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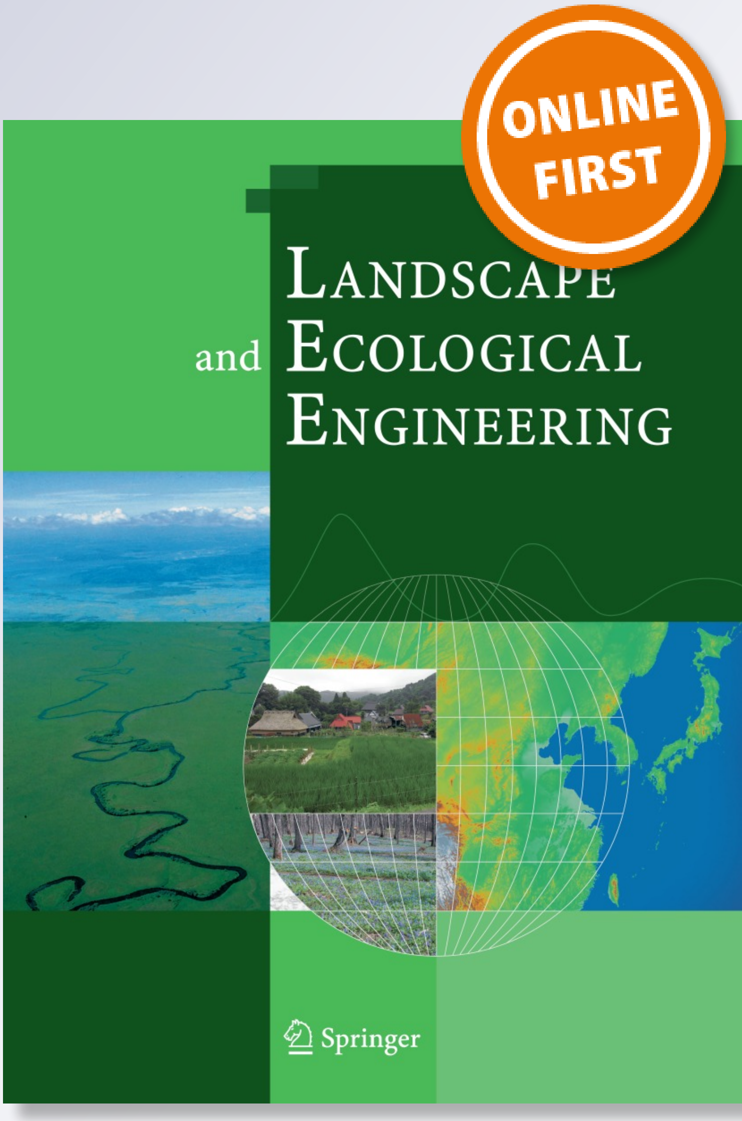

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SHORT COMMUNICATION

Water chemistry of headwater streams under stormflow conditions in catchments covered by evergreen broadleaved forest and by coniferous plantation

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Abstract It is important to determine the effects of vegetation on the water chemistry of headwater streams to ensure appropriate water resource management and landscape planning, particularly because vegetation is known to be one of the primary determinants of the chemistry in such streams and is easily altered by silvicultural operations. Previous studies of headwater stream water chemistry have investigated primarily the effects on baseflow. However, the sources and processes involved vary considerably between baseflow and stormflow due to rainfall. Stormflow water is supplied primarily through soil; accordingly, its chemistry is influenced by vegetation. The present study investigates the water chemistry of streams of headwater catchments, six with coniferous plantations and six with evergreen broadleaved forests, under four stormflow events and three times under baseflow conditions. The studied catchments were located in a hilly region in southwestern Japan and covered relatively small areas (0.7–3.6 ha). Inorganic ions, pH, and dissolved organic carbon were analyzed. A higher concentration of dissolved organic carbon and a lower concentration of Cl^- were found in the broadleaved catchments compared to the coniferous catchments under stormflow conditions, but no differences were detected under baseflow conditions. For catchments with older forests, the NO_3^- concentration was higher in the coniferous catchments than the broadleaved catchments under stormflow conditions. These results indicate that these three constituents were not diluted during stormflow and that their presence in soil water may be affected by the type of vegetation. The observed increased NO_3^- concentration under stormflow conditions may result in higher loading downstream.

