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Article

Relationship between seasonal trends in stream water chemistry and forest type in a snowy temperate region of northwestern Honshu, Japan

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Abstract

Stream water chemistry was compared between neighboring *Cryptomeria japonica* evergreen coniferous (CFs) and deciduous broad-leaved forests (BFs) in a snowy temperate region of northwestern Honshu, Japan. The stream water chemistry of the study area was characterized by extremely high concentrations of Cl^- and Na^+, which were thought to be mostly derived from sea salts. There were negative correlations between runoff and the concentrations of many ions, especially Cl^-, Na^+, and Mg^{2+}, from spring to mid-autumn. However, these correlations became weak in late autumn and winter due to the high influx of sea salt components transported by the northwest monsoon, as well as the acid shock phenomenon. As the runoff increased from late February to mid-March, the electrical conductivity (EC) of stream water rose abruptly, reached a maximum in early March, and then fell abruptly. The fluctuations during this period were extremely sharp in BFs. The pH of stream water in BFs (6.3–6.8) was significantly higher than in CFs (6.1–6.5) from spring to mid-autumn. The pH in late autumn and winter was lower than that from spring to mid-autumn, especially in BFs (5.5–6.3). This may be induced by the decline in the acid-neutralizing capacity (ANC), the supply of sea salts caused by the northwest monsoon, and the increase in NO_3^- concentration in late autumn and winter. Both the snow depth and total of chemical components in snow were greater in BFs than in CFs due to the difference in the accumulation pattern of snow on tree crowns and the ground. Approximately 80% of the chemical components in the snow were estimated to originate from sea salt. These chemical components in the snow dissolved more rapidly in BFs than in CFs from late winter to early spring due to the difference in the quantity of sunlight received at the snow surface and the density of the snowpack. Two patterns of pH drop (as low as 5.4–5.6) in stream water were recognized from late winter to early spring: one induced by an early snowmelt in BFs, and the other by the dilution of the ANC during the peak flow in the snowmelt season in both BFs and CFs. Acid shock was evident when the weather improved following cold snowy days in this snowy temperate region of Japan. This tendency was clearer in BFs than in CFs due to the different snowmelt patterns between the two forest types.

1. Introduction

Stream water chemistry is affected by the natural environment, *e.g.,* geology, climate (or weather), vegetation (or biology), and soil, as well as human impacts such as acid deposition, forest management, and land use (Kato, 1999). Several studies on the effect of vegetation on stream water chemistry have been conducted outside Japan. In the northeastern and eastern United States, Johnson *et al.* (2000) reported a higher organic acidity in stream water in a spruce-fir-white birch catchment than in a broad-leaved forest, while the broad-leaved forest had higher net production rates of basic cations. Johnson and Swank (1973) studied the input-output budgets in catchments covered by different vegetation types, and smaller losses of basic cations were recognized for broad-leaved or young forests than non-forest vegetation types. In France, Lelong *et al.* (1990) also recognized smaller losses of basic cations in an old beech forest than in other vegetation types (young spruce forest and grassland). Lower stream water pH was observed during stormflow in a forested catchment than in grassland in the UK, although the pH was almost the same during baseflow (Neal *et al.,* 1989). Grieve (1990) reported higher concentrations of mean dissolved organic carbon (DOC) and sulfate (SO_4^{2-}) in a forested catchment than in moorland catchments in southwestern Scotland. Edberg *et al.* (2001) reported that both the basic cation concentration and pH of stream water during the peak snowmelt flow were lower in watersheds above the tree line than in those of wetlands and forests in Sweden.

In Japan, Ishiguro *et al.* (1982) reported that the chemistry of stream water flowing from a forested watershed was more stable than that from a reclaimed watershed. Satoh *et al.* (1994) reported a higher total organic carbon (TOC) concentration of stream water during a rain event in watersheds covered by natural forests than those covered by *Sasa kurilensis* Makino et Shibata and/or *Sasa senanensis* Rehder (dwarf bamboo). The influences of forest management, such as harvesting (Kato, 1999; Hamabata, 2000) and forest age (Hirose *et al.,* 1988; Ohrui *et al.,* 1994; Asano *et al.,* 1996), have been well studied with reference to nitrate (NO_3^-) dynamics. Some studies have compared the stream water chemistry of broad-leaved and planted coniferous forests (Hirose *et al.,* 1988; Tokuchi *et al.,* 1991; Morisada and Hirai, 1995). However, they found no distinct correlations between stream water chemistry and forest type. This may be attributable to an insufficient sampling frequency, such as once a month, or a restricted study period, such as less than one year. No studies have examined the effect of forest type on stream water chemistry all the year around in Japan.

The emissions of air pollutants, especially sulfur emissions from Asian countries, have increased rapidly since the 1950s, in contrast to North American and European countries, where emissions have been leveling off since the 1980s (Lefohn *et al.,* 1999). Air pollution emissions from East Asian countries and chemical components originating from sea salt are transported to Japan by westerly winds and the northwest monsoon, especially in the regions of northwestern Honshu adjacent to the Sea of Japan (Ohizumi *et al.,* 1997). Of the total sulfur deposition in Japan, an estimated 40% had an East Asian continental source (Ichikawa *et al.,* 1998). Fukuzaki *et al.* (2001) observed greater deposition of non-sea-salt SO_4^{2-} and hydrogen (H^+) ions in winter precipitation in the regions along the coast of the Sea of Japan. The effects of snowmelt water on the freshwater and aquatic biota, the so-called acid shock phenomenon, in northern Europe and eastern Canada have been reported since the 1970s (*e.g.,* Hagen and Langeland, 1973; Jeffries *et al.,* 1979). In central to northwestern Japan, Shimizu and Tsuboyama (1990) and Sakurai (1998) reported a decrease in ion concentration due to snowmelt water and the absence of the acid shock phenomenon. Fukuzaki and Ohizumi (1995) predicted that the phenomenon of acid shock might be milder in the snowy temperate regions of Japan than in northern Europe and that it would appear from late winter to early spring. However, an increased ion concentration and a drop in the pH of stream water were recognized in mid-winter as well as in the snowmelt season in a snowy temperate watershed in northeastern Japan (Suzuki, 1995). Suzuki (1996, 2003) also reported seasonal trends in the stream water chemistry in the same watershed.

The purpose of this study is to clarify the effect of forest type on the seasonal trends in stream water chemistry by comparing the neighboring small watersheds covered by a *Cryptomeria japonica* D. Don evergreen coniferous forest and a deciduous broad-leaved forest in the snowy temperate region of northwestern Honshu, Japan. The influence of the northwest monsoon and snowmelt on stream water chemistry is also discussed. In central to northern Japan, most mountainous areas are covered by deciduous broad-leaved forests or planted coniferous forests, especially those of *C. japonica*. Therefore, a study to clarify the influence of forest types on the stream water chemistry is important for sound forest management given the increasing air pollutant emissions from East Asian countries and their consequent long-distance transport to Japan.

