soil solution (mmolc L⁻¹) from March to October in 1995.

Depth	Large (LD-plots)			Small (SD-plots)		Reference site	
Distance from the trunk	0.5 m	1.0 m	1.7 m	0.5m	1.7 m	1.0m	1.7 m
Calcium							
10 cm	0.181**0	0.127**S,**R,*2	0.198*5	0.215*0,*7,*R	0.287	0.313	0.282
20 cm	0.182*7,*R	0.206*7,*R	0.261	0.252	0.269	0.321	0.274**5
50 cm	0.190*0,**7,*R	0.511	0.377	0.297***R	0.409	0.339	0.409
Magnesium							
10 cm	0.151*R	0.138*S,*R,*5	0.292	0.199*0,*R	0.283	0.260	0.303
20 cm	0.200**7	0.202*7,*R	0.333*S	0.214*0,*7,*R	0.303	0.296	0.292*5
50 cm	0.181	0.435	0.357	0.282*0,**7,*R	0.320	0.306*R	0.418
Total-aluminum							
10 cm	0.351*S,**R,*2	0.277*R	0.360*S,*R	0.184**7,*R,*2	0.113*2	0.0790*2	0.0727
20 cm	0.231**S,0,*7,*R	0.101	0.107*S	0.0365	0.0380	0.00749	0.0285
50 cm	-.--	-.--	0.00373	-.--	0.00323	0.00218	0.00306

Legend is the same as that in Table IV-3

large trunk, the arithmetic mean of Mg²⁺ concentration at LD0510 was 0.151 mmolc L⁻¹, a value which was half of that at the depth of 10 cm at the reference site (0.303 mmolc L⁻¹). Magnesium concentration at the depths of 10 and 20 cm which was less than 1 m from the large trunk was lower than that at the corresponding depth at the reference site.

Tree size affected the aluminum concentration in the soil solution as well as the pH values. Aluminum showed the highest concentration of cations at the depth of 10 cm in the LD-plots, 0.351 mmolc L⁻¹ at the LD0510. Aluminum concentration at the depths of 10 and 20 cm in the LD-Plots increased significantly, compared with that at the corresponding depth at the reference site. Although aluminum was dissolved in the surface layer, it was immobilized by percolation to a depth of 50 cm.

IV-4 Discussion

IV-4-1. Factors responsible for soil solution acidification at RLL

Koch and Matzner (1993) revealed that the spatial variability of the soil solution chemistry was due to the stemflow in European beech (*Fagus silvatica*) and to the heterogeneity of throughfall input in the case of the Norway spruce (*Picea abies*), because the stemflow was negligible under the spruce forest. In the case of beech stemflow, the amounts were 14-20 % of the total precipitation. In this study, the amounts of Hinoki cypress stemflow ranged from 0.1 % to 7.7 % of the total rainfall at RLL, on the average, 4.3 % in 1995-1996. Stemflow, therefore, was an important factor of spatial variability of the soil solution chemistry at RLL.

The elemental input associated with stemflow should not be divided by the tree crown area but by the area which was affected by the stemflow, for estimating the effects on soil solution acidification around the trunk base. Sato and Takahashi (1996) estimated the area which was affected by the stemflow based on the soil pH around the trunk base. They then calculated stemflow fluxes using an area of 0.48 m² and compared them with throughfall fluxes. However, at RLL it was too difficult to estimate the area affected by the stemflow because of the slope (20°). Gersper (1970) who investigated radioisotope accumulation in soils around beech trunks, speculated that stemflow water on the slope (ca. 11°) was likely to flow vertically and also contribute significantly to internal downslope flow. In addition, Voigt (1960) noted that stemflow infiltration was more rapid along the large roots than in soils between roots, and that old root channels acted as an important pathway of water flow. As a result, estimating stemflow movement in solum was difficult. Therefore, emphasis of the

study was placed on the stemflow composition (Figure IV-5).

High proton and ammonium concentrations in Hinoki cypress stemflow promoted acidification around the tree trunk base. According to previous studies, the main cause of soil and soil solution acidification around the trunk base was the low pH (high proton concentration) of stemflow. Our results underscored the importance of ammonium ions for soil solution acidification. High proton and ammonium concentrations in Hinoki cypress stemflow were also reported by Sakai (1997) and soil acidification around the 35 year old Hinoki cypress trunk was revealed with a value of 4.0 on the average.

Heterogeneity of throughfall input was also a factor of spatial variability at RLL. Proton input at the proximal points was twice as high as that at distal points (Table IV-4). Beier *et al.* (1993) showed that the deposition of all the substances was considerably higher at 0.3 m from the Norway spruce trunk than that at the periphery of the canopy, 1.6 m away. Ammonium input associated with throughfall at 0.3 m increased by factors of 1.4-2.2, compared with that at 1.6 m. The ratio of the ammonium input at 0.5 m from the tree trunk to that at 1.5 m was 1.4 at RLL. However, no significant differences in base cation input were observed.

Higher proton and ammonium inputs at the proximal points also contributed to the acidification of the soil solution close to the tree trunks. At RLL, both stemflow and heterogeneity of throughfall input promoted soil solution acidification around the trunk base.

IV-4-2. Acidification processes and changes in Soil Solution Composition

The forested catchment at RLL has been saturated with nitrogen due to atmospheric deposition and nitrogen transformation became the main acid source (Baba and Okazaki, 1998). Increased acid production due to nitrogen transformation promoted the acidification of the soil solution. On the other hand, ion exchange with base cations and weathering was the dominant acid sink. Calcium and magnesium concentrations, therefore, were proportional to the nitrate concentration in the soil solutions. Soil solution pH decreased due to the portion of protons produced through nitrification, resulting in aluminum dissolution. Aluminum concentration, therefore, was also correlated with the nitrate concentration. Sulfate adsorption on Andisols alleviated the increase in acidification (Baba and Okazaki, 1998). Sulfate concentration in soil solution at RLL was controlled by the large sulfate adsorption capacity of Andisols (Baba et al., 1995b: Chapter III). Protons that were produced by nitrification contributed to a decrease in the pH levels of the soil solution. Sulfate adsorption capacity of Andisols increases with a decrease in pH levels. When the pH levels decreased, sulfate ions

were removed from the soil solution through sulfate adsorption on soils. Therefore, the sulfate concentration was positively correlated with the soil solution pH (Table IV-6) and negatively with the nitrate concentration or cation concentration.

Using the values listed in Tables VI-3 and VI-7, the relationship between the pH and cation concentration was examined (Figure IV-8). Soil solution pH decreased with a decrease in the calcium concentration ($R^2 = 0.638$, $p < 0.001$) and with a decrease in the magnesium concentration ($R^2 = 0.399$, $p < 0.01$). When the pH values decreased below 5.0, aluminum ions were dissolved in the soil solution and the concentration increased exponentially with a decrease in pH levels. Ohrui et al. (1993) also reported that aluminum ions were dissolved at the same pH levels in Azuma, Seta, Gunma Prefecture where Dystrochrepts had developed.

When the soil solution pH decreased to less than 4.4, the aluminum concentration in the soil solution exceeded 0.2 mmolc L^{-1}. This value was used to estimate the critical load of acidic deposition (de Vries et al., 1995; Shindo et al., 1995). The median value of the total-aluminum concentration at SD0510 was 0.202 mmolc L^{-1}, although the arithmetic mean concentration was 0.184 mmolc L^{-1}. Total-aluminum concentration at LD0520 also exceeded 0.2 mmolc L^{-1}. Total-aluminum concentration and soil solution pH were used in the classification criteria of the soil solution acidification processes.

The molar (Ca+Mg+K)/Al ratio, which was also used as a parameter to evaluate the critical load (Sverdrup and Warfvinge, 1993), decreased significantly at the depths of 10 and 20 cm around the large trunk (Table IV-8). This ratio at LD0510 where the lowest value was observed, ranged from 1.26 to 2.24 in 1995 and from 0.68 to 1.54 in 1991-1992. In the case of molar Ca/Al ratio (Table IV-9), at LD0510 the values ranged from 0.52 to 1.21, on the average, 0.85 in 1995. When the soil solution pH at the depth of 10 cm in the LD-plot became less than 4.2, these ratios became significantly low.

As a consequence, in this study, the soil solution acidification processes were tentatively clarified as follows;

Stage i) Soil solution pH range above 5.0: Protons, which were supplied from acidic deposition and N transformation, were consumed by ion exchange with abundant base cations, in particular calcium and magnesium. This stage was observed under the deciduous forest and at the depth of 50 cm under the coniferous forest. Soil solution at SD1720 also fitted to this stage.

Stage ii) Mean soil solution pH in the range of 4.4-5.0: Although the exchange reaction with base cations was still the main neutralizing process, small amounts of aluminum were dissolved. The acidification at a depth of 10 cm at the coniferous reference site
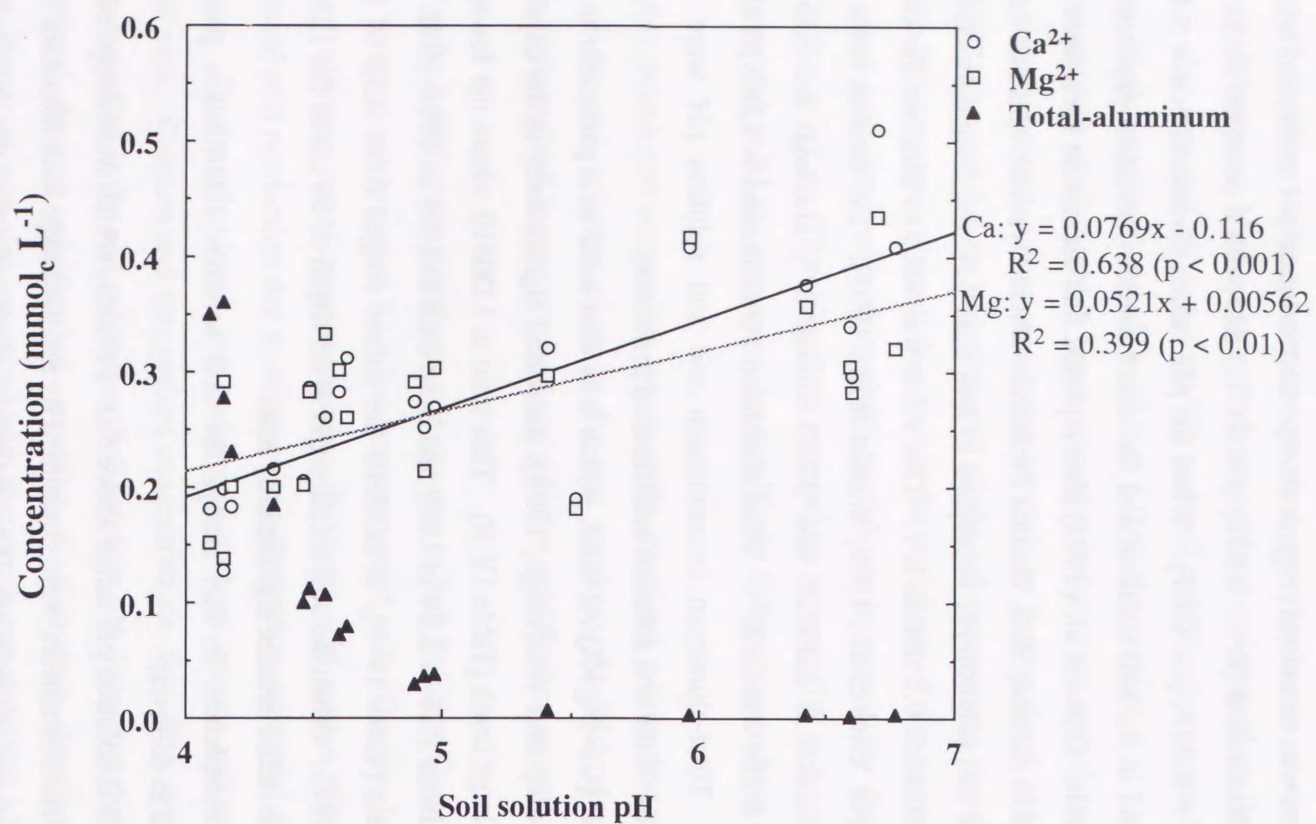
Ca^{2+}
Mg^{2+}
Total-aluminum

Ca: y = 0.0769x - 0.116
    R^2 = 0.638 (p < 0.001)
Mg: y = 0.0521x + 0.00562
    R^2 = 0.399 (p < 0.01)

Concentration (mmol$_c$ L^{-1})

Soil solution pH

**Figure IV-8 Relationship between pH and cation concentration
in soil solution in 1995-1996.**

Table IV-8 Molar ratio of the sum of calcium, magnesium and potassium to aluminum concentrations in soil solution from March to October in 1995.

Depth	Distance from the trunk Large (LD-plots)			Small (SD-plots)			Reference site
	0.5 m	1.0 m	1.7 m	0.5m	1.0m	1.7 m	
10 cm	1.71***S,*D,**2	1.73***S,**D,*2	2.96***S,*D,**2	3.93**1,**7,*D,**2	10.2***2	12.3	17.0
20 cm	2.82**S,*1,**7	7.49	8.77	21.8*1	25.2	139	42.7
50 cm			280		354	378	492

Legend is the same as that in Table IV-3

Table IV-9 Molar Ca/Al ratio of soil solution from March to October in 1995.

Depth	Distance from the trunk Large (LD-plots)			Small (SD-plots)			Reference site
	0.5 m	1.0 m	1.7 m	0.5m	1.0m	1.7 m	
10 cm	0.85***S,*D,*2	0.77**S,**D,**2	1.35**S,*D,*2	1.93**1,**7,*D,**2	4.93	6.44	8.05
20 cm	1.32**S,*1,**7	3.44	3.76	11.0	10.9	73.1	19.0
50 cm			153		354	150	232

Legend is the same as that in Table IV-3

corresponded to this stage. This group included the soil solutions at LD1020, LD1720, SD1010, SD1710, SD0520, and SD1020.

Stage iii) Soil solution pH in the range of 4.2-4.4: Aluminum concentration exceeded 0.2 mmolc L^{-1}, although exchangeable magnesium and calcium still contributed considerably to acid neutralization (LD0520, SD0510).

Stage iv) The soil solution pH below 4.2: Ultimately aluminum dissolution became the dominant acid sink. This process occurred at the depth of 10 cm in the LD-plot (LD0510, LD1010, LD1710).

It was thus considered that the spatial variability of the soil solution chemistry enabled to interpret the soil solution acidification processes. The soil solution classification we proposed was consistent with the soil buffer systems at various pH levels (Ulrich, 1986). Ion exchange was the main process in the removal of H^+ from the soil solution at Stage i). The pH range of Stage i) corresponds to the major part of the silicate buffer range (Ulrich, 1986). Baba and Okazaki (1998) showed that the ion exchange reaction and weathering processes contributed to the acid sink at RLL based on the results of elemental budget on a catchment scale. Presumably, primary silicates contributed to the consumption of acids at Stage i). The Stages ii) and iii) corresponded to the exchanger buffer range (Ulrich, 1986) and Stage iv) corresponded to with the aluminum buffer range. Ion exchange and weathering were quantitatively the major buffer reactions at RLL, although aluminum contributed to the buffer reaction around the trunk base.

Although the soil solutions were markedly acidified, no visible symptoms of forest decline have been observed at RLL. de Vries et al. (1995) concluded that excess over critical limits, which was estimated from the results obtained in laboratory experiments in relation to the effects on root (uptake), was not associated with actual forest decline. Falkengren-Grerup et al. (1995) also pointed out the difficulty in applying the evidence from laboratory experiments to field conditions, because many complex factors affected plant growth, including tree species. Kato and Shirai (1995) showed that the soils in Hinoki cypress stands were acidic compared with those of the Japanese cedar stands. The acid tolerance and the aluminum tolerance of Hinoki cypress were higher than those of Japanese cedar (Tsutsumi, 1962).

Nitrogen saturation also affects the plant growth (Aber et al., 1989). The forested catchment at RLL was saturated with nitrogen (Baba and Okazaki, 1998). Ammonium concentration in the Hinoki cypress stemflow was very high. Given the water fluxes around the tree trunks, the effect of ammonium should be quantitatively evaluated. Since the nitrate concentration affected the fluctuations of cation concentrations, nitrate leaching contributed to

the soil solution acidification around the tree trunks. The spatial variability of the soil solution chemistry could be an important factor in estimating the impact of soil solution acidification on plant growth, because soils around the trunk base are the most suitable rhizosphere soils for elucidating the effect of acidification.

IV-5 Conclusion

Atmospheric acid deposition promote the acidification of the soil solution at RLL, especially under the coniferous forest. The intensive acidification on the downslope side of tree trunks indicated effect of acidic stemflow rather than heterogeneity of throughfall fluxes. Protons were substituted with exchangeable base cations at RLL. Depletion of base cations in soils around tree trunks induced aluminum dissolution. Aluminum was the dominant cation in the soil solution in the surface horizon close to the Hinoki cypress trunk. The spatial variability of the soil solution chemistry enabled to interpret the soil solution acidification processes.