Keywords Evergreen broadleaved forest · Nitrate · Stormflow · Stream water chemistry

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Introduction

Controlling the water quality of headwater streams is one of the most important ecological services provided by forest ecosystems (Brauman et al. 2007). Major determinants of the chemistry of headwater streams include climate, geology, topography, rainwater chemistry, land use, and vegetation (Reynolds et al. 1994; Ohte et al. 2001b; Yoh et al. 2001; Tanaka and Suzuki 2005; Konohira et al. 2006; Ogawa et al. 2006; Koshikawa et al. 2011). Of these water chemistry determinants, vegetation is altered relatively easily by silvicultural operations, such as reforestation, abandonment of plantation in clearcut sites, and conversion of tree species. Therefore, determining the effect of vegetation on the water chemistry of streams is considered to be of vital importance for water resource management and landscape planning. In addition, the effects of anthropogenic sources on the water chemistry of streams, particularly in terms of nitrogen, have been reported recently in Japan (Ohrui and Mitchell 1997; Mitchell et al. 2001; Ohte et al. 2001a; Zhang et al. 2008a; Tabayashi and Koba 2011).

The age of forest cover also has an effect on the water chemistry of streams (Vitousek 1977; Reynolds et al. 1994; Stevens et al. 1994; Ohrui and Mitchell 1998; Goodale et al. 2003), but the effect of forest type (i.e. tree species composition) remains poorly understood. A number of studies have found differences in the water chemistry of

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streams depending on tree species. Lovett et al. (2002) and Williard et al. (2005) reported that NO_3^- exported from forested watershed was associated with variation in tree species composition in North America. Similarly, Zhang et al. (2008b) reported that concentrations of NO_3^- and total dissolved nitrogen under baseflow conditions were higher in coniferous forests than deciduous broadleaved forests in four areas in Japan.

One possible reason for the relatively limited understanding of the effects of forest type on stream water chemistry is the inadequate timing of sampling. The water chemistry of streams under baseflow and stormflow conditions is controlled by different sources in forested headwaters and by the connectivity of the source to the stream (Mulholland et al. 1990; Creed and Band 1998; Sidle et al. 2000). The major contributing source for baseflow is typically groundwater, whereas that for stormflow is soil water (Ohrui and Mitchell 1999; Katsuyama et al. 2000; Piatek et al. 2009). Soil water is influenced more strongly by vegetation type than groundwater because of the interactions between soil and vegetation, such as accumulation of litter, absorption by roots, and deposition of throughfall (Creed and Band 1998; van Verseveld et al. 2009). Therefore, to determine the effects of forest type on the water chemistry of streams, sampling under stormflow conditions is thought to be essential. In areas with limited snowfall in Japan, under stormflow conditions as a result of rainfall, the concentrations of NO_3^- and base cations have been shown to increase and decrease, respectively (Takagi et al. 2004; Chiwa et al. 2010a; Oda et al. 2011). However, the effects of forest type on these changes in concentration have not yet been determined.

The present study primarily aims to determine the effect of forest type on the water chemistry of streams using stormflow sampling. In the southern part of the Kyushu Islands in Japan, man-made forests of Japanese cypress (*Chamaecyparis obtusa*) and Japanese cedar (*Cryptomeria japonica*) are very common, whereas the native vegetation consists of evergreen broadleaved forest. Moreover, baseflow concentrations of NO_3^- could depend on forest age. Therefore, different headwater catchments containing coniferous plantations and evergreen broadleaved forests of various ages were investigated.

Study sites and methods

The present study was conducted in Miyazaki University Forests in a hilly region in southwestern Japan (31°51′N, 131°18′E), on the western edge of the Miyazaki Plain and 15 km inland from the Pacific coastline (Fig. 1). The bedrock of the study area consists of Cenozoic sedimentary rocks, and the dominant soil type is a Gleyic, Dystric Cambisol (brown forest soil). Based on climatological observations over the last 10 years, taken at the administration office building of Miyazaki University Forests (which is located in the study area), the annual mean precipitation and temperature in the area are 2800 mm and 17.4 °C, respectively.

Twelve small headwater catchments, six containing coniferous plantations and six containing evergreen broadleaved forests, were selected for stream water sampling (Fig. 1). The coniferous plantations consist of Japanese cypress (*Chamaecyparis obtusa*) and Japanese cedar (*Cryptomeria japonica*). The evergreen broadleaved forests are naturally regenerated and are dominated by evergreen Fagaceae species, such as *Castanopsis cuspidata*. A summary of the characteristics of the catchments is presented in