2. Materials and methods

2.1. Study area

The study area was located in Niigata Prefecture, northwestern Honshu, Japan, 35 km southeast of the coast of the Sea of Japan (37°41′N, 139°18′E; Fig. 1). The elevation of the watersheds ranged from 290 to 480 m. The aspect and average inclination of the slopes were W to WNW and 23–30°, respectively. The study watersheds were dominated by planted *C. japonica* forests and natural secondary forests composed of deciduous broad-leaved trees, including *Quercus mongolica* Fischer ex Turcz. var. *grosseserrata* Rehder et Wilson, *Sorbus alnifolia* C. Koch, and *Acer mono* Maxim. The parent rock in the study area was chert (Niigata Prefectural Government, 1983). The annual mean temperature in the study area estimated using data from the nearby Niitsu weather station (37°47′N, 139°05′E; 3 m elev.) was 10.0℃ at 480 m elevation and 11.2℃ at 290 m from 1979 to 2000. Similarly, the monthly mean temperature of the coldest month (February) was −1.4℃ (480 m elev.) and −0.2℃ (290 m). The annual mean precipitation from 1979 to 2000 was 1,828 mm at the Niitsu weather station. No meteorological snow depth data were available for the study area. Although the mean maximum snow depths at the Niitsu and Tsugawa (37°40′N, 139°27′E; 100 m elev.) weather stations from 1983 to 2000 were 68 and 111 cm, respectively, the author observed maximum snow depths in the study area to be 164 and 199 cm in 1997

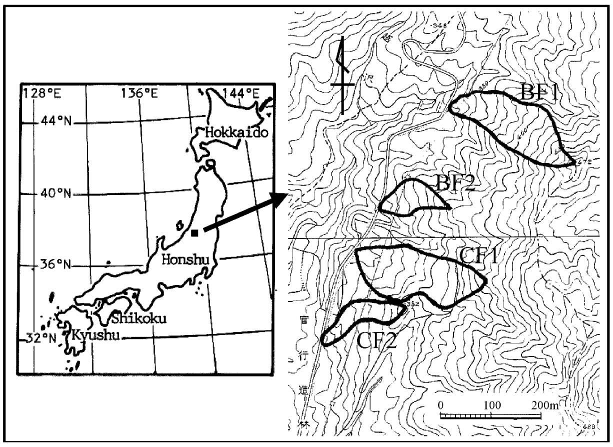

Fig. 1. Location of the study area.

and 1998, respectively.

2.2. Methods

Four small neighboring watersheds were chosen as study sites (Fig. 1); two were covered by *C. japonica* evergreen coniferous forests (CF1 and CF2) and two were covered by deciduous broad-leaved forests (BF1 and BF2). The areas of the four watersheds were 2.13 (CF1), 0.64 (CF2), 1.90 (BF1), and 0.57 (BF2) ha. Stream flow (runoff) was measured and water samples were collected weekly in each stream for one year (June 1996–May 1997). Stream water was collected completely at a cascade in each stream using a large plastic bag. The runoff was calculated by dividing the volume of the collected water by the collecting time. Stream water was measured and sampled roughly between 11 : 00 and 13 : 00 on each sampling day. The daily fluctuation in runoff with temperature has been reported for the snowmelt season (Ikeda, 1999). Since the field survey in this study during the snowmelt season was conducted on a day with a rather low temperature, the influence of the daily runoff fluctuation was considered to be small. A snow survey was carried out weekly from 19 January to 17 April in 1997. Snow depth was measured and snow samples were collected in CF1 (330 m elev.; N75° W) and BF1 (340 m elev.; N70° W). Two replicate snow core samples were collected by inserting a PVC pipe (2 m long, 5.5 cm diameter) into the snow vertically to the ground surface. The collected snow samples were weighed, and allowed to melt at room temperature.

The following chemical properties of the collected stream water and snowmelt water samples were measured. The pH was measured using a pH meter with a glass electrode (N-8F; Horiba, Japan). Electrical conductivity (EC) was measured with a conductivity meter (ES-14; Horiba). The inorganic ions (*i.e.,* anions: chloride (Cl^-), NO_3^-, and SO_4^{2-}; cations: sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+})) were measured using ion chromatography (LC-10A; Shimadzu, Japan) after each sample was filtered through a membrane filter (pore size, 0.45 μm). The acid-neutralizing capacity (ANC) of stream water was calculated as the difference between the sums of anions (Cl^-, SO_4^{2-}, and NO_3^-) and basic cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) (Inoue and Satake, 2000).

The temperature in the study area was estimated using data from the Niitsu weather station. The precipitation data during the study period were from the Muramatsu weather station (37° 42′N, 139° 11′E; 25 m elev.), the station nearest the study area. The maximum snow depth referred to data for both the Niitsu and Tsugawa weather stations.

Statistical analyses were performed using SPSS 8.0 (SPSS, USA). The significance of differences was tested using the Mann-Whitney *U*-test or Wilcoxon's signed-ranks test, and Spearman's coefficient of rank correlation was used to test correlations. Cluster analysis for the ion species of stream water was carried out using the Community Analysis Package (Pisces Conservation, UK). The concentrations of each ion species were standardized and dissimilarity among the ion species was calculated using the Euclidean distance in this cluster analysis.

3. Results and discussion

3.1. Seasonal trends in the chemical composition of stream water

The chemical properties for each stream water are summarized in Table 1. The data analysis was conducted separately for two periods: from spring to mid-autumn (June-October 1996 and April-May 1997) and from late autumn to winter (November 1996–March 1997), in order to study the influence of sea salts transported by the northwest monsoon, as well as the seasonal trends in the NO_3^- concentration and pH of the stream water.

The correlation coefficients for the runoff between each stream (Table 2) were extremely high ($r = 0.923$–0.989, $p = 0.000$; Spearman's *rho*), showing high synchronization of the four stream flows. The correlation coefficients were especially high in the same forest types ($r = 0.989$ between CF1 and CF2 and $r = 0.958$ between BF1 and BF2). The average runoff for the four streams ranged from 0.75 to 0.93 L sec^{-1} ha^{-1} in late autumn and winter, which were 1.27–1.66 times higher than those from spring to mid-autumn (0.53–0.65 L sec^{-1} ha^{-1}) for all streams ($p < 0.05$; Mann-Whitney), reflecting the weather characteristics of northwestern Honshu facing the Sea of Japan. The most abundant ions in the stream water were Cl^- and Na^+ (generally *ca.* 180–220 μmol_c L^{-1}). Ca^{2+} and Mg^{2+} averaged *ca.* 50–90 μmol_c L^{-1}, and the SO_4^{2-} levels were *ca.* 50–60 μmol_c L^{-1} year-round. Although the average runoff in late autumn and winter was higher than that from spring to mid-autumn, the average Cl^-, Na^+, and Mg^{2+} concen-

Table 1. Chemical properties for each stream water (average±standard error).