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Chapter V

Amorphous Aluminum Depletion from Andisols

Abstract

Andisols are rich in allophane and organic matter. Allophane, amorphous aluminosilicate, is readily dissolved at low pH when compared with crystalline clay minerals. Aluminum concentrations in soil solutions are not only controlled by inorganic clay minerals but also by organically bound aluminum. The aim of this study was to verify which pools (*or* solid phases) contribute to Al dissolution. Soil samples were taken at various distances from tree trunks and at various depths at Rolling Land Laboratory (RLL), Hachioji, Tokyo. Selective dissolution techniques were used to elucidate changes in solid-phase pools of aluminum. Exchangeable aluminum contents in soils under the Hinoki cypress were 100 mmol$_c$ kg^{-1}. This accounted for the cation exchange capacity (CEC) of Andisols at soil pH of 4. The relationship between soil pH and each aluminum pool showed that dissolved aluminum ions in soil solution were primarily derived from the amorphous Al pool and substituted with base cations of soils and/or complexed with organic matter. Dissolved aluminum ions were substituted with base cations of soils, resulting in exchangeable Al increases and/or complexed with organic matter which increased organically bound Al pools. Increase in organically bound Al pools exhibited importance of complexation with soil organic matters for controlling soil solution aluminum.

V-1 Introduction

Aluminum has been dissolved into soil solutions in the area where intensive soil acidification has occurred due to acidic deposition. Aluminum mobilization is the most important acid sink in intensively acidified soils (van Breemen and Jordens, 1983; Mulder *et al.*, 1987). Inorganic monomeric aluminum is toxic to biota (e.g. Foy *et al.*, 1978; Cleveland *et al.*, 1989; Parker *et al.*, 1989; Godbold, 1994). It has been suggested that the uptake of aluminum from drinking water may cause dementia as a result of accumulation in the brain (McLachlan, 1989; Kuroda, 1992; Kuroda, 1998). Aluminum speciation has been carried out to estimate inorganic monomeric forms of aluminum (Driscoll, 1984; Berggren, 1990; Clarke, 1994; Sparen, 1994). On the other hand, sources of aluminum are also a major concern to understand aluminum chemistry. Aluminum is a major component of soils, especially in crystalline forms of clay minerals. Therefore, inorganic clay minerals are an important source of Al and many studies have examined the equilibrium and the relationship between clay minerals and Al concentration in soil solution (e.g Gundersen and Beier, 1988; Mulder, *et al.*, 1989a ; van Grinsven *et al.*, 1992; LaZerte and Findeis,1994; Sjostrom, 1994). Recently,

some investigators revealed that organically bound Al contributes to Al dissolution (e.g. Cronan *et al.*, 1986; Mulder, 1989b; Berggren and Mulder, 1995; Ross and Bartlett, 1996). Concerning Japanese soils, Kato *et al.* (1995) showed that aluminum in soil solutions which were taken from Andisols and Entisols in the northern Kanto district were equilibrated with amorphous aluminum trihydroxides at pH 4 - 7. Andisols are abundant in amorphous clay minerals, such as allophane, and in organic matter. Therefore, it is important to verify which pools (*or* solid phases) contribute to Al dissolution. Based on the spatial variability of soil solution chemistry, it was proposed that aluminum pools would be different close to the tree trunk. The objective of this study was to examine this hypothesis and elucidate which pools of Andisols are important for soil solution aluminum.

V-2 Materials and Methods

Site description is presented in Chapter II and IV. The studied catchment (Nishinosawa) area is 2.15 ha (1.55 mixed deciduous forest and 0.6 ha mixed coniferous forest). The major species are oak (*Quercus serrata*) in the deciduous forest and Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) in the coniferous forest. The soil types are Andisols which developed on the basaltic volcanic ash derived from Mt. Fuji.

Soil samples were taken from various distances from the trunk of Hinoki cypress and oak. All samples were air-dried and passed through a 2 mm sieve. Then air-dried samples were used for analysis. The pH (H_2O) of a 1:5 air dried soil : water suspension was measured by glass electrode. Exchangeable cations were extracted by 1 M ammonium acetate (pH 7) and determined by atomic absorption spectrophotometry (Shimadzu, 670/AA Atomic Absorption Spectrophotometer). Subsequently, 200 mL of 1 M sodium acetate (pH 7) was added to replace exchangeable sites with sodium. Then, sodium ions in reagent were removed by ethyl alcohol. Retained sodium ions were extracted by 1 M ammonium acetate (pH 7) and sodium concentrations were determined to estimate cation exchange capacity (CEC).

Selective dissolution techniques were used for solid-phase pools of aluminum. Extracted aluminum pools were shown in Figure V-1 (Dahlgren and Walker, 1993; Saigusa and Matsuyama, 1996). Extraction procedure was performed according to van Langen (1993) and van Reeuwijk (1993). Briefly, a) exchangeable Al was extracted by 1 M potassium chloride solution and the extract was decanted into a 200 mL volumetric flask, this was repeated 5 times, b) organically bound Al was extracted by 0.1 M sodium pyrophosphate

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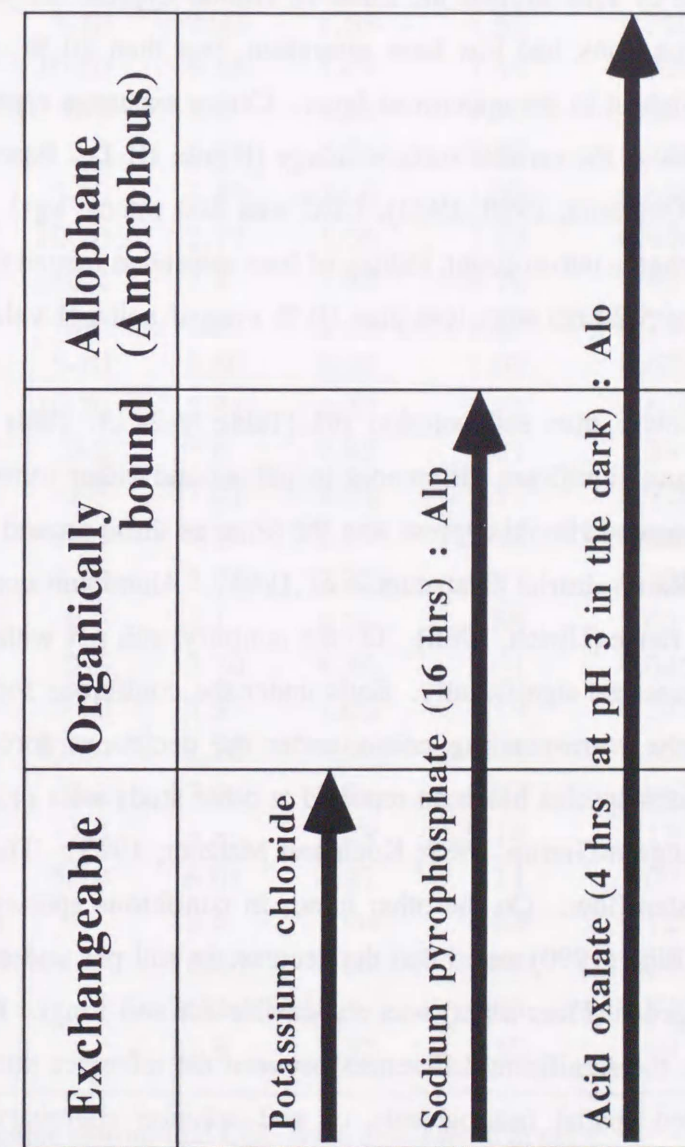
Figure V-1:
Pools of solid-phase aluminum extracted by selective dissolution technique
(Dahlgren and Walker, 1993; Saigusa and Matsuyama, 1996)

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solution overnight (16 hrs) and c) amorphous Al was extracted by acid ammonium oxalate solution (pH 3) for 4 hrs. Aluminum concentrations in extracts were determined by atomic absorption spectrophotometry (Shimadzu, 670/AA Atomic Absorption Spectrophotometer and Hitachi, Z-6100 Polarized Zeeman Atomic Absorption Spectrophotometer).

V-3 Results and Discussion

Chemical characteristics of soils around the trunk of Hinoki cypress are shown in Table V-1. Soils around the tree trunk had low base saturation, less than 10 %, although exchangeable cations were the highest in the uppermost layer. Cation exchange capacities of Andisols depend on pH values due to the variable surface charge (Figure III-1). Based on the equilibrium method (Wada and Okamura, 1980, 1983), CEC was 100 mmolc kg^{-1} at pH 4 (Figure III-2). Taking variable charge into account, indices of base saturation ranged from 6 to 31. These values at the depth of 5-20 cm were less than 10 % even if soil pH values were taken into consideration.

Soil pH values were lower than soil solution pH (Table V-2, cf. Table IV-2 in Chapter IV). There were not any significant differences in pH around either trunk size of Hinoki cypress. Soil pH range around Hinoki cypress was the same as those around declined Japanese cedar in the northern Kanto district (Matsuura *et al.*,1991). Aluminum compounds contribute buffer reaction in this range (Ulrich, 1986). On the contrary, soil pH within 0.5 m distance from the oak trunks decreased significantly. Soils under the coniferous forest were obviously lower than those at the corresponding points under the deciduous forest. Soil acidification close to the deciduous species has been reported at other study sites (e.g. Mina, 1967; Wolfe *et al.*, 1987; Falkengren-Grerup, 1989; Koch and Matzner, 1993). These cases were ascribed to the effects of stemflow. On the other hand, in coniferous species various causes were cited. Pallant and Riha (1990) stated that the decrease in soil pH under red pine (*Pinus resinosa*) and Norway spruce (*Picea abies*) was responsible for soil fungi. Koch and Matzner (1993) did not observe the significant differences between the reference site and the base of the stem, but exhibited spatial heterogeneity of soil solution chemistry. They concluded that spatial patterns were attributed to the differences in throughfall fluxes. In both cases, stemflows were negligible. Mina (1967) revealed that the soil acidity decreased outward. He concluded that throughfall and stemflow fluxes were small due to canopy structure of the spruce, although solute concentrations were high. The canopy structure affected the amount of stemflow (Ford and Deans, 1978; Sanada *et al.*, 1991). When

Table V-1 Chemical characteristics of soils close to the trunk of Hinoki cypress and soil at the distal points under the coniferous and the deciduous forest.

Plot	Soil Depth (cm)	Ca	Mg	K	Na	CEC	Base Saturation
			(mmolc kg^{-1})			(mmolc kg^{-1})	%
D-25	0-2	20.1	5.40	4.72	1.05	486	6.44
	2-5	3.86	2.06	2.02	0.680	309	2.79
	5-10	2.83	1.55	1.52	0.510	246	2.60
	10-20	6.13	1.24	1.34	0.528	207	4.47
D-50	0-2	17.9	6.22	4.76	1.27	551	5.47
	2-5	5.51	2.54	2.52	0.582	389	2.87
	5-10	3.55	2.06	1.79	0.636	314	2.56
	10-20	2.77	1.66	1.53	0.604	216	3.04
D-100	0-2	17.1	7.44	4.70	1.42	504	6.08
	2-5	5.47	2.49	1.87	0.742	332	3.18
	5-10	3.60	2.00	1.67	0.622	286	2.76
	10-20	2.81	1.47	1.13	0.618	199	3.03
D-150	0-2	17.6	7.45	3.81	1.39	499	6.05
	2-5	7.01	3.71	2.21	0.918	370	3.74
	5-10	4.20	2.17	1.45	0.623	254	3.32
	10-20	2.58	2.22	0.92	0.792	206	3.16
U-100	0-2	34.1	8.36	4.88	2.02	577	8.56
	2-5	7.70	4.36	3.01	0.645	238	6.60
	5-10	2.37	1.60	1.19	0.575	520	1.10
	10-20	2.76	1.94	1.04	0.653	215	2.98
CB	0-2	17.2	8.29	2.87	0.967	311	9.42
	2-5	13.8	7.48	2.14	1.12	380	6.44
	5-10	6.01	4.27	1.11	1.07	348	3.58
Plot II A		19.4	7.94	4.02	1.12	350	9.29
Plot II B		10.3	6.00	1.46	1.14	339	5.57
Plot III		26.2	18.4	6.64	0.820	389	13.4
Plot IV		22.8	7.52	3.30	1.09	406	8.55

Exchangable cations and CEC were determined at pH 7.
D represents downslope side of the trunk of Hinoki cypress.
U represents upslope side of the trunk of Hinoki cypress.
Number after hyphen represent the distance from the trunk of Hinoki cypress.
CB: 0.5 m distance from the Hinoki cypress; These samples were taken in 1991.
Plot II A and Plot II B: mixed coniferous forest.
Plot III and Plot IV: mixed deciduous forest.

Table V-2 Arithmetic mean soil pH around the tree trunks.

Depth	Distance from the trunk			
	0.25 m	0.5 m	1.0 m	1.7 m
Large trunk of Hinoki cypress				
0-2 cm	3.86	3.86#D	3.86**D, *7	3.95***D
2-5 cm	3.83#D, #7	3.95#D	3.84**D, #7	4.07**D
5-10 cm	3.92	4.05	4.04***D	4.14**D
10-20 cm	3.96*S	4.13	4.14*D	4.31*D
Small trunk of Hinoki cypress				
0-2 cm	3.62*D	3.73*D	3.69**D	3.82*D
2-5 cm	3.90*D	3.88*D	3.85*D	4.00*D
5-10 cm	4.09*D	4.02*D	4.02*D	4.16**D
10-20 cm	4.19*D, #7	4.11*D, #7	4.26*D	4.41*D
Trunk of oak				
0-2 cm	4.19#1, *7	4.61	4.63	4.66
2-5 cm	4.21**1, *7	4.38#1, #7	4.64	4.69
5-10 cm	4.32#5, **1, *7	4.39*1, #7	4.70	4.75
10-20 cm	4.43*1, **7	4.46*1, *7	4.89	4.94

#: $p < 0.1$, *: $p < 0.05$; **: $p < 0.01$, ***: $p < 0.001$.
S: Different from corresponding point around small tree trunk.
D: Different from corresponding point around deciduous trunk.
5: Different from soil at the same depth, 0.5 m distance from the same size trunk.
1: Different from soil at the same depth, 1.0 m distance from the same size trunk.
7: Different from soil at the same depth, 1.7 m distance from the same size trunk.

branches slope downwards towards the main trunk, this directs water towards the stem. Branches of Sakhalin fir (*Abies sachalinensis*) slope downwards towards the main trunk and those of Yezo spruce (*Picea jezoensis*) slope slightly upwards. As a consequence, the amount of stemflow from Sakhalin fir is larger than that from Yezo spruce (Sanada *et al.*, 1991). The amount of stemflow was in order as follows:

Sakhalin fir > Yezo spruce ≈ Japanese cedar > Hinoki cypress

where the amount of stemflow on the Japanese cedar and Hinoki cypress were referred from the results by Haibara and Aiba (1982). The similar results was obtained in 1995-1996; the average stemflow volume was 4.3 % of rainfall at open space of RLL.

The difference in acidity of soil (solution) between coniferous and deciduous forests was ascribed to the difference in acid load (Baba et al, 1995). Difference in acid load was attributed to the canopy function: larger amounts of acid substances were intercepted at the coniferous canopies than the deciduous canopies. By contrast, larger amounts of base cation were excreted at the deciduous canopies than the coniferous canopies. Proton and ammonium concentration in the coniferous stemflow were higher than the corresponding throughfall (Table II-5). On the other hand, Ca^{2+}, Mg^{2+}, and K^+ concentration were rather less than the throughfall. In the case of the deciduous stemflow, the opposite was true.

Exchangeable Al contents in soils around Hinoki cypress trunks were 100 $mmol_c$ kg^{-1} on the average and there were no significant differences between various distances and depths (Table V-3). Based on low base saturation (Table V-1) and CEC at soil pH around the trunks, exchangeable Al occupied the most cation exchange sites. Exchangeable aluminum in soils around oak trunks increased on approaching the trunk which corresponded to a decrease in pH levels. Exchangeable aluminum contents at 1 m and 1.7 m distance from cypress trunks were significantly higher than corresponding distances from oak trunks. Using values in Table V-2 and V-3, the correlation between soil pH and exchangeable aluminum contents was examined (Figure V-2). Exchangeable Al contents were inversely proportional to soil pH values ($R^2 = 0.71$, $p < 0.001$).

Organically bound Al reached a peak of 300 $mmol_c$ kg^{-1} at 1 m from the trunk (Table V-4). The lowest value in soils was found at the points closest to the Hinoki trunks (0.25 m). Organically bound Al pools were the largest at the 0-2 cm soil depth around Hinoki cypress. On the other hand, around oak trunks the greatest values were observed at the depth of 2-5 cm. Organically bound Al increased from 300 $mmol_c$ kg^{-1} at the edge of the oak crown to 400 $mmol_c$ kg^{-1} at the base of the trunk. Using values in Table V-2 and V-4, the relationship between soil pH and organically bound aluminum contents was examined (Figure V-3).

Table V-3 Arithmetic mean exchangeable aluminum in soils (mmolc kg^{-1}) around the tree trunks.