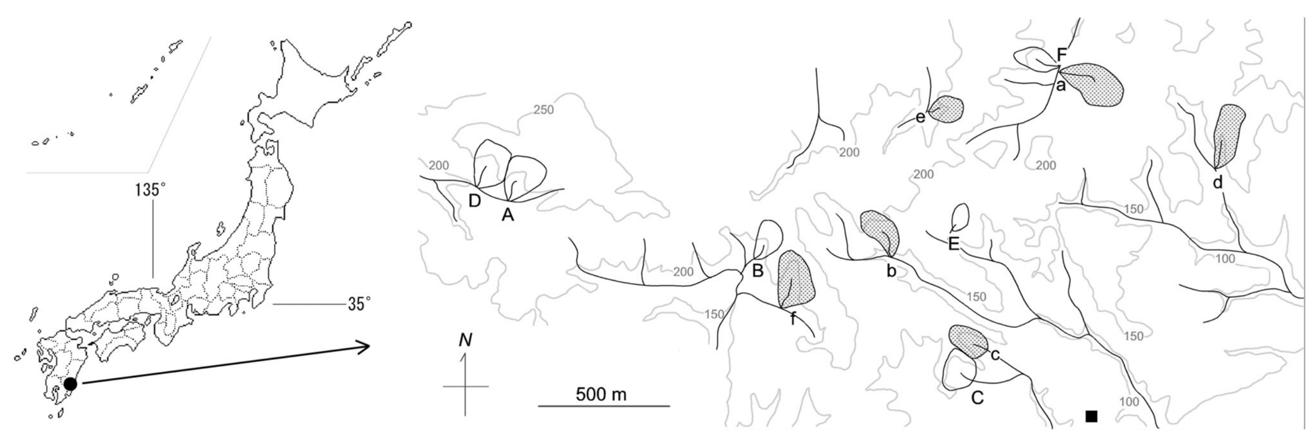

Fig. 1 Location of Miyazaki University Forests in Japan (*left*) and study catchments and major streams in Miyazaki University Forests (*right*). *Dotted areas* with *small letter* and *white areas* with *capital letter* indicate coniferous and broadleaved catchments, respectively. A *black square* in the *right panel* indicates the location of a rain gauge (administration office building of Miyazaki University Forests). Numbers on *grey lines* (*contours*) in the *right panel* indicate altitude

Table 1 Characteristics of the studied catchments

Catchments	Age (years)	Area (ha)	Slope (°)	Elevation (m)
Broadleaved				
A	21	2.0	16	215
B	53	1.2	24	170
C	66	1.9	10	135
D	89	1.6	22	195
E	87	0.7	16	160
F	93	1.2	19	145
Coniferous				
a	41	3.6	7	145
b	49	1.3	20	155
c	52	1.2	10	140
d	88	2.3	9	125
e	92	0.7	21	180
f	95	2.3	12	170

Table 1, including catchment area, forest age, mean catchment slope, and the elevation of the sampling point. The mean catchment slope was calculated by measuring the difference in height between the highest and lowest (i.e., sampling point) elevations of the catchment and dividing this by the distance between these two points. The smallest catchment area was 0.7 ha and the largest was 3.6 ha. All the streams of the catchments were first order. The maximum and minimum elevations of the sampling point were 215 and 125 m, respectively. The youngest and oldest forests were 21 and 95 years old in 2010. Broadleaved catchment E is equipped with a weir for stream flow observation. The water level of the weir, which has a 30° notch, was measured at 10-min intervals using a pressure transducer (CS-420, Campbell Scientific) and recorded using a datalogger (CR10X, Campbell Scientific).

Size and density of trees in all catchments were surveyed. The surveyed area in each catchment was greater than 5 % of the catchment area at least. The number and diameter at breast height (DBH; cm) of trees in the surveyed area were measured in 2009 or 2010, only trees exceeding 5 cm DBH were measured, and basal area (BA; m^2), that is, the cross-sectional area of tree stem at breast height, was calculated from the measured DBH as follows:

$$\mathrm{BA} = \pi\,(\mathrm{DBH}/2)^2/10000 \qquad (1)$$

Tree density was assumed to be tree number divided by the surveyed area and expressed as per hectare. In broadleaved catchments A, B, and C and coniferous catchments a and d, two or three square plots of 400 m^2 were located in both a valley and on ridges. Broadleaved catchment F and coniferous catchment e were both part of the existing forest monitoring programs, with plots of 1 ha each (Ishihara et al. 2011); the results from the monitoring programs were used for these two catchments. For the other catchments, a 10-m wide survey transect was placed perpendicular to the stream line, from one ridge to another.

The vegetation characteristics of each catchment are summarized in Table 2. The coniferous catchments had large BA, approximately double that of the broadleaved catchments. In the catchments with older coniferous forests (d, e, f), about one-third or one-quarter of total BA was BA of broadleaved trees. The broadleaved catchments showed no correlation between age and BA, tree density, or average DBH. In contrast, the average DBH of coniferous trees in the coniferous catchments was larger in catchments with older forests than in catchments with younger forests.