Stream	Runoff ($L\ sec^{-1} ha^{-1}$)	EC ($mS\ m^{-1}$)	pH	Cl^- ($\mu mol_c\ L^{-1}$)	NO_3^- ($\mu mol_c\ L^{-1}$)	SO_4^{2-} ($\mu mol_c\ L^{-1}$)	Na^+ ($\mu mol_c\ L^{-1}$)	K^+ ($\mu mol_c\ L^{-1}$)	Ca^{2+} ($\mu mol_c\ L^{-1}$)	Mg^{2+} ($\mu mol_c\ L^{-1}$)	ANC ($\mu mol_c\ L^{-1}$)
From spring to mid-autumn (June—October 1996 and April—May 1997); N = 31											
CF1	$0.59 \pm 0.12^{ab*}$	$3.80 \pm 0.05^{a*}$	6.33 ± 0.03^{a}	206.2 ± 4.6^{a}	$16.3 \pm 1.5^{a*}$	49.8 ± 1.1^{a}	186.1 ± 3.0^{ab}	5.3 ± 0.3^{a}	$91.6 \pm 13.0^{a*}$	$77.5 \pm 1.0^{a*}$	$88.1 \pm 13.9^{a*}$
CF2	$0.54 \pm 0.11^{cd*}$	$3.34 \pm 0.05^{b*}$	$6.29 \pm 0.03^{a*}$	$192.5 \pm 5.1^{b*}$	$0.2 \pm 0.1^{b*}$	$54.2 \pm 1.1^{b*}$	187.7 ± 3.8^{a}	2.6 ± 0.3^{b}	64.3 ± 10.7^{b}	$58.2 \pm 1.2^{b*}$	$65.8 \pm 11.4^{a*}$
BF1	$0.65 \pm 0.14^{ac*}$	$3.37 \pm 0.05^{b*}$	$6.50 \pm 0.04^{b*}$	$173.5 \pm 4.0^{c*}$	$8.3 \pm 1.1^{c*}$	$49.7 \pm 1.1^{a*}$	181.2 ± 4.0^{b}	4.5 ± 0.4^{c}	68.6 ± 7.8^{ab}	$55.0 \pm 1.2^{c*}$	$77.9 \pm 8.8^{ab*}$
BF2	$0.53 \pm 0.12^{bd*}$	3.59 ± 0.05^{c}	$6.53 \pm 0.03^{b*}$	185.6 ± 4.5^{b}	$1.7 \pm 0.4^{d*}$	60.9 ± 1.4^{c}	189.5 ± 3.9^{a}	$2.6 \pm 0.3^{b*}$	84.3 ± 17.0^{a}	68.0 ± 1.0^{d}	$96.3 \pm 17.3^{b*}$
From late autumn to winter (November 1996—March 1997); N = 22											
CF1	$0.75 \pm 0.09^{a*}$	$4.03 \pm 0.07^{a*}$	6.24 ± 0.05^{a}	212.3 ± 5.8^{a}	$28.6 \pm 1.4^{a*}$	50.5 ± 1.0^{a}	190.3 ± 2.5^{a}	4.5 ± 0.5^{ab}	$58.1 \pm 2.7^{a*}$	$84.6 \pm 1.7^{a*}$	$46.0 \pm 5.3^{a*}$
CF2	$0.79 \pm 0.09^{a*}$	$3.69 \pm 0.10^{b*}$	$6.10 \pm 0.05^{b*}$	$222.3 \pm 7.5^{b*}$	$0.9 \pm 0.3^{b*}$	$52.4 \pm 0.5^{ab*}$	190.8 ± 3.6^{a}	3.2 ± 0.4^{c}	44.7 ± 2.9^{b}	$70.8 \pm 2.2^{b*}$	$34.0 \pm 4.5^{b*}$
BF1	$0.93 \pm 0.13^{a*}$	$3.80 \pm 0.17^{b*}$	$6.18 \pm 0.06^{ab*}$	$203.6 \pm 9.9^{a*}$	$15.0 \pm 1.5^{c*}$	$55.5 \pm 2.5^{b*}$	196.7 ± 7.3^{a}	5.3 ± 0.8^{a}	51.0 ± 3.7^{c}	$66.6 \pm 3.3^{c*}$	$45.5 \pm 5.7^{a*}$
BF2	$0.88 \pm 0.12^{a*}$	3.83 ± 0.14^{ab}	$6.17 \pm 0.06^{ab*}$	202.8 ± 8.1^{a}	$4.1 \pm 1.2^{d*}$	62.7 ± 2.3^{c}	190.9 ± 5.9^{a}	$4.4 \pm 0.6^{b*}$	65.0 ± 12.8^{a}	72.9 ± 2.6^{b}	$63.7 \pm 11.1^{c*}$

Notes; Different letters indicate significant differences among the four streams by multiple comparisons with the Friedman test (Wilcoxon's signed-ranks test, $p < 0.05/6 = 0.0083$).
"*"indicates a significant difference between the two separated periods for each stream by Mann-Whitney *U*-test ($p < 0.05$).

Table 2. Correlation coefficients (Spearman's *rho*) for the runoff, EC, and pH between each stream.

Stream	Runoff	EC	pH
CF1—CF2	0.989	0.880	0.703
CF1—BF1	0.939	0.750	0.474
CF1—BF2	0.923	0.545	0.502
CF2—BF1	0.928	0.869	0.643
CF2—BF2	0.954	0.685	0.658
BF1—BF2	0.960	0.888	0.908

Note; All correlation coefficients were $p < 0.01$.

trations for all streams were also higher in late autumn and winter than from spring to mid-autumn ($p < 0.05$ in three and two of the four streams for Mg^{2+} and Cl^-, respectively). This may have been attributable to the high influx of chemical components originating from sea salt transported by the northwest monsoon. An influx of 12.1 $kmol_c\ ha^{-1} yr^{-1}$ of chemical components originating from sea salt was measured in a forested watershed in Niigata Prefecture, and most of this was concentrated in late autumn and winter (Nakata *et al.,* unpublished data).

The K^+ concentration was extremely low relative to the other ions, *i.e., ca.* 2–5 $\mu mol_c\ L^{-1}$ year-round. Nevertheless, the K^+ concentration increased to between 8 and 18 $\mu mol_c\ L^{-1}$ in early to mid-November, which may have been a result of leaching from fallen leaf litter.

The NO_3^- concentration was significantly higher in late autumn and winter (Fig. 2a) than from spring to mid-autumn for all streams ($p < 0.05$; Mann-Whitney) indicating a sound forest condition with respect to the nitrogen cycle (Aber *et al.,* 1989; Stoddard, 1994). It differed markedly between study sites; the average NO_3^- concentrations for the four streams throughout the study period were in the order CF1 > BF1 > BF2 > CF2 ($p = 0.000$; Wilcoxon's signed-ranks test). This may reflect the different mineralization process of nitrogen in each watershed. However, no mineralization data were available in this study.

The Cl^-, NO_3^-, SO_4^{2-}, Na^+, and Mg^{2+} concentrations were highest on 5 March. Although the Ca^{2+} and K^+ concentrations were also high on 5 March, they were highest in other seasons. The ANC was significantly lower in late autumn and winter (34.0–63.7 $\mu mol_c\ L^{-1}$ on average) than from spring to mid-autumn (65.8–96.3 $\mu mol_c\ L^{-1}$ on average) for all streams ($p < 0.05$; Mann-Whitney).

Watershed geology strongly affects the concentrations of ions in stream water (Bailey *et al.,* 1987). Table 3 compares the stream water chemistry for a watershed with the same geology (*i.e.,* chert) in Nagano Prefecture (Sakurai *et al.,* 1998; Fukushima *et al.,* 2000), which is located inland on Honshu and is adjacent to Niigata Prefecture. Although the ion concentrations are variable depending on the runoff, the relative proportions of major basic cations are roughly constant (Fukushima *et al.,* 2000). Of the four basic cations, the proportion of Ca^{2+} was highest (65–80%) in both streams in Nagano Prefecture, whereas that of Na^+ was low (*ca.* 10%). In contrast, the proportion of Na^+ exceeded 50% in the study area, and Ca^{2+} was *ca.* 20%, which was comparable to Mg^{2+}. The proportions of Na^+ and Mg^{2+} were higher in late autumn and winter than those from spring to mid-autumn in the study area. The average concentration of Cl^- in the study area was *ca.* 200 $\mu mol_c\ L^{-1}$, which was more than ten times higher than that in Nagano Prefecture. The dissolution rate of Cl^- from the parent rock is extremely low (Fukushima *et al.,* 2000). Therefore, most of Cl^- in the stream water was considered to have originated from precipitation or atmospheric deposition, and were also estimated to be of sea salt origin in the regions of northwestern Honshu adjacent to the Sea of Japan (Yasuda *et al.,* 1991; Suzuki and Endo, 1994). The concentrations of Cl^- and Na^+ increased in the following order: mid- to southern Nagano Prefecture, northern Nagano Prefecture, and Niigata Prefecture. This corresponds to the geographical gradient from the inland part of Honshu toward the Sea of Japan, reflecting the influence of sea salts.