Depth	Distance from the trunk			
	0.25 m	0.5 m	1.0 m	1.7 m
Large trunk of Hinoki cypress				
0-2 cm	97.2 [*S, *1]	106 [#D, #7]	122 [**D]	111 [**D]
2-5 cm	108	123	135 [*D]	108 [*D]
5-10 cm	96.5 [*1]	104	115 [**D, #7]	98.2 [*D]
10-20 cm	98.8 [#7]	86.9	93.9 [*D]	86.6 [**D]
Small trunk of Hinoki cypress				
0-2 cm	117 [*D]	122 [#D]	133 [*D]	120
2-5 cm	98.0	108	118	101
5-10 cm	90.8	98.2	104	87.1 [#D]
10-20 cm	86.7	92.2	80.2 [**D]	69.3 [#D]
Trunk of oak				
0-2 cm	80.2 [#1, *7]	46.3	36.9	42.0
2-5 cm	106	77.3	69.2	56.8
5-10 cm	94.2 [*1, #7]	87.2 [#1]	62.9	48.1
10-20 cm	81.5 [#1, #7]	81.8 [*1, *7]	39.8	35.0

#: $p < 0.1$, *: $p < 0.05$; **: $p < 0.01$, ***: $p < 0.001$.
S: Different from corresponding point around small tree trunk.
D: Different from corresponding point around deciduous trunk.
5: Different from soil at the same depth, 0.5 m distance from the same size trunk.
0: Different from soil at the same depth, 1.0 m distance from the same size trunk.
7: Different from soil at the same depth, 1.7 m distance from the same size trunk
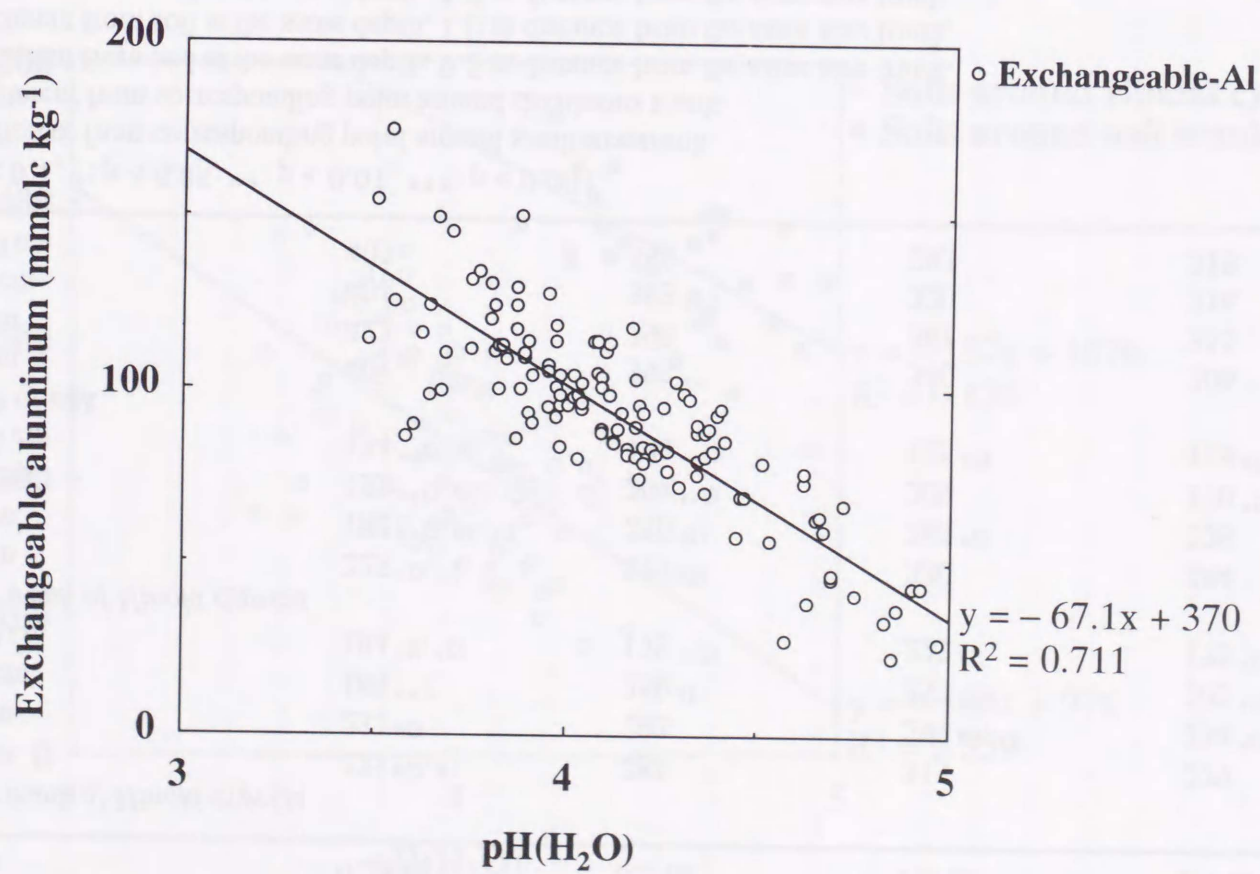
Figure V-2: Relationship between soil pH and exchangeable aluminum.

Table V-4 Arithmetic mean organically bound aluminum in soils (mmolc kg^{-1}) around the tree trunks.

Depth	Distance from the trunk			
	0.25 m	0.5 m	1.0 m	1.7 m
Large trunk of Hinoki cypress				
0-2 cm	225 [#D, #1]	285	315	279
2-5 cm	231 [#D]	293	297 [#S, *7]	234 [*D]
5-10 cm	188 [**1]	250 [#D]	257 [**7]	203 [**D]
10-20 cm	184 [*S, *D]	178 [**D]	222 [#S]	173 [*D]
Small trunk of Hinoki cypress				
0-2 cm	225 [*D, *1]	277 [#D]	320	284
2-5 cm	182 [**D, #5, *1]	250 [*D]	265 [*D]	228
5-10 cm	153 [**D, #5]	204 [**D]	209	170 [*D]
10-20 cm	134 [**D]	170 [**D]	125 [#D]	118 [#D]
Trunk of oak				
0-2 cm	401	393 [*7]	340	306
2-5 cm	423	398	361	355
5-10 cm	401	383 [**7]	320	316
10-20 cm	403	388	283	318

#: $p < 0.1$, *: $p < 0.05$; **: $p < 0.01$, ***: $p < 0.001$.
S: Different from corresponding point around small tree trunk.
D: Different from corresponding point around deciduous trunk.
5: Different from soil at the same depth, 0.5 m distance from the same size trunk.
0: Different from soil at the same depth, 1.0 m distance from the same size trunk.
7: Different from soil at the same depth, 1.7 m distance from the same size trunk
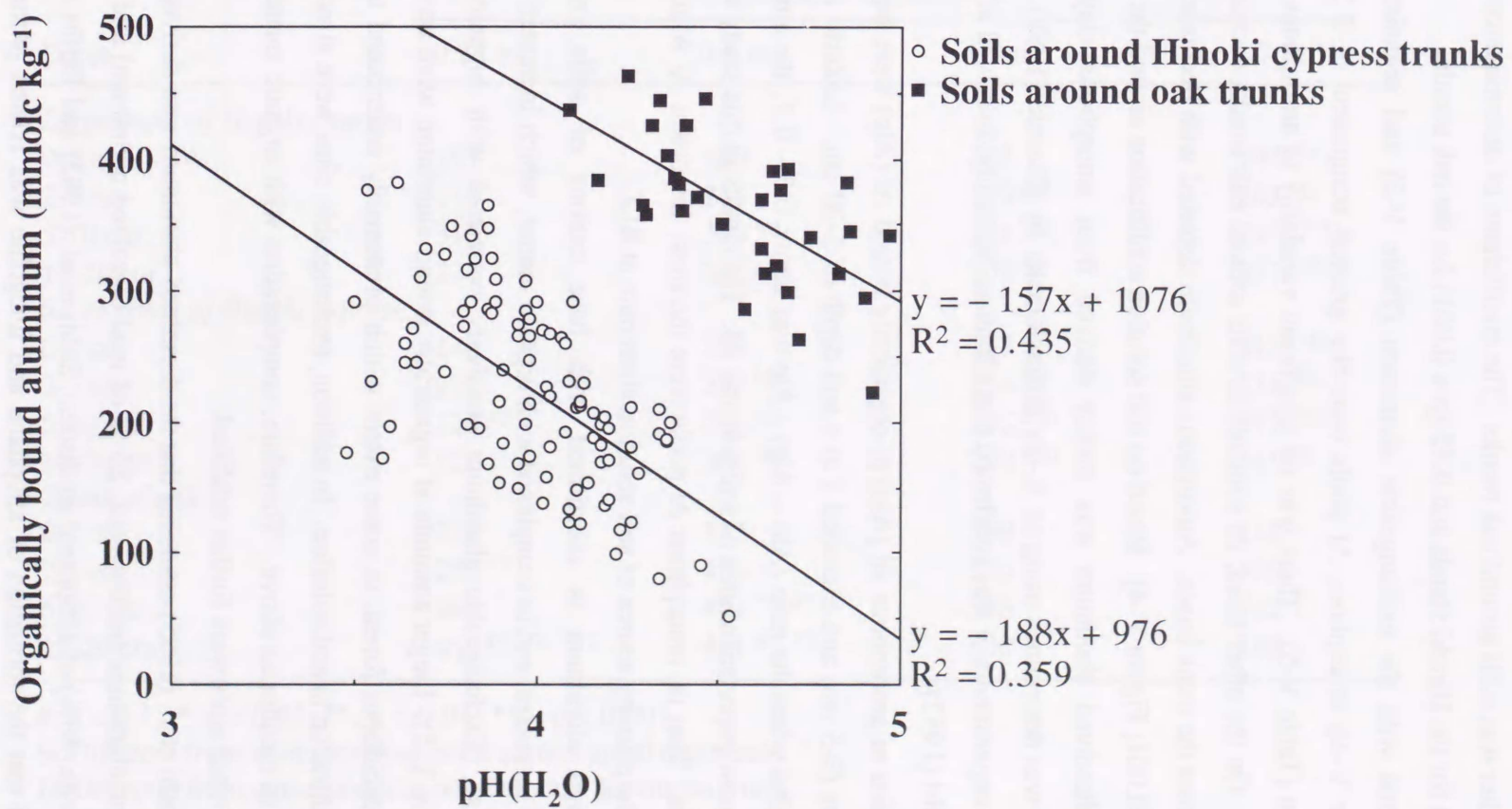
Figure V-3:
Relationship between soil pH and organically bound aluminum.

Scatter plots were apparently divided into 2 groups. One was soils close to the Hinoki cypress trunks and the other was soils around oak trunks. The coefficients of determination (R^2) were 0.36 (p < 0.001) for the Hinoki stands and 0.43 (p < 0.001) for the oak stands.

Compared with the exchangeable aluminum (Table V-3) and organically bound aluminum (Table V-4), amorphous Al pools were the greatest component at 5-20 cm soil depths each point (Table V-5). There was no significant variability of amorphous Al around Hinoki cypress. On the other hand, its contents in soils around oak trunks decreased within 0.5 m distance from the trunk bases. Amorphous aluminum depleted with decrease in soil pH (R^2 = 0.49, p < 0.001; Figure V-4). Based on soil solution acidification around the tree trunks (Chapter IV), dissolved aluminum was mainly derived from amorphous clay minerals, allophane which was determined using an X-ray diffractometer by Okazaki (1989). Based on field monitoring experiments, it was confirmed that allophane is readily dissolved at low pH as revealed by Shioiri (1952).

The ratios of amorphous Al (Alo) to organically bound Al (Alp) were less than 1 at the surface layers (0-5 cm) and exceeded 1 at a soil depth of 5-20 cm. LaZerte and Findeis (1995) revealed that when the ratio (Alo – Alp) / Alp was above 0.3 - 0.7, the amorphous Al pools were the most important source of soil solution Al. The results in this study were higher than their criteria. That is, amorphous Al pools were the most important Al source at RLL. Allophane was the primary source of soil solution aluminum at RLL.

Dissolved aluminum is substituted with base cations of soils, resulting in exchangeable Al increases, and/or complexed with organic matter, which increased organically bound Al pools. Exchangeable aluminum positively correlated with organically bound aluminum (Figure V-5). Larger amounts of organically bound aluminum were accumulated in soils under the deciduous forest, to some extent which presumably contributed to keep low aluminum concentration in soil solution. In addition, exchangeable sites were almost occupied with aluminum as mentioned above. Therefore, complexation with organic matter would be more important when soils were further acidified.

Takahashi et al. (1995) estimated that the dissolved aluminum was derived from both organically bound aluminum fractions (ca. 20 % of total dissolved aluminum) and amorphous aluminum fractions (80%) of allophanic Andisols. Shoji *et al.* (1982) and Parfitt and Saigusa (1985) revealed that the formation of allophane and imogolite was related primarily to soil acidity and that it occurred only in soils having pH (H_2O) > 4.9. When pH is less than 4.9, aluminum was preferentially bound by humic substances. This study results showed increases in organically bound Al with a decrease of soil pH, which agree with their findings. Based on

Table V-5 Arithmetic mean amorphous aluminum in soils (mmolc·kg⁻¹) around the tree trunks.

Depth	Distance from the trunk				
	0.25 m	0.5 m	1.0 m	1.7 m	
Large trunk of Hinoki cypress					
0-2 cm	197	180	203	193 *D	
2-5 cm	213	225	219 #D	263 *D	
5-10 cm	318	334 *D	281 *D	297 ***D	
10-20 cm	334	321	279 *D	257 **D	
Small trunk of Hinoki cypress					
0-2 cm	148	193	217	215 **D	
2-5 cm	277	232 #D	234 *D	231 **D	
5-10 cm	326 #D	296 #D	275 **D	297 **D	
10-20 cm	322	308 *D	298 **D	345 #D	
Trunk of oak					
0-2 cm	311	372	398	418	
2-5 cm	278 *7	454	546	495	
5-10 cm	465	491 *1, #7	586	592	
10-20 cm	453 #5, #1, **7	491 #1, *7	630	580	

#: p < 0.1, *: p < 0.05; **: p < 0.01, ***: p < 0.001.
S: Different from corresponding point around small tree trunk.
D: Different from corresponding point around deciduous trunk.
5: Different from soil at the same depth, 0.5 m distance from the same size trunk.
0: Different from soil at the same depth, 1.0 m distance from the same size trunk.
7: Different from soil at the same depth, 1.7 m distance from the same size trunk
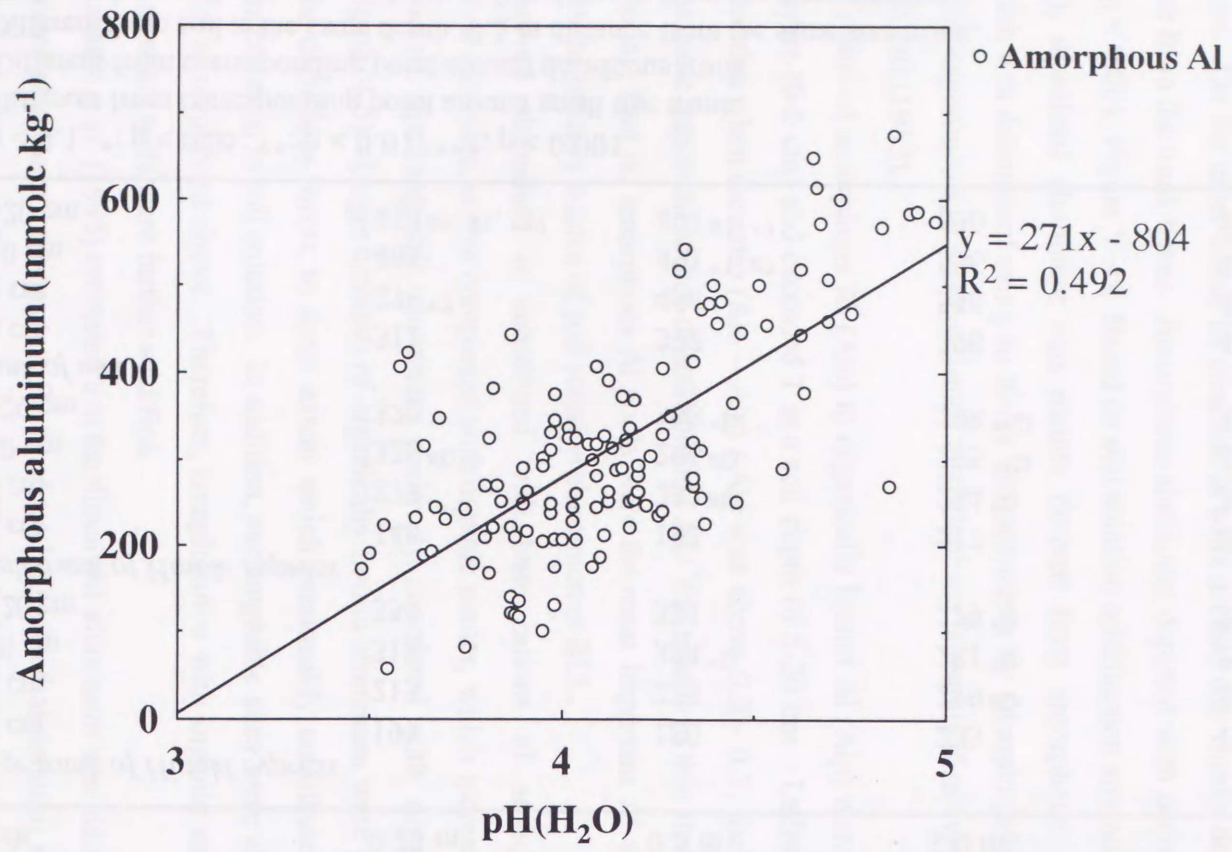
Figure V-4: Relationship between soil pH and amorphous aluminum.
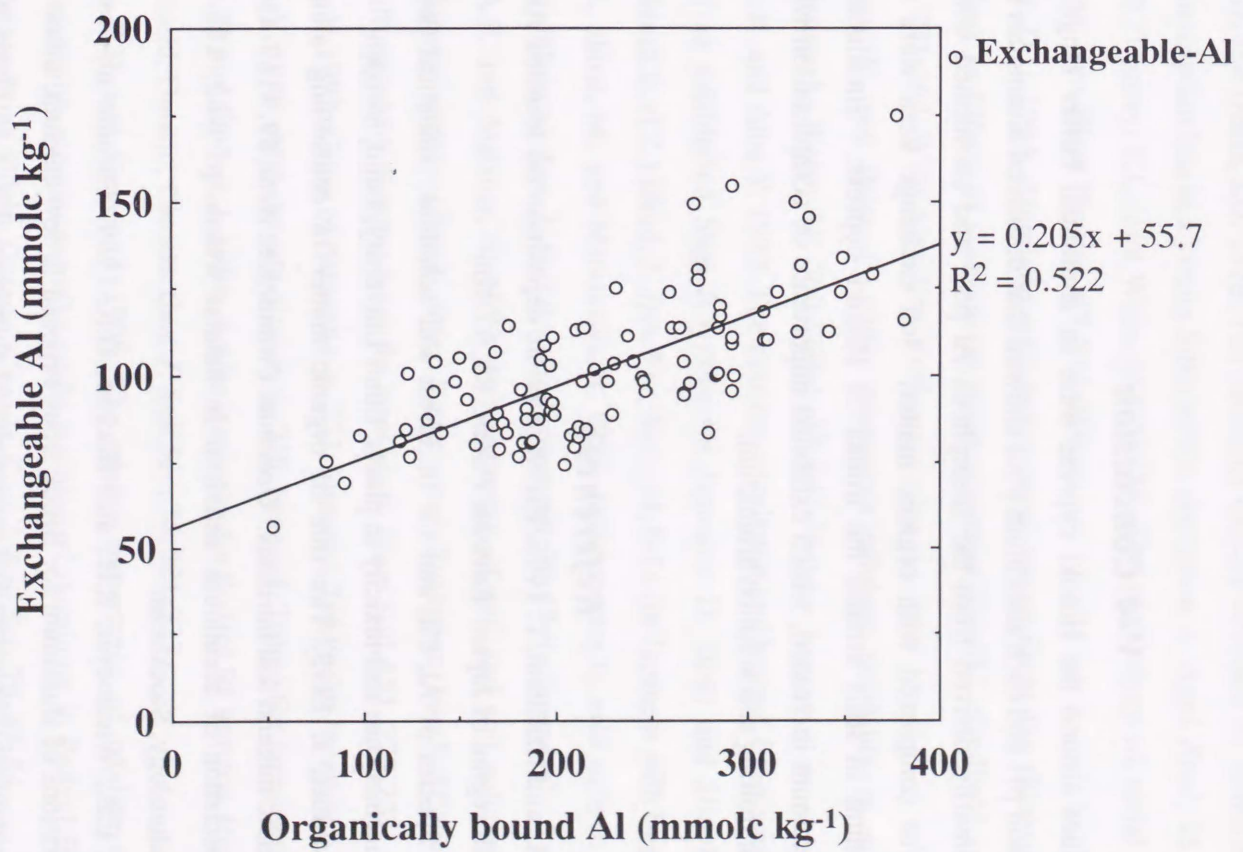
Figure V-5:
Relatioinship between exchangeable aluminum and organically bound aluminum.