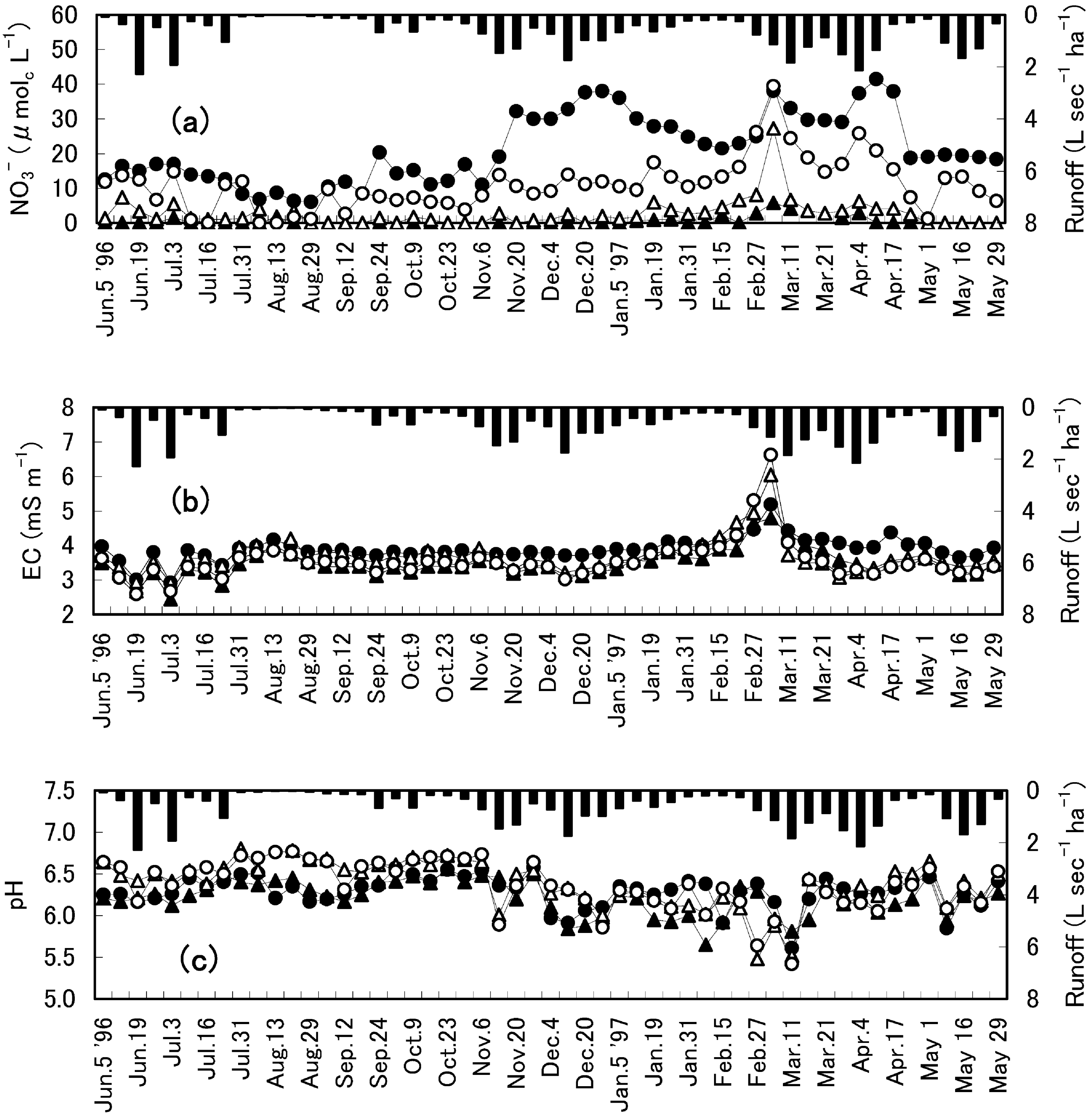

Fig. 2. The fluctuation in (a) NO_3^- concentration, (b) EC, and (c) pH relative to average runoff in the stream water of different forest types.

Notes: —●—, CF1; —▲—, CF2; —○—, BF1; —△—, BF2; vertical bar, average runoff from the four streams.

The high contribution of sea salts to the stream water chemistry in the study area was also indicated in a cluster analysis. Figure 3 shows dendrograms indicating the affinity of the ion species in each stream. Cl^-, Mg^{2+}, and Na^+ were very similar in all four streams, suggesting that most of these had the same origin, *i.e.*, sea salt.

Table 4 shows correlation coefficients (Spearman's *rho*) between runoff levels and chemical properties in each stream. There were significant negative correlations between runoff levels and ion concentrations, except for NO_3^- and K^+, from spring to mid-autumn. This may result from the dilution of ion concentrations by the runoff water during hydrological events (Kumagae *et al.*, 2000). The correlation coefficients were especially high for Na^+, Cl^-, and Mg^{2+}. However, these correlations weakened in late autumn and winter, which may have been caused by the high influx of chemicals originating from sea salt brought in by the northwest monsoon. Another reason for the weak correlation between ion concentrations and runoff levels in late autumn and winter was the rise in ion concentrations accompanied by the increase in runoff induced by snowmelt, resulting in an acid shock phe-

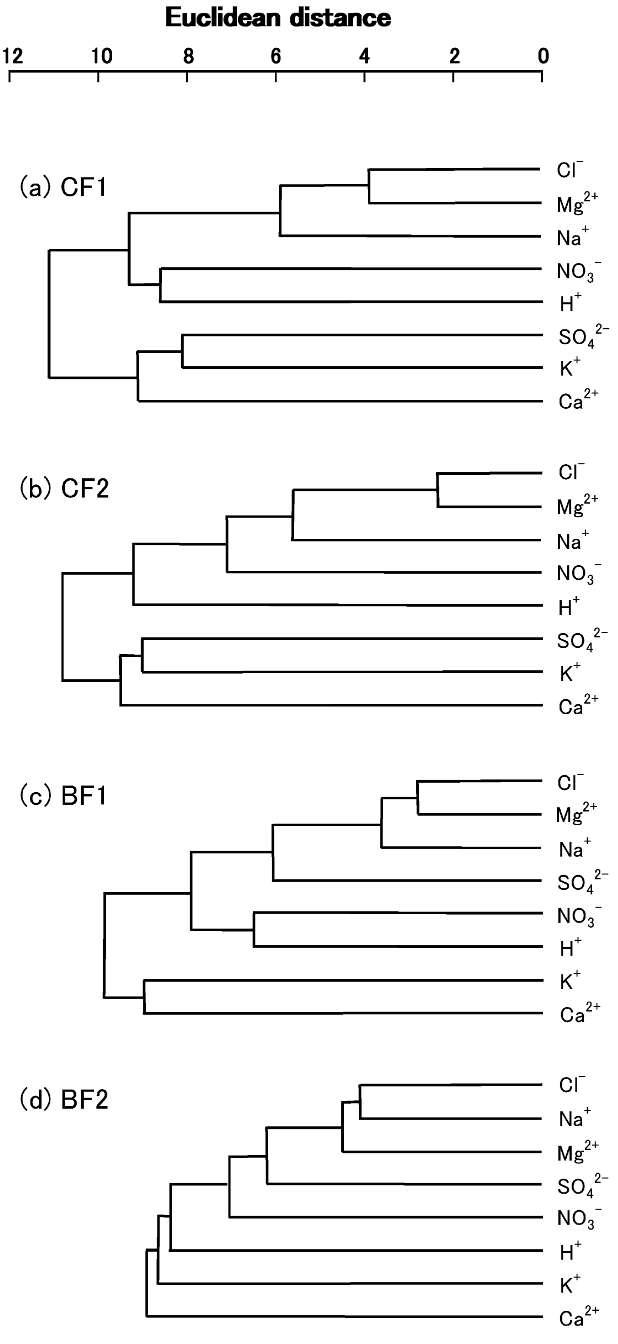

Fig. 3. Dendrograms indicating the affinity of ion species in each stream.

nomenon. There were strong positive correlations between runoff levels and the NO_3^- concentration in CF 1 and BF1 from spring to mid-autumn ($p=0.000$). This phenomenon was explained as an effect of the washout of NO_3^-, which was held in the upper soil layers, with increased water movement near the ground surface during hydrological events (Kumagae *et al.*, 2000).

The fluctuation in EC relative to runoff in the stream water of different forest types is shown in Fig. 2b. The EC of the four streams fluctuated in a similar manner, especially in the same forest types ($r=0.880$ between CF1 and CF2 and $r=0.888$ between BF1 and BF2, $p=0.000$; Spearman's *rho*; Table 2). The EC fluctuated between 3 and 4 $\mathrm{mS\,m^{-1}}$ from spring to mid-autumn, and fell to 2.4–3.0 $\mathrm{mS\,m^{-1}}$ at times of high runoff. The relatively low EC and low ANC (average value $<100\,\mu\mathrm{mol_c\,L^{-1}}$ in all study streams) indicated the susceptibility of the study streams to acidification (The Committee for Acid Deposition Measures, 2004). There were strong negative correlations between EC and runoff from spring to mid-autumn ($p<0.01$; Spearman's *rho*; Table 4). However, the negative correlation weakened in late autumn and winter and there were no significant correlations between EC and runoff in CF ($p>0.05$). This may have been due to the high influx of chemicals originating from sea salt and the acid shock phenomenon. Although the average runoff in late autumn and winter was higher than that from spring to mid-autumn, the runoff decreased gradually from mid-December 1996 to mid-February 1997, resulting in a gradual increase in EC. As the runoff increased from late February to mid-March, EC rose abruptly, reached a maximum on 5 March, with peaks of 6.63, 6.05, 5.19, and 4.79 $\mathrm{mS\,m^{-1}}$ for BF1, BF2, CF1, and CF2, respectively, and then fell abruptly. The fluctuations during this period were extremely sharp in the BFs, and the concentrations of all ions varied in the same manner during this period. Acid shock was evident, and was clearer in the BFs than in the CFs. After reaching a maximum on 5 March, the EC in the BFs was lower than that in the CFs until the end of March.

3.2. *Seasonal trends in stream water pH in different forest types*

The fluctuation in pH relative to runoff in the stream water of different forest types is shown in Fig. 2c. The stream water pH fluctuated in a similar manner in the same forest types ($r=0.703$ between CF1 and CF2 and $r=0.908$ between BF1 and BF2, $p=0.000$; Spearman's *rho*; Table 2). However, the correlation coefficients were relatively low between the different forest types ($r=0.474$–0.658). The pH of stream water in BFs was significantly higher than in CFs from spring to mid-autumn ($p=0.000$; Wilcoxon's signed-ranks test; Table 1 and Fig. 2c). The pH in BFs was 6.3–6.8 (average 6.50 and 6.53 for BF1 and BF2, respectively). The pH in BFs was especially high during the summer drought (6.7–6.8). In contrast, the pH in CFs was relatively low, ranging from 6.1 to 6.5 (average 6.33 and 6.29 for CF1 and CF2, respectively) from spring to mid-autumn. The soil type in this area was brown forest soil and did not differ between the two forest types (Niigata Prefectural Government, 1983). However, the stemflow of *C. japonica* is extremely low ($<$ 4.0; Sassa *et al.*, 1991), and organic acids and SO_4^{2-} leached from its bark tend to acidify its soil (Matsuura, 1992; Sakai, 2001). This might lower the pH in the stream water of CFs. However, definite evidence of a difference in pH between CFs and BFs from spring to

Table 3. Comparison of stream water chemistry of this study to other watersheds with the same geology (*i.e.,* chert) in Nagano Prefecture.

Stream	Cl^- ($\mu mol_c L^{-1}$)	NO_3^- ($\mu mol_c L^{-1}$)	SO_4^{2-} ($\mu mol_c L^{-1}$)	Na^+ ($\mu mol_c L^{-1}$)	K^+ ($\mu mol_c L^{-1}$)	Ca^{2+} ($\mu mol_c L^{-1}$)	Mg^{2+} ($\mu mol_c L^{-1}$)
From spring to mid-autumn (June—October 1996 and April—May 1997); N = 31							
CF1	206.2	16.3	49.8	186.1	5.3	91.6	77.5
CF2	192.5	0.2	54.2	187.7	2.6	64.3	58.2
BF1	173.5	8.3	49.7	181.2	4.5	68.6	55.0
BF2	185.6	1.7	60.9	189.5	2.6	84.3	68.0
Average	189.5	6.6	53.7	186.1	3.8	77.2	64.7
				(56.1)	(1.1)	(23.3)	(19.5)
From late autumn to winter (November 1996—March 1997); N = 22							
CF1	212.3	28.6	50.5	190.3	4.5	58.1	84.6
CF2	222.3	0.9	52.4	190.8	3.2	44.7	70.8
BF1	203.6	15.0	55.5	196.7	5.3	51.0	66.6
BF2	202.8	4.1	62.7	190.9	4.4	65.0	72.9
Average	210.3	12.2	55.3	192.2	4.4	54.7	73.7
				(59.1)	(1.3)	(16.8)	(22.7)
Northern part of Nagano Pref.	18.9	8.2	149.6	105.7	9.7	516.5	161.3
(Source; Sakurai *et al.,* 1998)				(13.3)	(1.2)	(65.1)	(20.3)
Mid- to southern part of Nagano Pref.	11.8	—	46.0	79.6	5.6	682.7	86.4
(Source; Fukushima *et al.*, 2000)				(9.3)	(0.7)	(79.9)	(10.1)

Note; The figure in parentheses indicates the relative composition (%) of each basic cation to total ones.

Table 4. Correlation coefficients (Spearman's *rho*) between runoff levels and chemical properties in each stream.