batch experiments, Berggren and Mulder (1995) revealed that when the pH < 4.1 aluminum solubility was explained both qualitatively and quantitatively by equilibrium complexation with soil organic matters. Decrease in organically bound Al at the points closest to trunks of Hinoki cypress (Table V-4) suggested effect of organically bound Al on soil solution aluminum at RLL. Dissolved aluminum ions from allophane could be speculated to be controlled by complexation with soil organic matters.

V-4 Conclusion

Soil pH values around the Hinoki cypress were in aluminum buffer range. The relationship between soil pH and each aluminum pool showed that dissolved aluminum ions in soil solution were primarily derived from the amorphous Al pool and substituted with base cations of soils and/or complexed with organic matter. Ion exchange sites were almost occupied with aluminum in soils around the trunks of Hinoki cypress. Simultaneously, organically bound aluminum increased, which exhibited importance of complexation with soil organic matters for controlling soil solution aluminum.

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Chapter VI

Acidification in Nitrogen Saturated Catchment

Abstract

Continuous monitoring studies focused on nitrogen saturation were conducted at the Rolling Land Laboratory (RLL) of the forest experimental station located in the Tama Hill region in Central Japan. Based on the nitrate concentration in stream water and nitrogen budget, it was estimated that the forest ecosystems at RLL could be classified into Stage 2 of nitrogen saturation. The stream water pH decreased when the nitrate concentration increased. Proton production due to N transformation (= $([NH_4^+]_{th}-[NH_4^+]_{out}) - ([NO_3^-]_{th}-[NO_3^-]_{out})$) amounted to 1.24 kmolc ha^{-1} yr^{-1} in 1991-1992, a value 1.5 times as high as the total atmospheric proton input. Sulfate adsorption buffered the impact of the acid load. Protons were mainly consumed by ion exchange with base cations and weathering processes. Both acidic deposition and N transformation accelerated base cation mobilization. Nevertheless, soil pH values at RLL have not decreased due to the abundance in base cations.

VI-1 *Introduction*

Nitrogen saturation occurs when the nitrogen input exceeds nitrogen requirements of plants and microbes in ecosystems (Aber et al., 1989). Responses of the forest ecosystems to nitrogen input depend on the nitrogen saturation status. Aber et al. (1989) classified nitrogen saturation into 4 stages. Stoddard (1994) developed a classification based on the concentration of nitrogen compounds in stream water and nitrogen budget. The export of nitrogen compounds (mainly nitrate ions) from the forest ecosystems was negligible or low in Stage 0 systems regardless of the nitrogen input. Atmospheric nitrogen deposition benefited forest ecosystems when available nitrogen compounds were limited (Abrahamsen, 1980). Additional atmospheric nitrogen deposition resulted in an increase in the foliar nitrogen content and an increase in the foliar biomass, resulting in the promotion of tree growth. With the increase of the nitrogen input, available nitrogen may satisfy the requirements for organisms and nitrogen input in the winter dormant season exceeds the requirements. This excess nitrogen resulted in a seasonal (episodic) increase of nitrogen output (Stage 1). Wright et al. (1995) revealed that 10 kg N ha^{-1} yr^{-1} was the minimum threshold for nitrogen saturation. Further increase in nitrogen input induced the export of nitrate even in the growing season (Stage 2). Chronic nitrate leaching may lead to the depletion of base cations. Foliage colour turned yellow due to magnesium deficiency (Krahl-Urban et al., 1988; Hüttl, 1990). Enhanced base cation mobilization may induce an imbalance in nutrients and results in a reduction in plant growth (Abrahamsen, 1980; Nihlgård, 1985; Aber et al., 1989). When the amount of base cations

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was low in the systems, aluminum was mobilized to toxic levels. Large amounts of atmospheric ammonium sulfate (3 kmolc NH_4^+ ha^{-1} yr^{-1} = 52 kg N ha^{-1} yr^{-1}) caused aluminum mobilization in Dutch forest ecosystems (van Breemen et al., 1982). Nitrogen output exceeded the input in the decline phase (Stage 3). Wright et al. (1995) reported that ecosystems would reach this stage when the input became above 25 kg N ha^{-1} yr^{-1}. In addition it was pointed out that increased amount of leaf nitrogen caused a decrease in frost hardiness (Friedland et al., 1984; Soikkeli and Kärenlampi, 1984), an increase in susceptibility to water stress (Aber et al., 1989), and to fungal diseases (Roelofs, 1985).

Measures to lower the sulfur emission has made some progress according to the sulfur protocols of the United Nation's Economic Commission for Europe and European Community's (European Union in present) directive (Freemantle, 1995). After the reduction of sulfur dioxide emissions in Europe, nitrogen cycles were extensively studied in terms of acidification (e.g. Freemantle, 1995; Wright and van Breemen, 1995; Wright and Rasmussen, 1998). Sulfur dioxide emissions have also decreased in Japan since the late 1960s (Japan Environment Agency: JEA, 1996). On the other hand, no decrease in nitrogen oxide concentration in the air have been observed. Baba et al. (1995a) reported the presence of a high nitrogen deposition at the Rolling Land Laboratory (RLL) of the forest experimental station located in the Tama Hill region, Kanto district. Total inorganic nitrogen deposition associated with throughfall was 1.4 - 2.8 kmolc ha^{-1} yr^{-1} (= 20 - 40 kg N ha^{-1} yr^{-1}) which exceeded the nitrogen saturation criteria proposed by Wright et al. (1995). Ohrui (1997) revealed that the forested watershed at Seta, Gunma Prefecture, northern Kanto district had reached nitrogen saturation. However, the effects of nitrogen saturation on abnormal forest growth have not been examined in Japan although it was assumed that frost damage or water stress was the cause of abnormal forest growth (Matsumoto et al., 1992; Yoshitake 1996). Estimate of nitrogen saturation status is essential to elucidate the mechanisms of decline. This Chapter is focused on the effect of nitrogen saturation on acidification.

Long-term monitoring of precipitation, throughfall, and stream water has been carried out on a catchment scale and the elemental budget was estimated. The objective of this study was to estimate i) the stage of nitrogen saturation and ii) the contribution of acidic deposition and nitrogen transformation to acidification based on the determination of elemental budget in a small catchment.

VI-2 *Materials and Methods*

VI-2-1 Study site

RLL is on the fountainhead of the Ohguri River, a branch of the Tama River. The forested area of RLL covers 11.3 ha and the area of the studied catchment covered 2.15 ha (1.55 ha of mixed deciduous forest and 0.6 ha of mixed coniferous forest at an elevation of 148-184 m above sea level). The annual mean temperature and annual precipitation were 14.0 °C and 1780 mm during the period from 1985 to 1994 (Tomizawa et al., 1992; Tomizawa et al., 1995). The major species were oak (*Quercus serrata*) in the deciduous forest and Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) in the coniferous forest. The Tama Hill is a terrace underlain by interglacial marine deposits which emerged from the sea 300,000 to 500,000 years ago. The aeolian volcanic ashes from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji have deposited on the Tama Hill resulting in the formation of thick Andisols. The Andisols, Melanudands and Hapludands, derived from volcanic ash are observed on the flat hill tops and gentle slopes (Okazaki and Matsui, 1990). Meanwhile, Dystrochrepts cover parts of the steep slopes. The chemical and mineralogical properties of Andisols were reported by Okazaki (1989), Baba et al. (1995a), and Chishima and Okazaki (1997). According to Ogura et al. (1986), 53 kg urea was applied to the coniferous forest in 1978. However, they concluded that there were no effects on the stream water chemistry. After that any fertilizers were not applied.

Open bulk precipitation and throughfall were collected using 200 cm^2 polyethylene funnels with 5 L glass bottles in 1990-1992 and with 10 L polyethylene bottles in 1995-1996. Throughfall samplers were set up under the canopy close to the edge of canopy projection. Canopy gaps were negligible or very small. The samplers were set up close to the tree trunk in 1995-1996. Therefore, weighted mean flux was used as the throughfall flux. Samples were collected at least once every two weeks in 1990-1992 and once a month in 1995-1996. Stemflow of Hinoki cypress and oak was collected through spirally rolled and glued vinyl tubes (28 mm in diameter) using 20 L polyethylene collection vessels in 1990-1992 and 200 L vessels in 1995-1996. The stream water was collected at the V-notch weir located at the end of the catchment, which has been installed by Ogura et al. (1986). Water level was automatically recorded at this weir. The discharge rate of water was calculated based on the relationship between water levels and water flux according to the method of Ogura et al. (1986). The weir was replaced in 1992. After 1992, the discharge rate was calculated using equation 1) based on the relationship between water levels and water flux (Figure VI-1);

$$Q = 0.0117 * H^{2.43} \qquad \qquad ...1)$$
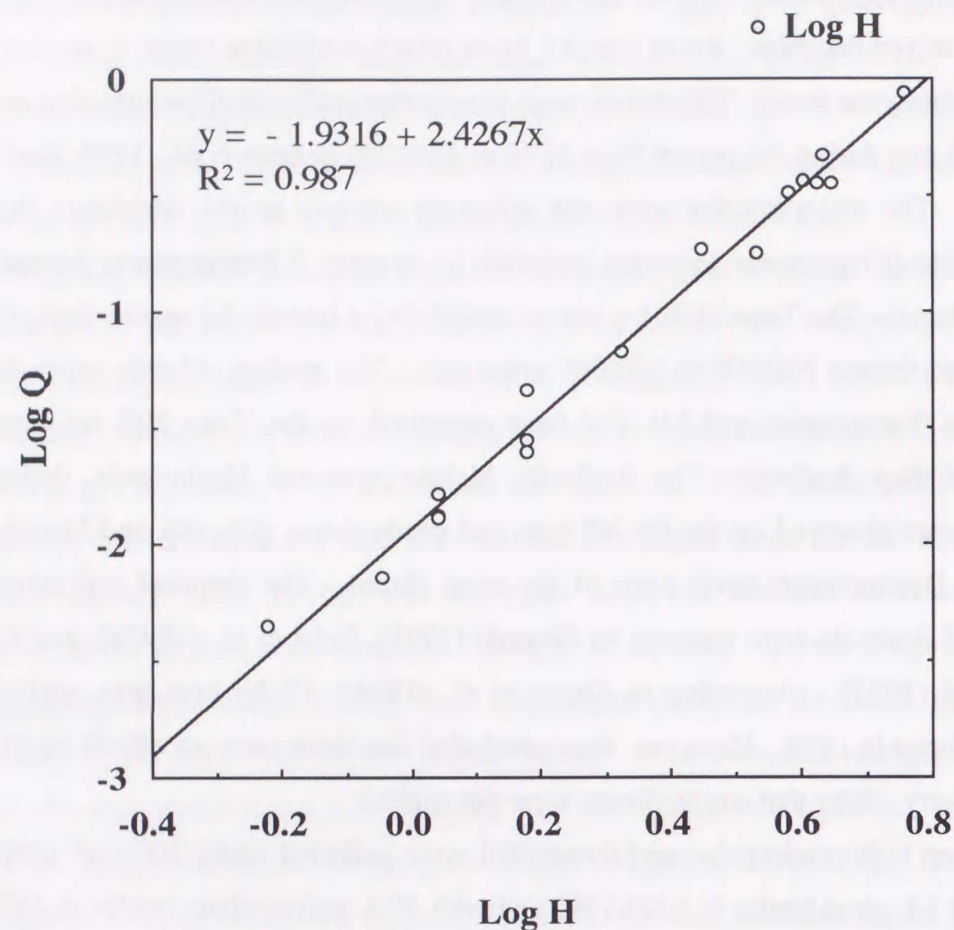
Figure VI-1
Relationship between water level (cm)
and water flux (L Sec⁻¹)

$Q = 0.0117 * H^{2.43}$

Q: Water flux (L Sec⁻¹)

H; Water level (cm)

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Where Q is the water flux in $L\ s^{-1}$ and H is the water level at the V-notch weir (cm).

Water samples were immediately analyzed for the pH and electric conductivity. Subsequently, all the samples were filtered using membrane filters (Millipore 0.45 μm in pore size) and stored at –20 °C. The concentration of nitrate (NO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) were analyzed by ion chromatography (Yokogawa, IC 200 Ion Chromatographic Analyzer). The concentration of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) were determined by atomic absorption spectrophotometry (Shimadzu, 670/AA Atomic Absorption Spectrophotometer). Ammonium (NH_4^+) analysis was performed by colorimetry (Shimadzu, Spectrophotometer UV-140-01) based on the indophenol-blue method. Silica concentration was also measured by colorimetry according to the method of Mullin and Riley (1955).

VI-2-2 Calculation of H⁺ budget and base cation mobilization

Proton budgets associated with N transformation were calculated according to the method of van Breemen et al. (1987). The total acid production caused by proton (H^+), NO_3^-, NH_4^+, SO_4^{2-}, and Cl^- fluxes and mobilization of base cations ($kmolc\ ha^{-1}\ yr^{-1}$) and silicate ($kmol\ ha^{-1}\ yr^{-1}$) were calculated according to the method of Mulder et al. (1987). The equations are as follows;

$$[H^+]load = ([NH_4^+]th - [NH_4^+]out) - ([NO_3^-]th - [NO_3^-]out) \quad ...2)$$

$$[H^+]prod = [H^+]in - [H^+]out + [NH_4^+]th - [NH_4^+]out + [NO_3^-]out -$$
$$[NO_3^-]th + [SO_4^{2-}]out - [SO_4^{2-}]th + [Cl^-]out - [Cl^-]th \quad ...3)$$

$$[H^+]in = [H^+]pr + [H^+]dry \quad ...4)$$

$$[H^+]dry = [SO_4^{2-}]th - [SO_4^{2-}]pr + [NO_3^-]th - [NO_3^-]pr + [NH_4^+]pr -$$
$$[NH_4^+]th \quad ...5)$$

$$[Cat]mob = [Na^+]out - [Na^+]th + [K^+]out - [K^+]pr + [Ca^{2+}]out -$$
$$[Ca^{2+}]pr + [Mg^{2+}]out - [Mg^{2+}]pr \quad ...6)$$

$$[SiO_2]mob = [SiO_2]out - [SiO_2]pr \quad ...7)$$

where "pr" represents the open bulk precipitation input, "th" indicates the throughfall input to the small catchment and "out" indicates the stream water output. Both atmospheric H^+ input ($[H^+]in$) and proton budgets due to N transformation ($[H^+]load$) are the part of $[H^+]prod$.