Stream	EC	pH	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	ANC
From spring to mid-autumn (June—October 1996 and April—May 1997); N = 31										
CF1	−0.566**	−0.316	−0.369*	0.753**	−0.435*	−0.735**	−0.201	−0.537**	−0.312	−0.564**
CF2	−0.761**	−0.396*	−0.665**	0.101	0.502**	−0.788**	−0.001	−0.442*	−0.664**	−0.470**
BF1	−0.882**	−0.776**	−0.577**	0.679**	0.250	−0.744**	−0.459**	−0.434*	−0.709**	−0.585**
BF2	−0.895**	−0.739**	−0.769**	0.259	−0.414*	−0.844**	0.258	−0.360	−0.790**	−0.402*
From late autumn to winter (November 1996—March 1997); N = 22										
CF1	−0.224	−0.301	−0.056	0.492*	−0.366	−0.029	0.338	−0.237	−0.031	−0.255
CF2	−0.148	−0.132	−0.067	0.142	0.230	−0.108	0.167	−0.128	−0.067	−0.225
BF1	−0.493*	−0.098	−0.361	0.251	−0.514*	−0.569**	0.075	−0.429*	−0.406	−0.269
BF2	−0.518*	−0.011	−0.365	0.031	−0.473*	−0.534*	0.077	−0.280	−0.523*	−0.200

Notes; $^*p<0.05$, $^{**}p<0.01$.

mid-autumn was not obtained in this study. The pH of stream water was negatively correlated with runoff from spring to mid-autumn ($p<0.05$; Spearman's *rho*; Table 4), except for CF1. The correlation coefficient was extremely high in BFs ($r=-0.776$ and -0.739 for BF1 and BF2, respectively, $p=0.000$). The acidification of freshwater during hydrological events was explained as a depression of alkalinity due to the dilution of basic cations and an increase in strong acid anions (Tranter *et al.,* 1994). Almost all of the basic cations in the four streams in this study had negative correlations with the runoff from spring to mid-autumn. In contrast, of the strong acid anions, Cl^- had a negative correlation, NO_3^- had a positive correlation, and SO_4^{2-} had both positive and negative correlations with the runoff during this period (Table 4). This resulted in a significantly negative correlation ($p<0.05$; Spearman's *rho*) between the ANC and runoff in all streams from spring to mid-autumn. The ANC correlated with pH significantly and positively ($r=0.456$, $p=0.010$ for CF1, $r=0.639$, 0.626, and 0.624, $p=0.000$ for CF2, BF1, and BF2, respectively). The washout of organic acids from forest soils was proposed as another cause of the acidification of stream water induced by rainstorms (Jansson and Ivarsson, 1994).

The pH in late autumn and winter was lower than that from spring to mid-autumn (Table 1 and Fig. 2c). That was especially evident ($p=0.000$; Mann-Whitney) in BFs (average 6.18 and 6.17 for BF1 and BF2, respectively). There were no significant differences in pH between BFs and CFs ($p>0.05$; Wilcoxon's signed-ranks test) in late autumn and winter. A similar fluctuation pattern of stream water pH between warm and cold seasons was reported in a snowy temperate area of northeastern Japan (Suzuki, 2005). The drop in stream water pH in late autumn and winter was attributed to the lower ANC. Almost all strong acid anions increased in late autumn and winter. Conversely, of the basic cations, Na^+ and Mg^{2+} increased slightly, but Ca^{2+} decreased considerably in those periods. Therefore, the ANC became significantly lower in late autumn and winter than from spring to mid-autumn in all four streams (Table 1). Another reason for the drop in stream water pH in late autumn and winter is thought to be the supply of sea salts (Neal *et al.,* 1986; Vogt and Muniz, 1997) caused by the northwest monsoon. Winter precipitation or snow in the regions of northwestern Honshu adjacent to the Sea of Japan contains many sea salt components (Yasuda *et al.,* 1991; Suzuki and Endo, 1994). Cation exchange with sea salt occurs in the soil and H^+ is consequently released (Haraguchi *et al.,* 2003). There were no significant correlations between pH, ANC, and runoff in late autumn and winter ($p>0.05$; Spearman's *rho*). However, the NO_3^- concentration had a significantly negative correlation with pH ($r=-0.436, p=0.043$ for CF1, $r=-0.609, p=0.003$ for BF1, and $r=-0.645, p=0.001$ for BF2), except for CF2. Furthermore, the NO_3^- concentration was significantly higher in late autumn and winter than from spring to mid-autumn in all four streams ($p<0.05$; Mann-Whitney; Table 1). Therefore, the pH fluctuation in late autumn and winter may be regulated primarily by the NO_3^- concentration (Suzuki, 2003).

The stream water pH was considerably lower in late winter and early spring (27 February–11 March), and was as low as 5.4–5.6. At that time, the pH in BFs was lower than in CFs. The pH in BFs had two minima (27 February and 11 March), whereas there was only one in CFs (11 March). The ANC was extremely low (5.0–$17.6\,\mu mol_c\,L^{-1}$) when the pH in all streams had the lowest value on 11 March. An experiment demonstrated that the propagation of two Japanese trout species was reduced at a pH below 6 (Ikuta *et al.,* 1999). Although the streams in this study were too small for such freshwater fish, the lower pH (5.4–5.6) in late winter and early spring may influence the aquatic biota. However, there was no faunal or floral information for these streams. The cause of the episodic pH drop in late winter and early spring is discussed in relation to snowmelt in the next section.

3.3. *Snow properties of different forest types in relation to stream water chemistry in winter*

The depth, water equivalent, density, EC, and pH of snow for the different forest types (CF1 and BF1) in 1997 are shown in Fig. 4a-e, respectively. Snow depths (Fig. 4a) increased from January (50–70 cm) to February, reaching a maximum on 23 February (165 and 136 cm for BF1 and CF1, respectively). The period from 1 to 23 February 1997 was the coldest part of the winter, *i.e.,* the estimated daily mean maximum temperature at the study site was 3.0℃, and the daily mean minimum temperature was −2.8℃ (Fig. 5). Much snow fell during this period (101 mm in terms of precipitation) and snowmelt was at its lowest level. After 23 February, the weather improved and the daily maximum temperature exceeded 10℃ periodically. There were several clear days and some rain fell during this period. Consequently, the snow depth decreased after 23 February and the snow disappeared in early to mid-April. The snow was deeper in BF1 than in CF1 from January until the end of March ($p=0.003$; Wilcoxon's signed-ranks test). The main reason for this was the greater snowfall interception rate by the crowns in CFs (evergreen trees) than in BFs (deciduous trees) (Ishibashi and Takizawa, 1983). The snow water equivalent (Fig. 4b) changed in almost the same manner with the snow depth, reaching a maximum on 23 February in CF1 (528 mm) and on 27 February in BF1 (628 mm). However, the snow water equivalent decreased somewhat rapidly on 5 March and increased slightly on 11 March in CF1. This may have been attributable to the lag in snow accumulation on the ground due to the interception by the tree crowns in CFs. Snow density (Fig. 4c) increased gradually from January (*ca.* $0.3\,g\,cm^{-3}$) to early April (*ca.* $0.5\,g\,cm^{-3}$) due to snow recrystallization and the gravitational compression of the snowpack. The snow density in CF1 was higher than in BF1 from January to 23 February ($p=0.043$; Wilcoxon's signed-ranks test), while it was higher in BF1 than in CF1 from 27 February to 21 March ($p=0.043$). During the cold snowy period, the accumulated snow was more compact in CFs than in BFs, because in CFs the snow first accumulated on the evergreen tree crowns and then fell to the ground in blocks. In contrast, most of the snow accumulated on the ground directly and evenly in BFs. After 23 February, however, the weather improved and the snow surface in BFs received more sunlight than that in CFs on sunny days (Ohta *et al.,* 1990). Consequently, the melted snow may have increased the snow density in BF1 more than in CF1.

The EC of snow (Fig. 4d) rose from January (2.1–$2.8\,mS\,m^{-1}$) to February, reaching a maximum on 15 February in CF1 ($3.73\,mS\,m^{-1}$) and 23 February in BF1 ($4.36\,mS\,m^{-1}$). The EC in BF1 was higher than that in CF1 until 23 February ($p=0.043$, Wilcoxon's signed-ranks test), perhaps due to the dissolution of ions from the snow on tree crowns in CFs. After 23 February, the weather improved and the EC of snow dropped, reflecting the preferential dissolution of ions from the snow (Johannessen and Henriksen, 1978). The EC decreased to between 0.7 and 1.0 mS m^{-1} in early April just before the snow disappeared. No significant difference was seen between the EC of snow in BF1 and CF1 after 23 February ($p=0.499$; Wilcoxon's signed-ranks test). The pH of snow (Fig. 4e) rose gradually from January (4.6–4.8) to early April (5.2–5.5), showing a significantly negative correlation with the EC of snow ($r=-0.577$, $p=0.039$ for CF1 and $r=-0.937$, $p=0.000$ for BF1; Spearman *rho*). This indicated a preferential dissolution of ions, especially H$^+$, from the snow (Satoh *et al.,* 1996). However, the lowest pH value was observed on 23 February in BF1 (4.21). The pH in BF1 was significantly lower than that in CF1 ($p=0.012$; Wilcoxon's signed-ranks test) throughout the snow period. That may also have been attributable to the dissolution of ions, especially H$^+$, from the snow on the tree crowns of CFs.

The amounts of chemical components in snow for the different forest types in 1997 are shown in Fig. 6. Of the chemical components in snow, Cl$^-$ and Na$^+$ were the dominant ion species, constituting *ca.* 70% of the totals. Other than Cl$^-$ and Na$^+$, SO$_4^{2-}$ and Ca^{2+} were rather abundant ion species, constituting *ca.* 20% of the totals. The total amount of chemical components in snow was greater in BF1 than in CF1, except on 16 March and 10 April, and the maximum total amount in BF1 (338.7 mmol$_c$ m^{-2}, 23 February) was much greater than that in CF1 (205.4 mmol$_c$ m^{-2}, 15 February). This may also have been attributable to the dissolution of ions from the snow on tree crowns in CFs. Figure 7 shows the amounts of non-sea-salt chemical components in snow for different forest types calculated using the chemical composition of seawater provided by the Oceanographic Society of Japan (1990). The amounts of non-sea-salt components in snow corresponded well with the total amounts of chemical components in snow ($r=0.890$, $p=0.000$ for CF1 and $r=0.608$, $p=0.036$ for BF1; Spearman's *rho*), and they always constituted *ca.* 20% of the totals throughout the snow period. Therefore, *ca.* 80% of the chemical components in snow were estimated as sea salt origin. SO$_4^{2-}$ and Ca^{2+} were the dominant ion species among the non-sea-salt components in snow, occupying more than 80% of the totals. The difference of dissolution rate among the ions species (Suzuki, 1991) was not clear in this study, with the exception of H$^+$. The contribution of dry deposition on the snow may mask the dissolution trend of each ion species from the snow (Satoh *et al.,* 1996).

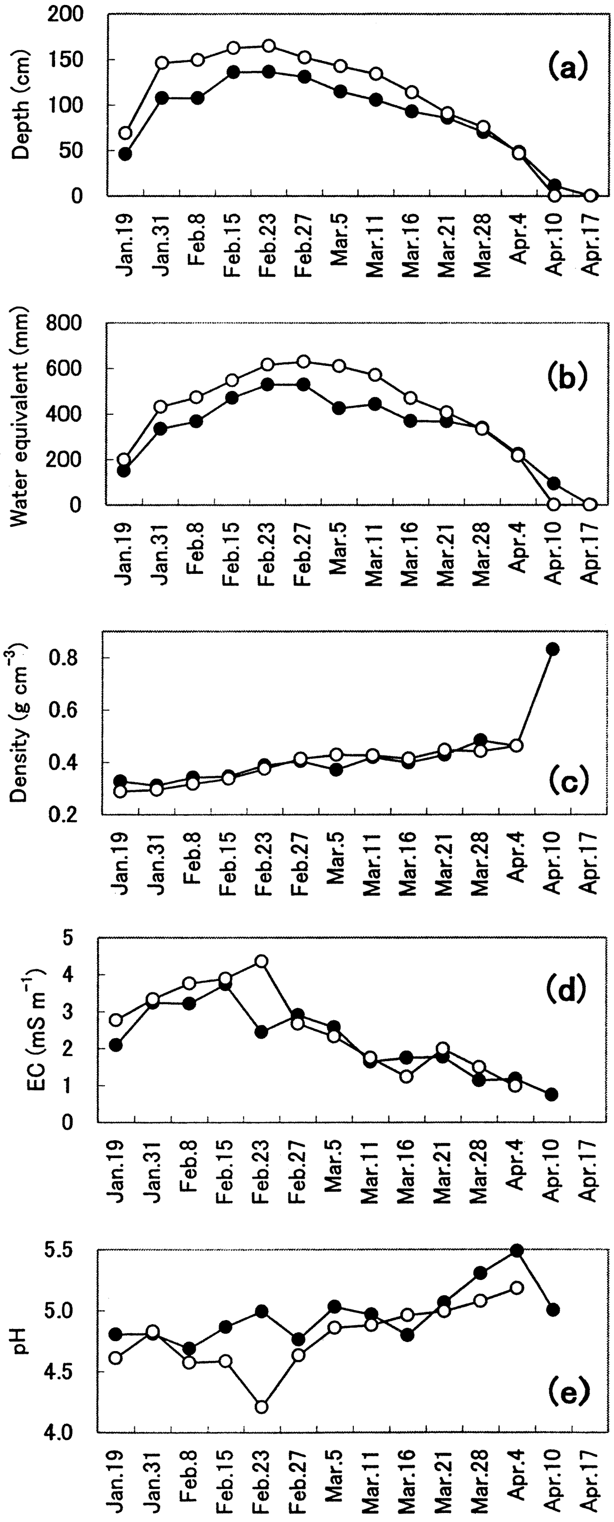

Fig. 4. (a) The depth, (b) water equivalent, (c) density, (d) EC, and (e) pH of snow for the different forest types (CF1 and BF1) in 1997.
Notes: —●—, CF1; —○—, BF1.

From late February to mid-March, a large ion loss in the snow was observed for both the total and non-sea-salt components (Figs. 6 and 7), *e.g.,* between 23 and 27 February (BF1) and between 5 and 11 March (both BF1 and CF1). The greatest loss of chemical components from the snow was seen in BF1 (155.5 mmol$_c$ m^{-2}) between 23 and 27 February. This was also the period when the EC decreased rapidly (from 4.36 to 2.67 mS m^{-1}; Fig. 4d) and the pH increased (from 4.21 to 4.63; Fig. 4e) in the snow of BF1. From 31 January to 23 February in 1997, the stream water runoff was extremely low (average value < 0.25 L sec^{-1} ha^{-1}) due to cold snowy weather conditions. However, the weather turned warm between 23 and 27 February (Fig. 5), and

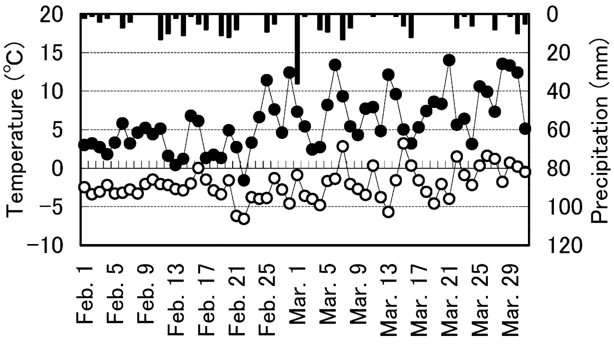

Fig. 5. Weather conditions in the study area in February and March in 1997.
Notes: —●—, daily maximum temperature; —○—, daily minimum temperature; vertical bar, daily precipitation.