Throughfall flux corresponded to the sum of the fluxes associated with bulk precipitation, dry deposition, and leaching (or adsorption) as reported by Cape and Lightowlers (1988). In spite of various attempts (e.g. Kobayashi et al., 1995; Takenaka and Win, 1998), it

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still remains difficult to estimate the contribution of each factors to throughfall chemistry. Since the dry deposition of K^+, Ca^{2+}, Mg^{2+}, and silicate is negligible (van Breemen et al., 1989), open bulk precipitation fluxes of these elements were used for the calculation. Average throughfall flux was used for these calculation. Average flux corresponded to the weighted average of throughfall fluxes in coniferous and deciduous forests in the forest areas. Throughfall input under the deciduous forest in 1995-1996 was extrapolated from that under the coniferous forest based on the relationship determined in 1991-1992. Monthly total acid production, mobilization of base cations and silicate were also calculated in 1995-1996.

VI-3 Results and Discussion

VI-3-1 Nitrogen saturation

VI-3-1-1 Precipitation chemistry

Element input from March 15 to March 15 in the following year is represented as annual input in Table VI-1. Nitrate input associated with open bulk precipitation gradually decreased from 0.64 kmolc ha^{-1} yr^{-1} in 1990-1991 to 0.43 kmolc ha^{-1} yr^{-1} in 1995-1996. On the contrary, ammonium input increased from 0.48 kmolc ha^{-1} yr^{-1} in 1990-1991 to 0.63 kmolc ha^{-1} yr^{-1} in 1995-1996. As a result, total inorganic nitrogen input exceeded 1 kmolc ha^{-1} yr^{-1} (= 14 kg N ha^{-1} yr^{-1}). Nitrogen input exceeded the minimum threshold (10 kg N ha^{-1} yr^{-1}) for nitrogen saturation proposed by Wright et al. (1995). Nitrate and ammonium input in 1995-1996 in Shinjuku, Tokyo monitoring station by JEA was 0.61 kmolc ha^{-1} yr^{-1} and 0.64 kmolc ha^{-1} yr^{-1}, respectively (JEA, 1997), the highest values recorded in Japan. Deposition chemistry in Tokyo could be characterized by a high nitrogen input. Since sulfate input associated with open bulk precipitation also tended to decrease, the equivalent ratio of non-sea salt sulfate to nitrate (nss-SO_4^{2-} / NO_3^-: S/N ratio) was stable. The S/N ratio at RLL was 1.1 during the study periods, a value markedly lower than the Japanese average of 2.7 recorded in 1988-1992 and 2.0 in 1995 (JEA, 1994, 1997). High nitrate input was attributed to the non-point source emissions of nitrogen oxides mainly from cars in Tokyo (JEA, 1991, 1996). According to the annual report of the Air Quality Bureau, JEA (1996), the mean sulfur dioxide concentration in the air in 1995 was 0.21 μmol m^{-3} at Katakura, Hachioji, the closest measurement station to RLL, whereas the concentration of nitrogen dioxide was 1.13 μmol m^{-3}. The sum of nitrogen oxide and nitrogen dioxide concentration was 2.25 μmol m^{-3} on average. Air quality affected the deposition chemistry at RLL.

The coniferous throughfall fluxes of nitrate and ammonium were enriched to 2 or 3

Table VI-1 Average throughfall flux of major ions at the Rolling Land Laboratory

	H$^+$	H$_{dry}$*	Cl$^-$	NO$_3^-$	SO$_4^{2-}$ (kmolc ha^{-1} year^{-1})	nss-SO$_4^{2-}$	NH$_4^+$	Ca^{2+}	Mg^{2+}	K$^+$	Na$^+$
Open-bulk											
1990-1991	0.290		0.927	0.635	0.766	0.662	0.482	0.834	0.200	0.0767	0.881
1991-1992	0.398		0.823	0.532	0.710	0.623	0.536	0.501	0.153	0.0626	0.714
1995-1996	0.443		0.376	0.432	0.490	0.472	0.632	0.229	0.0727	0.0921	0.152
Throughfall											
1990-1991	0.0877	0.207	1.63	0.973	1.44	1.36	1.28	1.62	0.680	1.14	0.664
1991-1992	0.235	0.406	1.16	0.651	1.19	1.13	0.727	1.10	0.566	0.812	0.465
1995-1996	0.293	0.404	0.968	0.908	0.827	0.784	1.04	1.14	0.189	0.292	0.356

*: [H$^+$]dry = [SO$_4^{2-}$]th - [SO$_4^{2-}$]pr + [NO$_3^-$]th - [NO$_3^-$]pr + [NH$_4^+$]pr - [NH$_4^+$]th ; th = throughfall, pr = open bulk precipitation; Equation 5

fold compared with those associated with open bulk precipitation. Nitrate input associated with coniferous throughfall ranged from 1.08 $kmol_c$ ha^{-1} yr^{-1} to 1.40 $kmol_c$ ha^{-1} yr^{-1} and the ammonium input ranged from 1.21 $kmol_c$ ha^{-1} yr^{-1} to 1.57 $kmol_c$ ha^{-1} yr^{-1}. On the other hand, fluxes associated with deciduous throughfall were increased by a factor of 2. The input of both ammonium and nitrate was larger than that in other study areas (e.g. Haibara and Aiba, 1982; Shibata and Sakuma, 1996) except for the results at Isogo, an industrial area (Katou, 1996).

Ammonium input correlated well with the nitrate input (R^2 = 0.81, p < 0.001). High ammonium concentration in aerosols was attributed to the formation of ammonium nitrate (Matsumoto and Ogura, 1992). Accordingly, dry deposition from aerosols may have contributed to the large input of nitrate and ammonium at RLL, especially in the coniferous forest.

VI-3-1-2 Stream water chemistry

Anion concentrations and pH values of stream water are shown in Figure VI-2. Sulfate and chloride concentrations were relatively stable, while the nitrate concentrations fluctuated markedly. Stream water pH decreased when the nitrate concentrations increased (R^2 = 0.30, p < 0.001). This episodic acidification was also observed in Noland Divide catchment on the North Carolina and Tennessee border (Nodvin et al., 1995). Changes in pH in the Noland Divide catchment were more conspicuous than at RLL, although the nitrate concentrations were markedly lower than at RLL. Inceptisols have developed on sandstone composed of quartz and potassic feldspar in the Noland Divide catchment. On the other hand, at RLL, Andisols developed on basaltic volcanic ashes. Differences in base cation content might be attributed to the difference in the pH of stream water. The Noland Divide catchment has been saturated with nitrogen and was classified into Stage 2 of nitrogen saturation. Elevated nitrate leaching contributed to both chronic and episodic acidification (Nodvin et al., 1995). Ulrich (1986) stated nitrate leaching is the most powerful source of soil acidification. Aber et al. (1989) postulated that increases in base cation mobilization induced a nutrient imbalance resulting in a forest decline. Abrahamsen (1980) revealed that atmospheric nitrogen promoted plant growth in Norwegian nitrogen deficient ecosystems. He pointed out the imbalance of nutrients may lead to the decrease of plant production. Kolling et al. (1997) reported that nitrogen application induced a decrease in the concentration of soil magnesium resulted in magnesium deficiency for leaves (yellowing).

The water discharge depended on rainfall (Figure VI-3, R^2 = 0.81, p < 0.001). Since annual period is from March 15 to March 15 in the following year in this study, March in
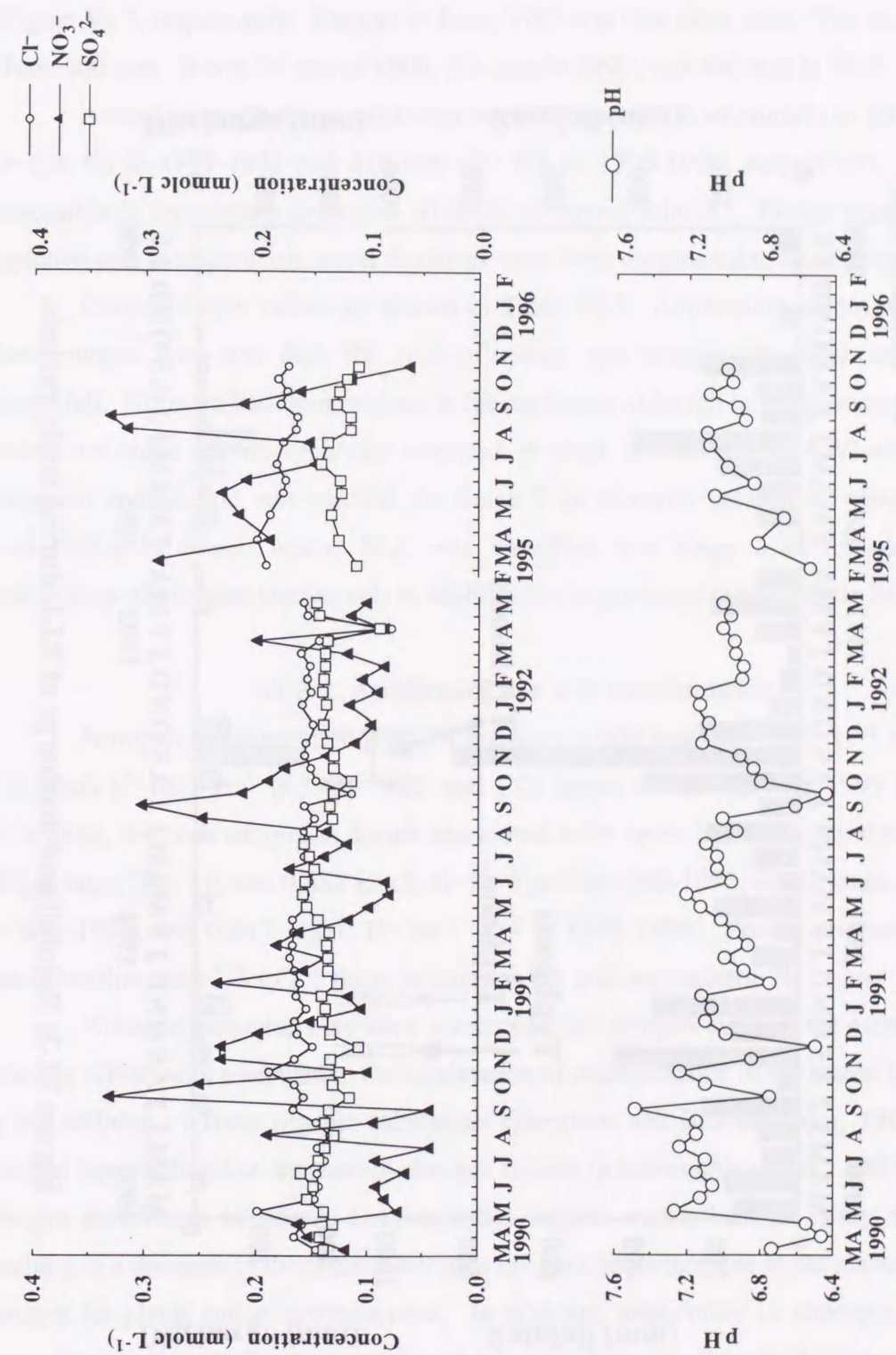
Figure VI-2: Changes in anion concentration and pH values of stream water.
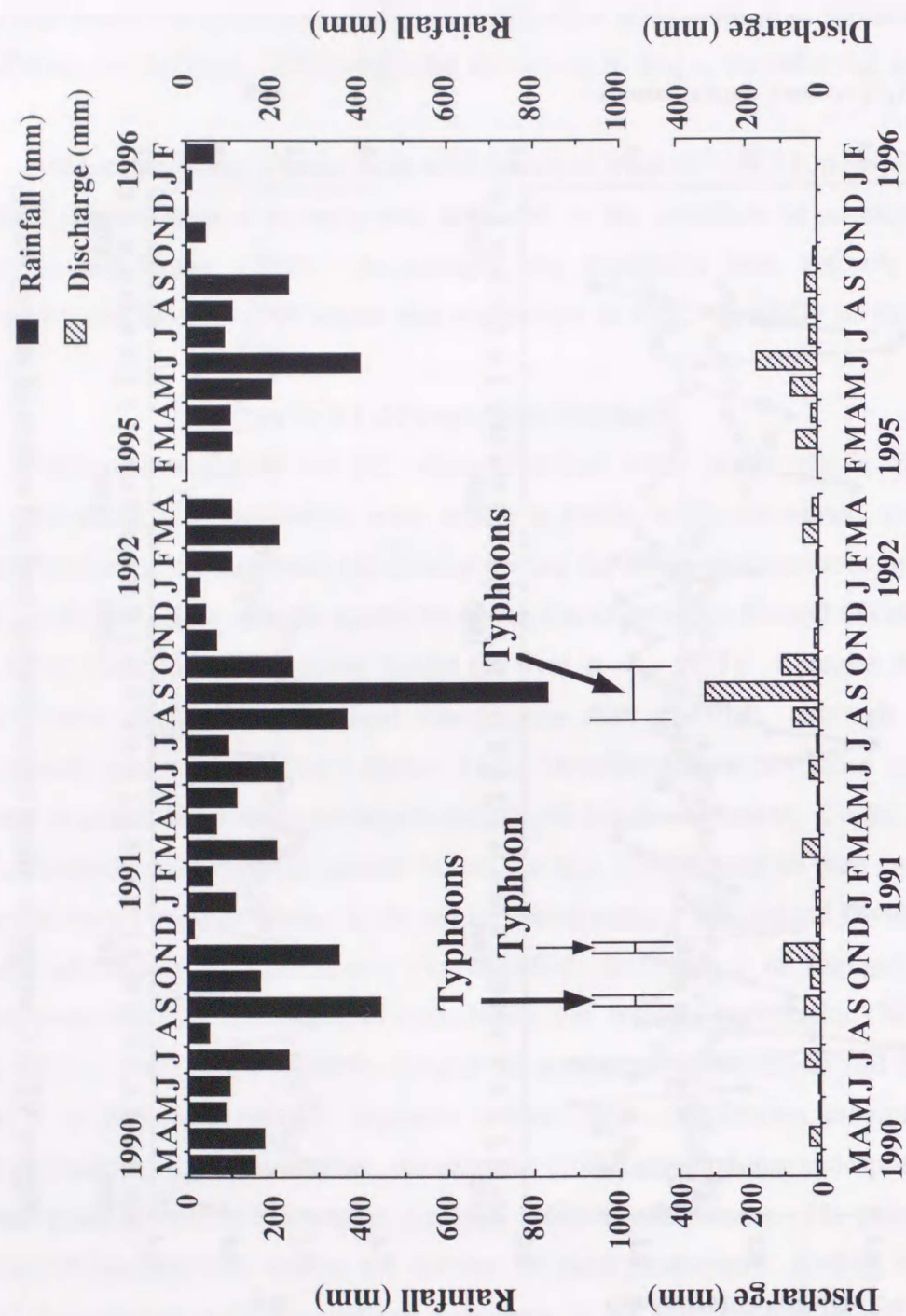
Figure VI-3: Rainfall and discharge at RLL during study periods.

Figure VI-3 is from March 15 to April 15. Fist half of October in 1990 and first half of December in 1990, which typhoon(s) affected, was included in September and October in 1990 in Figure VI-3, respectively. Rainfall in June, 1995 was first rainy term. The average rainfalls in June 200 mm. It was 94 mm in 1990, 220 mm in 1991, and 390 mm in 1995.

Annual water discharge rates were was 295 mm (15 % of rainfall) in 1990-1991, 606 mm (25 %) in 1991-1992 and 410 mm (30 %) in 1995-1996, respectively (Table VI-2). Evaporation in open space amounted 40-60 % of annual rainfall. Taking transpiration from vegetation into consideration, water discharge rates were considered to be adequate.

Element output values are shown in Table VI-3. Ammonium output was negligible. Nitrate output was less than the sum of nitrate and ammonium input associated with throughfall. Nitrogen had been retained in the catchment although large amounts of nitrate had leached out when several typhoons occurred at short intervals (Figure VI-4). The forest ecosystem at RLL has not reached the Stage 3 of nitrogen saturation. Based on nitrate concentration in stream water, RLL was classified into Stage 2 of nitrogen saturation. Contribution of nitrogen compounds to acidification is examined quantitatively below.

VI-3-2. Acidification due to N transformation

Nitrogen transformation [Eq. 2)] provided 0.909 kmolc H^+ ha^{-1} yr^{-1} in 1990-1991, 1.24 kmolc H^+ ha^{-1} yr^{-1} in 1991-1992, and 1.08 kmolc H^+ ha^{-1} yr^{-1} in 1995-1996. On the other hand, the sum of proton inputs associated with open bulk precipitation and average $[H^+]_{dry}$ input [Eq. 4)] was 0.437 kmolc H^+ ha^{-1} yr^{-1} in 1990-1991, 0.804 kmolc H^+ ha^{-1} yr^{-1} in 1991-1992, and 0.847 kmolc H^+ ha^{-1} yr^{-1} in 1995-1996. Proton production due to N transformation were 1.3 to 2.1 times as much as the total atmospheric H^+ input.

Nitrogen saturation may have accelerated the nitrogen cycle in the ecosystems. This "priming effect" was attributed to the acceleration of mineralization of the stable humus in soils by the addition of fresh organic substances (Harmsen and Kolenbrander, 1965). Elevated nitrogen input induced an increase in nitrogen content in leaves (Aber et al., 1989), resulting in nitrogen enrichment in litter. Consequently, organic matter became easily decomposable, resulting in a decrease in the organic nitrogen pool and in an increase in the amount of available nitrogen for plants and microorganisms. In addition, ammonium in atmospheric deposition may stimulate the nitrification activity which contributes to the nitrification of mineralized nitrogen.

During the nitrification process, a portion of nitrogen may be removed to the atmosphere as nitrous oxide under aerobic conditions (Minami, 1990; Yoh and Minami, 1991).

Table VI-2 Annual rainfall and water discharge rate from the subcatchment of the Rolling Land Laboratory

	Annual rainfall (mm)	Annual water discharge (mm)	Evaporation (mm)
1990-1991	1918.8	295.1 (15.4)	1118.0 (58.3)
1991-1992	2397.9	605.6 (25.3)	895.0 (37.3)
1995-1996	1357.1	409.8 (30.2)	820.4 (60.5)

Parentheses represent the respective percentage of water discharge and evaporation to annual rainfall.

Table VI-3 Annual stream water output of major ions and silica from the subcatchment of the Rolling Land Laboratory

	H^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	SiO_2
				(kmolc ha^{-1} year^{-1})						(kmol ha^{-1} year^{-1})
1990-1991	0.000547	0.458	0.598	0.371	0.000148	0.766	0.758	0.0162	0.444	
1991-1992	0.00131	0.849	1.18	0.788	0.0115	1.47	1.34	0.0421	0.847	
1995-1996	0.000599	0.745	0.951	0.512	0.000873	1.12	1.14	0.0202	0.699	1.60
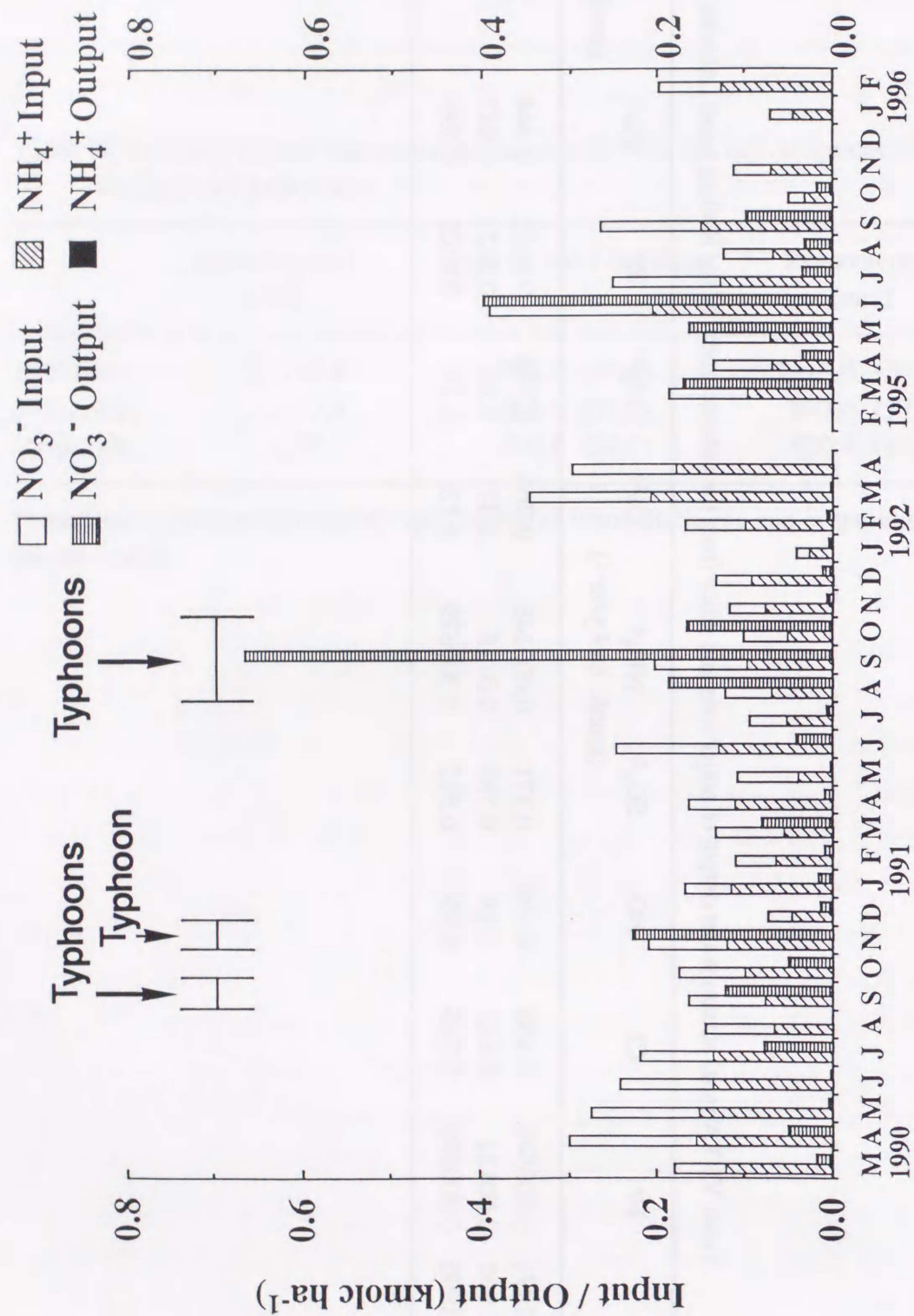
Figure VI-4: Nitrogen budget at RLL.

NH_4^+ Input
NH_4^+ Output
NO_3^- Input
NO_3^- Output

Typhoons
Typhoons
Typhoon
Typhoons
Typhoon

Input / Output (kmolc ha^{-1})

MAMJJASONDJFMAMJJASONDJFMAMJJASONDJFMA FMAMJJASONDJF
1990   1991   1992   1995   1996

Minami (1990) revealed that 0.1 - 0.5 % of nitrogen fertilizers released to the atmosphere. Based on their evaluation, most of the ammonium ions derived from atmospheric deposition could be transformed into nitrate ions with proton production. Baba et al. (1995a) suggested that nitrate ions in the soil solution at RLL were derived from nitrification and provided protons contributed to soil acidification. The importance of nitrogen in atmospheric deposition for the proton load was quantitatively confirmed based on elemental budget.

As for the denitrification, no data were available for estimating how the increase of nitrogen input affected the denitrification process although denitrification potential in the water saturated zone at RLL was estimated (Konohira et al., 1997) and calculation showed that 34 $\mu molc\ L^{-1}\ day^{-1}$ of nitrate in the soil solution was denitrified. If stream water passed through this saturated zone before flowing out, the nitrate concentration could be reduced by denitrification. Based on annual discharge of stream water (Table VI-2) and denitrification rate, an amount of 0.1 - 0.2 $kmolc\ NO_3^-\ ha^{-1}\ yr^{-1}$ was removed with H^+ consumption. Further information would be necessary to estimate effect of nitrogen saturation on the denitrification process.

Various factors affected nitrogen cycle as mentioned above. Gundersen and Rasmussen (1990) reviewed the contribution of nitrogen in atmospheric deposition to the proton budget. Nitrogen transformation provided large amounts of proton and it was an important acid source at RLL.

The total acid production which was calculated by equation 3), was −0.868 $kmolc\ H^+\ ha^{-1}\ yr^{-1}$ in 1990-1991, 1.34 $kmolc\ H^+\ ha^{-1}\ yr^{-1}$ in 1991-1992, and 1.39 $kmolc\ H^+\ ha^{-1}\ yr^{-1}$ in 1995-1996. Proton production due to N transformation accounted for the main portion of the total acid production. The total acid production in 1990-1991 was significantly lower than the proton production due to N transformation. Sulfate output in 1990-1991 was 0.371 $kmolc\ ha^{-1}\ yr^{-1}$ (Table VI-3) which was less than half of sulfate input associated with open bulk precipitation (Table VI-1). Andisols at RLL have large sulfate adsorption capacity (Baba et al., 1995a, 1995b: Chapter III). Sulfate output was larger in 1991-1992 and in 1995-1996 than the open bulk precipitation input, but lower than the throughfall input. The discharging rate (output / input) of sulfate was remarkably lower than that of chloride and nitrate. Heavy rainfall caused by several typhoons in 1991-1992 removed the adsorbed sulfate and typhoons prevented soil from being saturated with sulfate (Figure VI-5A). The large sulfate output in 1995-1996 was attributed to the export of sulfate in June when 30 % of annual rainfall was occurred and water discharge reached 40 % of the annual discharge. Sulfate adsorption at RLL contributed to the buffer reaction (Yoshida and
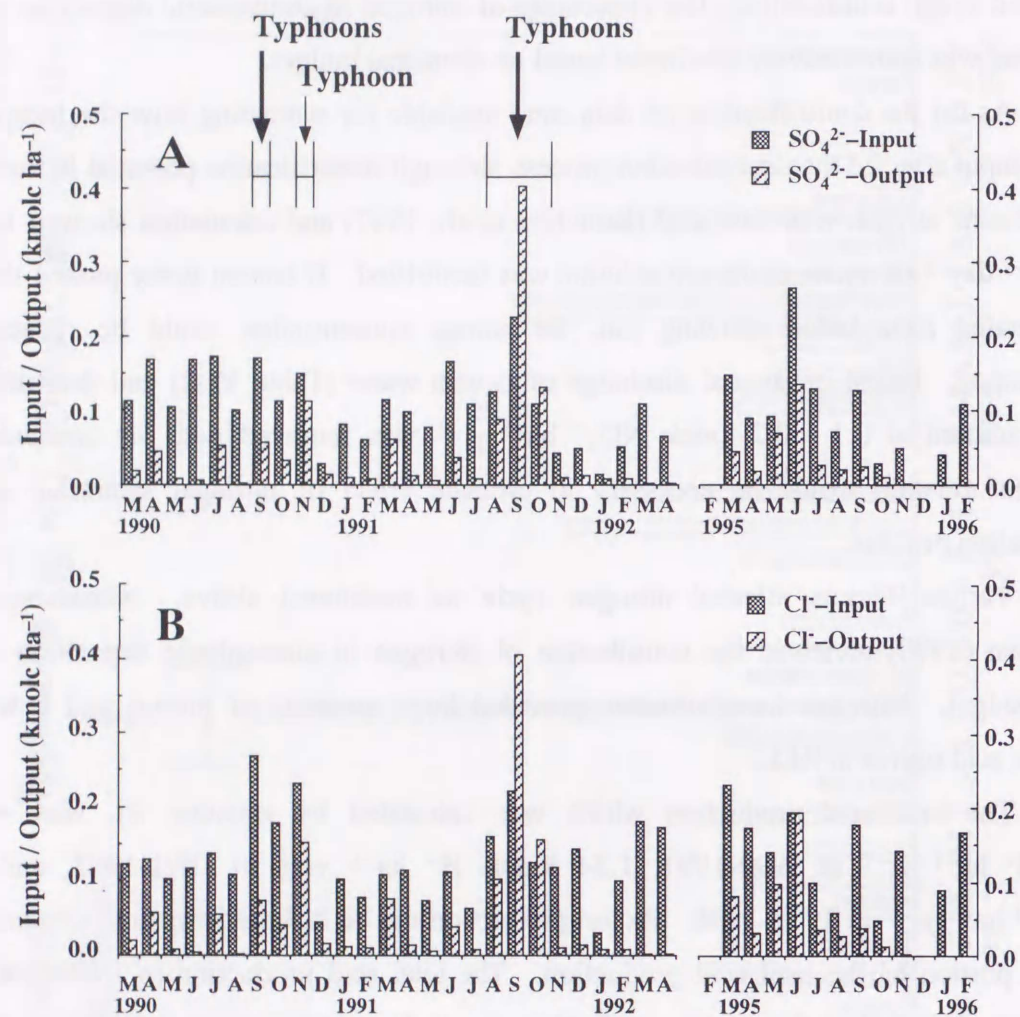
Figure VI-5: Sulfate and chloride budgets at RLL.
A: Sulfate, B: Chloride

Kawahata, 1988) and mitigated to accelerate acidification.

Chloride output also increased when typhoons came across (Figure VI-5B). Simultaneously, typhoons enhanced cation mobilization, calcium and magnesium output increased when they occurred (Figure VI-6). Sodium output also increased, although it was quantitatively smaller than calcium and magnesium output (Figure VI-6C). Annual potassium output was markedly lower than other base cation outputs (Table VI-3) and its monthly output was 0.027 kmol$_c$ ha^{-1} (not shown in Figure), which was larger than annual potassium output in 1990-1992 and 1995-1996 (Table VI-3).

Excess nitrogen relative to the requirements of plants and microorganisms is likely to be exported and to contribute to the mobilization of base cations. Tamm et al. (1995) revealed that an increase in additional amounts of nitrogen induced a decrease in the Ca^{2+} and Mg^{2+} content in the soil, while the contents in the trees were also inversely proportional to N addition. Cronan (1985) reported that the weathering rate increased with the increase in acid input. On the other hand, base cation weathering rates were independent of the acid load in Dutch Spodosols where weatherable base cations were extremely depleted and aluminum mobilization was the main acid sink (Mulder et al., 1989). When the depletion rate of exchangeable base cations was higher than the weathering rate, soil acidification accelerated. Monthly cation mobilization [Eq 6)] was proportional to the total acid production [Eq 3)] ($R^2 = 0.96$, $p < 0.001$: Figure VI-7A), that is, mobilization of base cations was the main acid sink. Monthly mobilization of base cations in 1995-1996 was well correlated with silica mobilization [Eq 7)] ($R^2 = 0.99$, $p < 0.001$: Figure VI-8) which was proportional to calcium mobilization ($[Ca^{2+}]_{out} - [Ca^{2+}]_{pr}$), magnesium mobilization ($[Mg^{2+}]_{out} - [Mg^{2+}]_{pr}$), and sodium mobilization ($[Na^{+}]_{out} - [Na^{+}]_{th}$), respectively (Figure VI-9). Silica mobilization was also correlated with the total acid production (Figure VI-7B). Acid input influenced the weathering rate at RLL in contrast to the Dutch forest, presumably due to the basaltic volcanic ashes which contain large amounts of easily weatherable primary minerals. Volcanic ashes in the southern Kanto district are mainly derived from Mt. Fuji which is rich in olivine, pyroxene, and anorthite (Ohkura et al., 1993). Soil pH values at RLL ranged from 4.6 to 6.0 (Baba et al., 1995a; Chishima and Okazaki, 1997), which corresponded to the silicate buffer range and cation exchange buffer range (Ulrich, 1986). Exchangeable base cations acted as intermediate response reservoir and were replenished by weathering (Cronan, 1985). Both ion exchange and weathering contributed to the buffer reaction.