both the runoff and EC of the stream water began to increase (Fig. 2b). Consequently, the abrupt drop in the pH of the stream water of BF (5.64 and 5.48 for BF 1 and BF2, respectively; Fig. 2c) on 27 February was thought to have resulted from the early snowmelt, *i.e.,* the abrupt and preferential dissolution of chemical components from the snowpack, with their transport near the ground surface to the streams in both BF1 and BF2. The lowest pH of stream water in Norway was observed during early snowmelt due to the release of snowmelt water highly enriched in sea salts (Vogt and Muniz, 1997). In this study, *ca.* 80% of the dissolved ions from the snow were thought to be of sea salt origin. Therefore, dissolved ions of sea salt origin from the snow might contribute to the drop in the pH of the stream water in BFs. However, no such rapid dissolution of ions from the snow and consequent drop in stream water pH was recognized in either CF1 or CF2. This may have been because the snow surface in CFs received less sunlight than that in BFs on sunny days (Ohta *et al.,* 1990). Consequently, ions in the snow dissolved more slowly in CFs than in BFs. Furthermore, the accumulated snow during the cold snowy period was more compact in CFs than in BFs (Fig. 4c), which contributed to the delayed snowmelt relative to that in BFs.

The pH in all of the streams showed episodic acidification on 11 March. The ANC was extremely low on that day (5.0–17.6μmol$_c$ L^{-1}). Although large ion loss from the snow was observed in both BF1 and CF1 between 5 and 11 March, the peak ion concentration in the stream water, as expressed by EC (Fig. 2b), was observed on the previous sampling day (5 March). In contrast, the maximum runoff during the snowmelt season, *i.e.,* from late February to late March, was on 11 March. Therefore, the drop in pH on 11 March in all four streams may have been due to the dilution of basic cations in groundwater by the surficial organic-horizon/overland flow of snowmelt water, which may be high in DOC (Kendall *et al.,* 1999; Laudon and Bis-

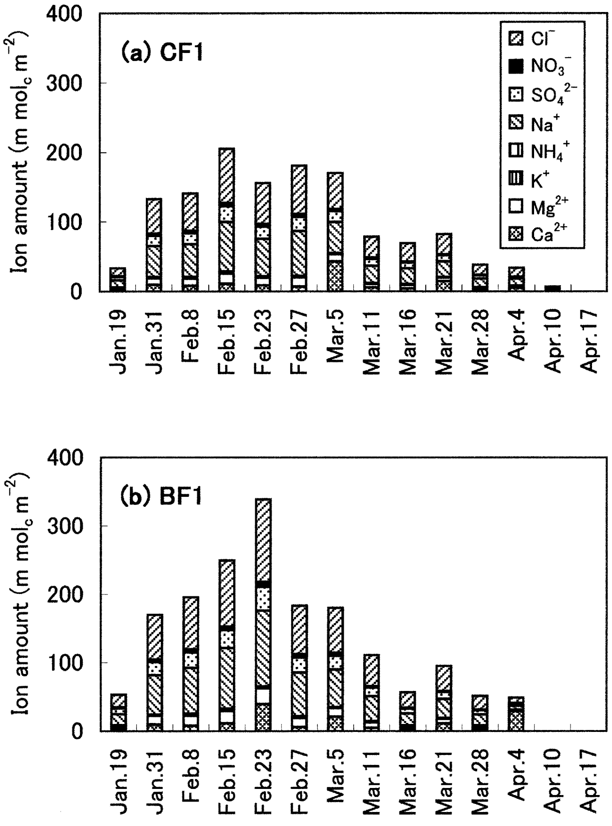

Fig. 6. The amounts of chemical components in snow for the different forest types (CF1 and BF1) in 1997.

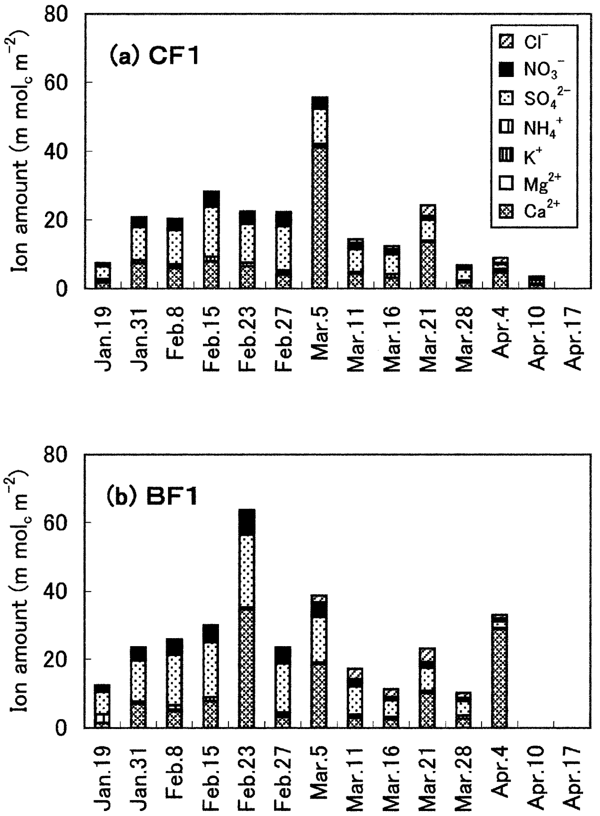

Fig. 7. The amounts of non-sea-salt chemical components in snow for the different forest types (CF1 and BF1) in 1997.

hop, 1999).

4. Conclusion

The stream water chemistry in the study area was characterized by extremely high concentrations of Cl^- and Na^+, most of which was derived from sea salts. There were negative correlations between runoff and the concentrations of many ions, especially Cl^-, Na^+, and Mg^{2+} from spring to mid-autumn. However, these correlations weakened in late autumn and winter probably due to the high influx of sea salt components transported by the northwest monsoon, as well as the acid shock phenomenon. The pH of stream water in BFs (6.3–6.8) was significantly higher than in CFs (6.1–6.5) from spring to mid-autumn. The pH in late autumn and winter was lower than that from spring to mid-autumn, especially in BFs (5.5–6.3). This may have resulted from the drop in the ANC, the supply of sea salts, and the increase in NO_3^- concentration in late autumn and winter.

Both the snow depth and total chemical components in snow were greater in BFs than in CFs due to the difference in the accumulation patterns of snow on the tree crowns and ground. Approximately 80% of the chemical components in the snow were estimated to be of sea salt origin. These chemical components in the snow dissolved more rapidly in BFs than in CFs from late winter to early spring due to the differences in the quantity of sunlight received at the snow surface and the density of the snowpack.

As the runoff increased from late February to mid-March due to snowmelt, the EC of stream water rose abruptly, reached a maximum in early March, and then fell abruptly. The fluctuation during this period was extremely sharp in BFs. Two patterns of the pH drop (as low as 5.4–5.6) in stream water were recognized from late February to mid-March induced by an early snowmelt in BFs, and the dilution of the ANC during the peak flow in the snowmelt season in both BFs and CFs. Acid shock was evident when the weather improved following cold snowy days in this snowy temperate region of Japan. This tendency was clearer in BFs than in CFs due to the difference between the snowmelt patterns of the two forest types.

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