Tsurumi and Ichikuni (1989) analyzed stream water chemistry in the mountainous areas at the fountainhead of Tama River and its branches. Nitrate concentration in the Hachioji
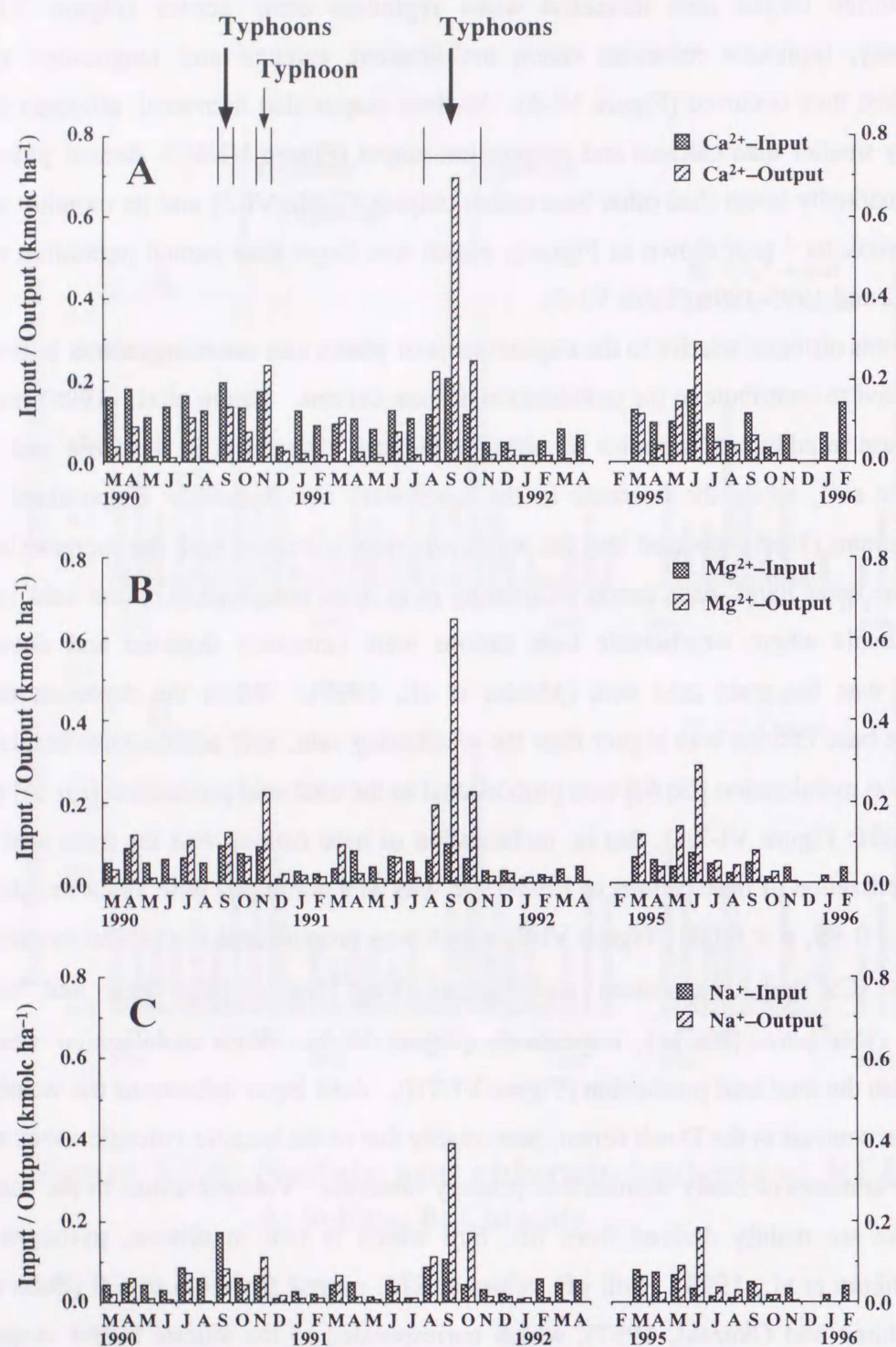
Figure VI-6: Cation budgets at RLL.
A: Calcium, B: Magnesium, and C: Sodium
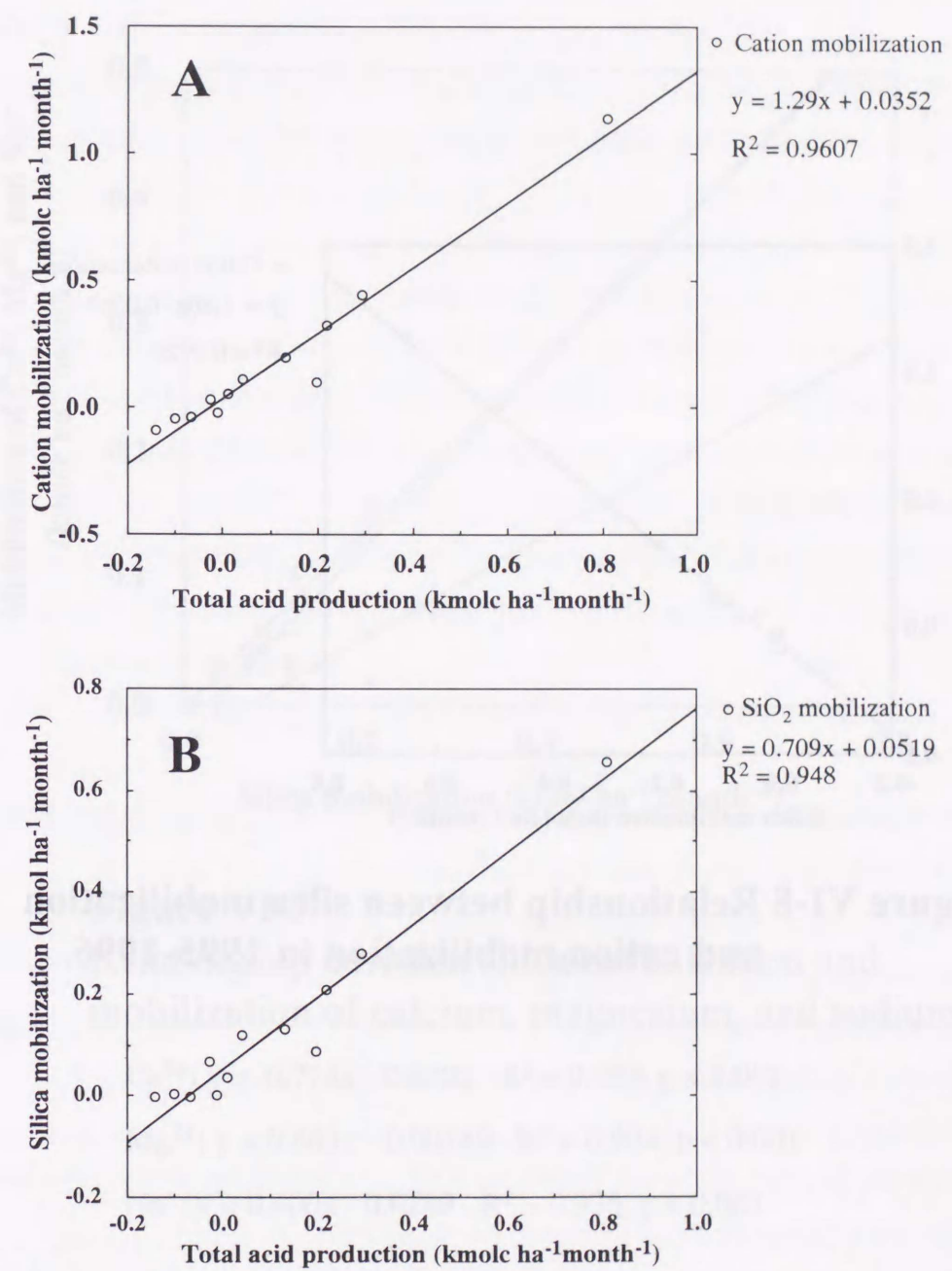
Figure VI-7: Relationship between total acid production and cation mobilization (A) and between total acid production and silica mobilization (B) in 1995-1996.

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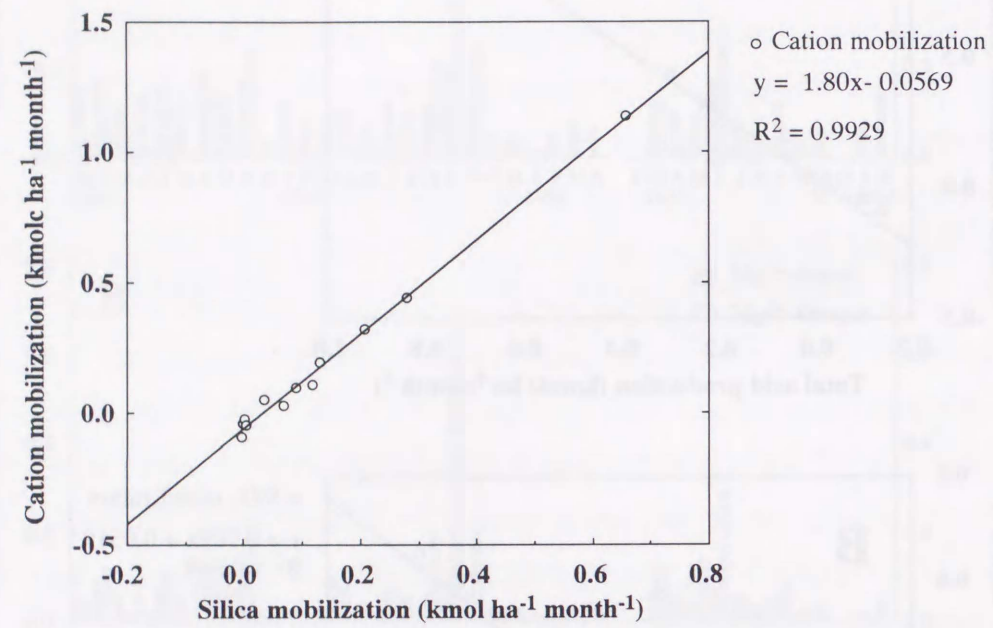
Figure VI-8 Relationship between silca mobilization and cation mobilization in 1995-1996.

Legend on figure:
o Cation mobilization
y = 1.80x - 0.0569
$R^2 = 0.9929$

X-axis: Silica mobilization (kmol ha^{-1} month^{-1})
Y-axis: Cation mobilization (kmolc ha^{-1} month^{-1})
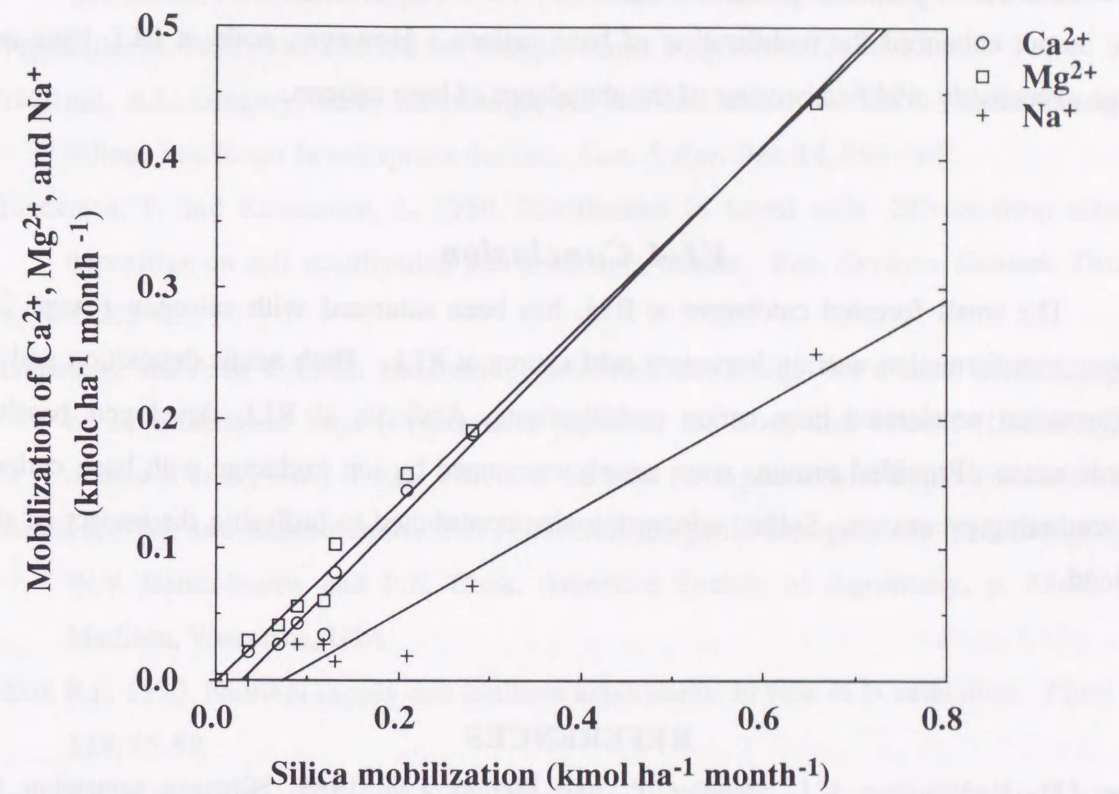
Figure VI-9
Relationship between silica mobilization and
mobilization of calcium, magnesium, and sodium.

Ca^{2+}: y = 0.716x - 0.0202 $R^2 = 0.989$, p < 0.001

Mg^{2+}: y = 0.683x - 0.00149 $R^2 = 0.994$, p < 0.001

Na^+: y = 0.400x - 0.0289 $R^2 = 0.930$, p < 0.001

Legend on figure:
o Ca^{2+}
□ Mg^{2+}
+ Na^+

X-axis: Silica mobilization (kmol ha^{-1} month^{-1})
Y-axis: Mobilization of Ca^{2+}, Mg^{2+}, and Na^+ (kmolc ha^{-1} month^{-1})

area was higher than that around the Okutama lake. They concluded that the elevated nitrate concentration was due to the anthropogenic nitrogen in atmospheric deposition, suggesting that forest ecosystems in these areas had undergone nitrogen saturation. The small forested catchment at RLL has also been saturated with nitrogen. High concentration of nitrogen compound in the air promoted a large nitrogen input resulting in nitrogen saturation. Increased nitrate output enhanced the mobilization of base cations. However, soils at RLL have not become excessively acidified because of the abundance of base cations.

VI-4 Conclusion

The small forested catchment at RLL has been saturated with nitrogen (Stage 2). Nitrogen transformation was an important acid source at RLL. Both acidic deposition and N transformation accelerated base cation mobilization. Andisols at RLL developed basaltic volcanic ashes. Provided protons were mainly consumed by ion exchange with base cations and weathering processes. Sulfate adsorption also contributed to buffering the impact of the acid load.

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Chapter VII

General Discussion

Japan Environment Agency (1989, 1994) stated that there were no symptoms of forest decline due to acidic deposition. Precipitation pH values in Japan are almost in the same range as Europe and North America where acidic deposition has severely affected the forest ecosystems. Large acid neutralizing capacity of the soils is one of the factors in differences in responses to acidic deposition. Recently nitrogen saturation is also pointed out as an important factor which govern the forest response (Aber *et al.*, 1989). Atmospheric nitrogen deposition benefited forest ecosystems when available nitrogen compounds were limited (Abrahamsen, 1980). Additional atmospheric nitrogen deposition resulted in an increase in foliar nitrogen content and an increase in foliar biomass, resulting in the promotion of tree growth. However, increased amounts of leaf nitrogen caused a decrease in frost hardiness (Friedland et al., 1984; Soikkeli and Kärenlampi, 1984) and an increase in susceptibility to water stress (Aber et al., 1989) and to fungal diseases (Roelofs, 1985). Frost damage or water stress has been speculated as the cause of abnormal forest growth in Kanto district (Matsumoto et al., 1992; Yoshitake 1996). Therefore, estimate of nitrogen saturation status is essential to elucidate the mechanisms of decline.

The weighted mean pH values of open bulk precipitation at RLL were 4.5-4.8. This was the same range as the results by Japan Environment Agency (1994, 1997). Annual proton input was comparable to those in Europe and North America, taken between polluted sites and reference sites. Nitrogen input was relatively high at RLL compared to the results by the Japan Environment Agency. The S/N (nss-SO_4^{2-} / NO_3^-) ratio was significantly lower than that of the Japanese average. High nitrate input were attributed to the non-point source emissions of nitrogen oxides in Tokyo (Japan Environment Agency, 1991). Although emission sources in this region are not clear, ammonium input correlated well with nitrate input ($R^2 = 0.81$, p < 0.001). High ammonium concentration in aerosols was attributed to the formation of ammonium nitrate (Matsumoto and Ogura, 1992). As a result, total inorganic nitrogen input exceeded 1 kmol$_c$ ha^{-1} yr^{-1} which exceeded the minimum threshold for nitrogen saturation proposed by Wright *et al.* (1995).

Nitrate and ammonium was enriched in throughfall and stemflow, especially in the coniferous forest. The crown of coniferous trees could intercept large amounts of air pollutants. The total nitrogen input associated with the coniferous throughfall exceeded 2 kmol$_c$ ha^{-1} yr^{-1} and reached 3 kmol$_c$ ha^{-1} yr^{-1} in maximum. Nitrogen output is substantial in this range (Wright *et al.*, 1995). Nitrogen input in deciduous forest, 1.0-1.8 kmol$_c$ ha^{-1} yr^{-1}, was in the range to undergo a transition to nitrogen saturation. Based on nitrogen budget and

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nitrate concentration in stream water, the forest ecosystem at RLL was classified into Stage 2 of nitrogen saturation (Stoddard, 1994). Proton production due to N transformation was significantly higher than atmospheric proton input. Accordingly, N transformation was the most important acid source at RLL.

Nitrogen saturation is an important factor to plant growth. Therefore, it is the key to estimating the effects of acidic deposition on forest ecosystems. Blow down of Hinoki cypress due to typhoons in 1996 would induce a decrease in nitrogen retention, undergoing nitrogen saturation. In march 1996 the forest catchment at RLL have not reached Stage 3 of nitrogen saturation which was presumed that forest decline would occur (Aber et al., 1989). It was verified that atmospheric deposition contributed to nitrogen saturation and coincidently to soil acidification. However, effects of these factor on plant growth still remained controversial.

Total acid production, base cation mobilization, silicate mobilization were estimated after Mulder et al. (1987). Base cation mobilization was the main acid sink at RLL. Monthly cation mobilization was proportional to the total acid production ($R^2 = 0.96$, $p < 0.001$) and to silicate mobilization ($R^2 = 0.99$, $p < 0.001$). This would be attributed to the basaltic volcanic ashes which abundant in easily weatherable primary minerals. Volcanic ashes in the southern Kanto district are mainly derived from Mt. Fuji which abundant in olivine, pyroxene and anorthite (Ohkura et al., 1993). Soil pH values at RLL ranged from 4.6 to 6.0 (Baba et al., 1995; Chishima and Okazaki, 1997). This was represented the silicate buffer range and the cation exchange buffer range (Ulrich, 1986). Exchangeable base cations acted as the intermediate response reservoir and were replenished by weathering (Cronan, 1985). Both ion exchange and weathering contributed to the buffer reaction. In addition, sulfate adsorption, which was the important acid buffer reaction in Andisols, also mitigated the impact of acid load at RLL.

The soil acidification processes were estimated based on the field data. Different acidity of soil (solution) and spatial variability around tree trunks were focused to verify the acid buffering system of Andisols which was classified as the soils having high tolerance to acid substances.

Differences in H^+ and NH_4^+ input under the coniferous forest and the deciduous forest contributed to soil (solution) acidity. The soils under the coniferous forest was acidified compared with those under the deciduous forest. Calcium and magnesium was the codominant cation species in soil solution taken at the depth of 10 cm at the reference site under the coniferous forest. Aluminum was dissolved into soil solutions when nitrate concentration markedly increased. The soil solution pH was inversely proportional to NO_3^- concentration in

soil solution, because nitrification simultaneously produced large amounts of protons. When nitrification was accelerated in the summer, excess protons contributed to a decrease in pH below 5.0 and induced aluminum dissolution. Aluminum dissolution was negligible under the deciduous forest although NO_3^- concentration were higher than those under the coniferous forest. The input of nitrate and ammonium associated with the deciduous throughfall was half and three quarters of those under the coniferous forest, respectively. Accordingly, the produced amount of nitrate ions due to nitrification under the deciduous forest was larger than that under the coniferous forest. Simultaneously protons were produced by nitrification. Nevertheless, soils under the coniferous forest were more acidic than those under the deciduous forest. It was reflected by the difference of canopy functions; interception capacity of acid substances, reaction of foliage against acid substances, and so on. The coniferous canopy trapped larger amount of acid substances in atmospheric deposition than the deciduous canopy. On the other hand, the acidity at the deciduous canopy was neutralized by the excretion of base cations from the foliage and/or assimilation of nitrogen. Imbalance of elemental input induced the difference in soil solution chemistry. In other words, the differences in soil properties under the coniferous forest and the deciduous forest is attributed to the differences in supplied amount of acid substances.

Acidic stemflow which enriched with H^+ and NH_4^+, promoted soil (solution) acidification around the bases of tree trunks. Based on spatial variability of soil solution chemistry, soil solution acidification processes were divided into 4 stages. Soil solution pH values were above 5 at Stage i) and aluminum was not dissolved but Ca^{2+} and Mg^{2+} dominated. This stage corresponded to the silicate buffer range (Ulrich, 1986). The pH values of soil solution at the depth of 50 cm and stream water were above 5. The results of elemental budget in catchment scale were consistent with this phase. When pH became below 5, aluminum ions were dissolved in the soil solution. However, Ca^{2+} and Mg^{2+} were dominant cation species [Stage ii)]. The Stages ii) and iii) corresponded to the exchanger buffer range (Ulrich, 1986). Aluminum became the codominant cation species in Stage iii) with decrease in Ca^{2+} concentration and aluminum concentration exceeded 0.2 mmolc L^{-1}, which was applied to estimate the critical load of acidic deposition (de Vries et al., 1995; Shindo et al., 1995). The pH range of this stage was 4.2 - 4.4. Soil solution pH became less than 4.2, aluminum dissolution became a dominant acid sink [Stage iv)], which corresponded the aluminum buffer range named by Ulrich (1986). Dissolution of aluminum and/or base cations were proportional to NO_3^- concentration. It indicated that nitrogen was not retained but leached out with cations. In other words, it was verified that nitrogen leaching promoted soil acidification.

The molar (Ca+Mg+K)/Al ratio or Ca/Al ratio (< 1) were also used as the criteria. The molar (Ca+Mg+K)/Al of Stage iii) and iv) was significantly decreased compared with Stages i) and ii). The lowest value (1.71) was obtained in Stage iv). In the case of Ca/Al ratio, the lowest average was 0.77. However, no visible symptoms of forest decline have been observed at RLL. de Vries et al. (1995) concluded that excess over critical limits, which was estimated from the results obtained in laboratory experiments in relation to the effects on root (uptake), was not associated with actual forest decline. Falkengren-Grerup et al. (1995) pointed out the difficulty to apply the evidence from laboratory experiments to the field conditions, because many complex factors affected plant growth. Complexation with organic matter, for example, contributes to reduce aluminum toxicity. Based on spatial variability of soil aluminum pools, amorphous aluminum was the primary source of soil solution aluminum at RLL. Dissolved aluminum ions were substituted with base cations of soils which resulted in exchangeable Al increases and/or complexed with organic matter which increased organically bound Al pools. Exchangeable sites have been almost occupied with aluminum, especially under the coniferous forest. Shoji *et al.* (1982) and Parfitt and Saigusa (1985) revealed that the formation of allophane and imogolite was related primarily to the soil acidity and that it occurred only in soils having pH (H_2O) > 4.9. When pH is less than 4.9, aluminum was preferentially bound by humic substances. Increases in organically bound Al with a decrease of soil pH agree with their finding. Based on batch experiments, Berggren and Mulder (1995) revealed that when the pH < 4.1 aluminum solubility was explained both qualitatively and quantitatively by equilibrium complexation with soil organic matters. Aluminum solubility was not only governed by pH but also activities of inorganic aluminum and dissolved organic carbon concentration. At RLL, dissolved aluminum ions from allophane could be speculated to be controlled by complexation with soil organic matters, which would contribute to reduce aluminum toxicity

Acidic deposition with high nitrogen induced nitrogen saturation and promoted soil acidification. Nitrogen transformation was the most effective acid source in nitrogen saturating forest ecosystems. On the other hand, base cation mobilization was the major acid sink. Geological features governed the response to acidic deposition at RLL. Basaltic volcanic ash derived from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji had been deposited on the Tama Hills resulting in the formation of thick Andisols. Andisols at RLL are abundant in i) base cations which contribute to the consumption of protons by substitution and ii) allophane which contributes to the buffer reaction especially in low pH range. Andisols have large sulfate

adsorption capacity which mitigates the impact of acidic deposition.

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Chapter VIII

Conclusion

Conclusion

Precipitation chemistry at RLL was characterized by high nitrogen input, which enough to induce nitrogen saturation. In fact, the forest ecosystem at RLL was classified into Stage 2 of nitrogen saturation based on nitrate concentration in stream water and nitrogen budget. Nitrogen transformation was the most effective acid source. On the other hand, base cation mobilization was the most important acid sink. Both ion exchange and weathering contributed to buffer reaction in soil (solution) pH range above 5. Geological features governed the response to acidic deposition at RLL. Basaltic volcanic ashes, which were derived from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji, contained Ca^{2+} and Mg^{2+} abundantly, deposited on the Tama Hills resulting in the formation of thick Andisols. Aluminum ions were dissolved exponentially into solution below pH 5. Amorphous aluminosilicate, allophane, was the primary source of soil solution aluminum at RLL. Ion exchange with Ca^{2+} and Mg^{2+} was still main acid buffer reaction till pH 4.4. Exchangeable aluminum increased with a decrease in pH levels. When soil solution pH decreased below 4.4, aluminum concentration exceeded 0.2 mmolc L^{-1}, which were comparable to Ca^{2+}, Mg^{2+} concentration. Soils in this stage could be called the acidified soil. When soil solution pH became less than 4.2, aluminum dissolution was the main acid sink.

The total aluminum concentration exceeded the critical limit. Although effects of nitrogen saturation and/or soil acidification on plant growth still remained controversial, increased organically bound aluminum suggested that aluminum ions were complexed with organic matter which would contribute to reduce aluminum toxicity. The comprehensive monitoring studies are essential to elucidate the relationship between soil acidification and forest vitality. Investigation on spatial variability of soil (solution) chemistry should be useful to estimate the impacts of soil (solution) acidification on plant growth, because soils around the trunk bases are the most suitable rhizosphere to elucidate the effects.

Acidic deposition at RLL promoted soil acidification through nitrogen saturation. Acidification processes in relation to buffering systems were elucidated based on the field data. Andisols at RLL are abundant in i) base cations which contribute to the consumption of protons by substitution and ii) allophane which contributes to the buffer reaction especially in low pH range. Andisols have the large sulfate adsorption capacity which mitigates the impact of acidic deposition. Cation mobilization was quantitatively the most important acid sink at RLL at present. These buffering systems alleviated the effect of acidic deposition and increase in acidification.

Summary

Acidic precipitation has been observed in Japan. The cause of the decline of Japanese forests remains controversial. Responses of the forest ecosystem to acidic deposition are dependent on soils and on the nitrogen saturation status. Field data on soil acidification and/or nitrogen saturation are insufficient to estimate their contribution to forest decline in Japan. Continuous monitoring studies on open bulk precipitation, throughfall, stemflow, soil solution, and stream water were conducted at the Rolling Land Laboratory (RLL) of the forest experimental station located in the Tama Hills in Central Japan. The objectives of this study are

i) to investigate acidic deposition and characterize its chemistry,

ii) to estimate the effects of nitrogen saturation at RLL based on stream water chemistry and elemental budgets,

iii) to elucidate the soil (solution) acidification due to acidic deposition based on spatial variability of soil (solution) chemistry,

and finally

iv) to examine effects of nitrogen saturation and soil acidification on forest vitality.

Soil type at RLL was Hapludand, Andisol. The aeolian volcanic ashes from Mt. Hakone, Mt. Yatsugatake, and Mt. Fuji have deposited on the Tama Hill resulting in the formation of thick Andisols. Andisols have the large proton adsorptive capacity. Aluminum, however, is easily dissolved from Andisols when soils were acidified. Soil and soil solution samples were taken at various distances from trunk bases of the Hinoki cypress (*Chamaecyparis obtusa*) and at various depths.

The weighted mean pH values of open bulk precipitation was 4.5-4.8. Proton input asociated with open bulk precipitation was 0.30-0.44 kmol$_c$ ha^{-1} yr^{-1}. High nitrogen input resulted in a lower S/N ratio (ratio of non-sea salt sulfate to nitrate). The high nitrate input was attributed to the high nitrogen oxide gas concentration in the air, which is derived from the non-point sources. Coniferous canopies intercept large amounts of acidic substances. Consequently, coniferous throughfalls and stemflows were high in protons and ammonium ions. High nitrogen contents in acidic deposition induced nitrogen saturation.

The forested catchment at RLL was classified into Stage 2 of nitrogen saturation. Nitrogen transformation was the most effective acid source. The stream water pH decreased when the nitrate concentration increased. Proton production due to nitrogen transformation $(=\{[NH_4^+]_{th}-[NH_4^+]_{out}\}-\{[NO_3^-]_{th}-[NO_3^-]_{out}\})$ was 1.28 kmol$_c$ ha^{-1} yr^{-1} in 1995-1996 which was 1.3 times as much as the total atmospheric proton input. Sulfate adsorption

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mitigated the impact of the acid load.

Soil (solution) acidification processes were divided into 4 stages as follows;

Stage i) pH > 5.0: Both ion exchange and weathering contributed to the buffer reaction. The results of elemental budget in catchment scale were consistent with this stage.

Stage ii) 5.0 > pH > 4.4: Ion exchange with Ca^{2+} and Mg^{2+} was still the main acid buffer reaction. Aluminum ions were dissolved from amorphous aluminosilicate, allophane, into soil solution. Simultaneously exchangeable aluminum increased with the decrease in pH levels in this stage.

Stage iii) 4.4 > pH > 4.2: Aluminum concentration exceeded 0.2 $mmolc$ L^{-1}, which was applied to estimate the critical load. Calcium and magnesium concentrations were comparable to the total-aluminum concentration. Soils in this stage could be called the acidified soil.

Stage iv) 4.2 > pH: Aluminum dissolution was the main acid sink.

The molar (Ca+Mg+K)/Al of sStages iii) and iv) was significantly decreased compared with Stages i) and ii). The lowest value (1.71) was obtained in Stage iv). In the case of Ca/Al ratio, the lowest average was 0.77. No visible symptoms of forest decline have been observed at RLL, although aluminum concentration or other factors exceeded the critical limit. Presumably other factors counteracted the adverse effects. For instance, increased organically bound aluminum suggested that aluminum complexed with organic matter which would reduce aluminum toxicity. Comprehensive monitoring studies are essential for further understanding of the relationship between soil acidification and forest vitality. The soils around the tree trunk bases are the most suitable rhizosphere soils for elucidating the effects of soil and soil solution acidification on plant growth. Investigation on soil and soil solution chemistry and its changes with distances from the trunks would be useful.

Acidic deposition at RLL promoted soil acidification through nitrogen saturation. Acidification processes in relation to buffering systems were elucidated based on the field data. Andisols at RLL are abundant in both base cations which contribute to the consumption of protons by substitution and allophane which contributes to the buffer reaction especially in the low pH range. Andisols have large sulfate adsorption capacity which mitigates the impact of acidic deposition. These buffering systems alleviated the effect of acidic deposition and increase in acidification. Cation mobilization was quantitatively the most important acid sink at RLL.

要　旨

　本邦においても、酸性雨が観測されているが、その森林生態系に対する影響は未だに明かにされていない。森林生態系の酸性沈着に対する反応は、森林土壌の性質や系における窒素の飽和状態によって異なる。本研究は、1. 降水の化学性について特徴を明かにすること、2. 窒素飽和について渓流水中の硝酸イオン濃度および森林小流域における物質収支から評価すること、3. ヒノキ（*Chamaecyparis obtusa*）樹幹周辺における土壌および土壌溶液の化学性の違いから黒ボク土の酸性化の過程と酸緩衝作用について明かにすること、4. 窒素飽和および土壌酸性化が森林生態系に与える影響について検討することを目的として、東京農工大学農学部付属波丘地利用実験実習施設（東京都八王子市堀之内：以下波丘地とする）においてモニタリング研究を実施した。波丘地において林外雨、林内雨、樹幹流、土壌溶液および渓流水を定期的に採取し、主要イオンについて分析を行なった。また、土壌を採取し、化学分析を行なった。

　波丘地における林外雨の加重平均 pH 値は 4.5〜4.8 で酸性雨が観測され、水素イオンの負荷量としては 0.30〜0.44 kmolc ha^{-1} yr^{-1} であった。また、窒素の負荷量が比較的多く、S/N（非海塩起源性硫酸イオン/硝酸イオン）比は低かった。この多い窒素負荷量は、移動発生源から排出される窒素酸化物に起因していると考察された。針葉樹の樹冠は、多くの酸性物質を捕集するため、針葉樹林における林内雨および樹幹流には水素イオンやアンモニウムイオンが多く含まれていた。多量の窒素を含んだ酸性沈着は森林生態系の窒素飽和に寄与していた。

　波丘地の西の沢流域は窒素化合物（主に硝酸イオン）の流出量が多く、窒素飽和の段階 2 の状態にあると判断された。渓流水の pH は 7 前後であったが、硝酸イオン濃度が上昇すると共に低下した。1995 年 3 月からの 1 年間に窒素の形態変化に伴う酸の生成量（{[NH$_4$$^+$]$_{th}$-[NH$_4$$^+$]$_{out}$}-{[NO$_3$$^-$]$_{th}$-[NO$_3$$^-$]$_{out}$}）は 1.28 kmolc ha^{-1} yr^{-1} で、酸性沈着による酸の負荷量の 1.3 倍に達した。窒素飽和の段階 2 の状態では、窒素の形態変化に伴って生成される酸の量が重要な酸性化の要因となっていることが明かになった。

　波丘地の土壌型は淡色黒ボク土である。黒ボク土は酸緩衝能が大きいが、pH が低下すると多量のアルミニウムが溶出するようになる。硫酸イオンの吸着は黒ボク土の重要な酸緩衝作用の一つであり、土壌溶液中の硫酸イ

オン濃度を左右していることが明かとなった。また、ヒノキ樹幹周辺における土壌および土壌溶液の化学性の違いから、土壌（溶液）の酸性化の過程を以下のように4段階に分けることができた。

i) pH > 5.0：イオン交換反応および風化が酸緩衝作用に寄与している段階。これは、森林小流域での物質収支から得られた結果と一致していた。

ii) 5.0 > pH > 4.4：カルシウムイオン、マグネシウムイオンとのイオン交換が主要な緩衝作用であるが、アルミニウムイオンが土壌溶液中に溶出し始める段階。アルミニウムイオンは非晶質粘土鉱物であるアロフェンから供給されており、カルシウムイオン、マグネシウムイオンとのイオン交換により交換基に保持される量が次第に増加していく。

iii) 4.4 > pH > 4.2：土壌溶液中のアルミニウムイオン濃度が臨界負荷量を評価される際に用いられる基準値 0.2 mmolc L^{-1} より高くなる段階。この段階ではカルシウムイオン、マグネシウムイオン濃度が減少し、これらの濃度はアルミニウムイオン濃度とほぼ同じであった。

iv) 4.2 > pH：アルミニウムイオンの溶出に伴って、土壌溶液から酸が取り除かれる段階。土壌溶液中の(Ca+Mg+K)/Al比は 1.71 まで、Ca/Al比は 0.77 まで低下していることが明かになった。

幹周辺において生物に影響があるとされる臨界値を超えていたものの、波丘地においては針葉の黄化や落葉など可視的な兆候は見られなかった。土壌酸性化と樹木の生育との関係については、さらに検討する必要あるが、pHの低下に伴い、アルミニウム腐植複合体の画分が増加していたことから、アルミニウムの影響が緩和されていることが推察された。

波丘地における酸性沈着は土壌の酸性化に寄与していた。特に、窒素の負荷は森林生態系における窒素飽和に寄与し、硝酸イオンの流出量を増大させ、酸性化を加速していた。黒ボク土の持つ大きな硫酸吸着能はこれらの酸性沈着の影響を緩和していた。樹幹周辺において、アロフェンの溶解が酸の緩衝に寄与するほど酸性化していたが、波丘地の黒ボク土はイオン交換や溶解などの反応を通じて緩衝作用に寄与する塩基に富んでおり、著しく酸性化している場所は限られていた。これらの緩衝作用に寄り酸性沈着による土壌酸性化は緩和されていた。波丘地では、特に塩基による酸緩衝作用が量的に最も重要であった。

Table Content

Figure Content

Publication list

1. *Papers consisting this thesis*　（学位論文を構成する論文・著書）

1) Baba, M., M. Okazaki, and T. Hashitani. Effect of Acidic Deposition on Forested Andisols in the Tama Hill Region of Japan. *Environmental Pollution* **89**, 97-106, 1995（平成7年6月）

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3) Baba, M. and M. Okazaki. Acidification in nitrogen-saturated forested catchment. *Soil Science and Plant Nutrition* **44** (4) 513-525, 1998（平成10年12月）

4) Baba, M. and M. Okazaki. Spatial variability of soil solution chemistry under Hinoki cypress (*Chamaecyparis obtusa*) in Tama Hills *Soil Science and Plant Nutrition* （Accepted：平成11年2月）

2. *Other papers*　（その他の論文・著書）

1) Okazaki, M., M. Baba, K. Sato, and Hashitani, T. Effects of atmospheric acidic deposition on soils. *Pedologist*, **36**, 159-166, 1992 (*in Japanese*)
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2) Baba, M. Nitrogen cycling and its relation to soil acidification *In* Ecological study in acidic environment. Ed. K. Satake, p.120-134 Aichi Publishers, Hino, Tokyo (*in Japanese*)
（馬場光久　窒素の循環および土壌酸性化　佐竹研一（編）　酸性環境の生態学　p. 120-134（第8章）愛智出版, 平成11年1月）