Stream water was collected at four different times under stormflow conditions resulting from rainfall events (S1, S2, S3, and S4) and at three different times under baseflow conditions (B1, B2, and B3) from May 2008 to May 2010 (Table 3). Stormflow samplings S1 and S4 took place during the rising phase of the hydrograph (before peak flow) during precipitation, whereas samplings S2 and S3 took place during the recession phase (after peak flow) (Fig. 2). The stormflow and baseflow conditions were expressed using specific discharge measured in broadleaved catchment E and antecedent precipitation index (API_3) (Welsch et al. 2001). The API_3 indicates the contribution of antecedent precipitation amount to discharge, weighing recent precipitation more heavily than earlier precipitation, and was defined as follows:

$$\mathrm{API}_3 = \sum_{i=0}^{3} (P_i/i) \qquad (2)$$

where P_i was the precipitation amount (mm) of i days beforehand. Sampling in all 12 catchments took approximately 4 h. The water temperature of the streams was measured in situ at each sampling point. Immediately after sampling, the pH and electrical conductivity (EC) were measured using a pH meter (CH-40V, DKK-TOA) and an EC meter (CM-40V, DKK-TOA), respectively, using a non-filtered sample in a laboratory of Miyazaki University Forests. Additional chemical analyses were conducted after a filtering sampling using a PTFE membrane filter (0.2 µm) (DISMIC-25HP, ADVANTEC). The concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} was measured using ion chromatography (LC-10, Shimadzu). The concentration of NH_4^+ was determined using the indophenol method. Dissolved organic carbon (DOC) was analyzed using a TOC analyzer (TOC-V, Shimadzu). All analyses were conducted within 2 days after sample collection. The NO_3^- concentrations of precipitation and baseflow stream water were monitored throughout the

Table 2 Vegetation of the catchments

Catchment	Total BA (m^2/ha)	BA of broadleaved trees in survey plots (m^2)	BA of coniferous trees in survey plots (m^2)	Tree density (/ha)	Average DBH (cm)
Broadleaved					
A	34.1	3.5	0	5140	9.1
B	44.2	3.5	0	1900	16.1
C	39.2	4.7	0	1580	15.6
D	41.6	4.2	0	3080	10.3
E	45.1	22.5	0	2440	12.2
F	40.3	4.5	0.1	1470	14.0
Coniferous					
a	71.1	0	11.4	1530	24.6
b	80.1	0	6.4	2340	20.7
c	86.5	0	6.9	1790	25.2
d	58.2	10.0	19.1	1700	11.1 (29.5)
e	72.0	4.3	6.8	1660	18.7 (31.7)
f	67.2	2.7	6.5	1820	17.3 (30.9)

Values in parentheses of catchment d, e, and f are average DBH of only conifer trees

BA denotes the basal area of trees, *DBH* denotes the diameter at breast height of trees

Table 3 Outline of the sampling

Year/month/day	Abbreviation	API_3 (mm)	Specific discharge (mm/h)	Water temperature (°C)
2008/05/22	B1	0	0.013	16.2
2008/06/02	S1	85	1.1	17.3
2008/07/31	B2	1	0.006	23.4
2008/08/28	S2	122	2.3	20.9
2009/05/15	B3	0	0.012	17.2
2009/10/08	S3	84	0.70	19.5
2010/05/19	S4	89	2.4	16.8

Specific discharge and water temperature were measured at broadleaved catchment E

B and *S* mean baseflow and stormflow, API_3 denotes antecedent precipitation index

study period. Precipitation was collected for each precipitation event at the administration office building of Miyazaki University Forests using a bulk sampler. The stream water was collected bi-weekly under baseflow conditions at the weir of catchment E. The concentration of NO_3^- was analyzed following the method described above.

To determine any differences in the concentrations of the constituents between forest types on each sampling day, a nonparametric Wilcoxon test was conducted. Two-way analysis of variance (ANOVA) was used to examine the effect of flow conditions (stormflow or baseflow) and forest types (coniferous or broadleaved) on concentration. In the first ANOVA, flow condition and catchment were used as regressors and catchment was a repeated measure, for both forest types. In the second ANOVA, forest type and sampling day were used as regressors and sampling day was a repeated measure, for both flow conditions. For the six catchments with older forest age (i.e., over 80 years; D, E, and F of the broadleaved catchments and d, e, and f of the coniferous catchments), another ANOVA (in which forest type and sampling day were used as regressors and sampling day was a repeated measure) was conducted for both flow conditions. Statistical analyses were conducted using the JMP(R) 4 (SAS Institute) software. The level of significance was 0.05 for all tests.

Results

The API_3 and specific discharge of baseflow (stormflow) samplings were less than 1 mm (more than 80 mm) and less than 0.015 mm/h (more than 0.70 mm/h), respectively (Table 3). Specific discharge was measured using a weir in only one catchment (E). However, sampling of all catchments took about 4 h and the catchments were located within a relatively small area (3.0 × 1.5 km rectangle); therefore, the sampling of all catchments was conducted under high flow conditions.

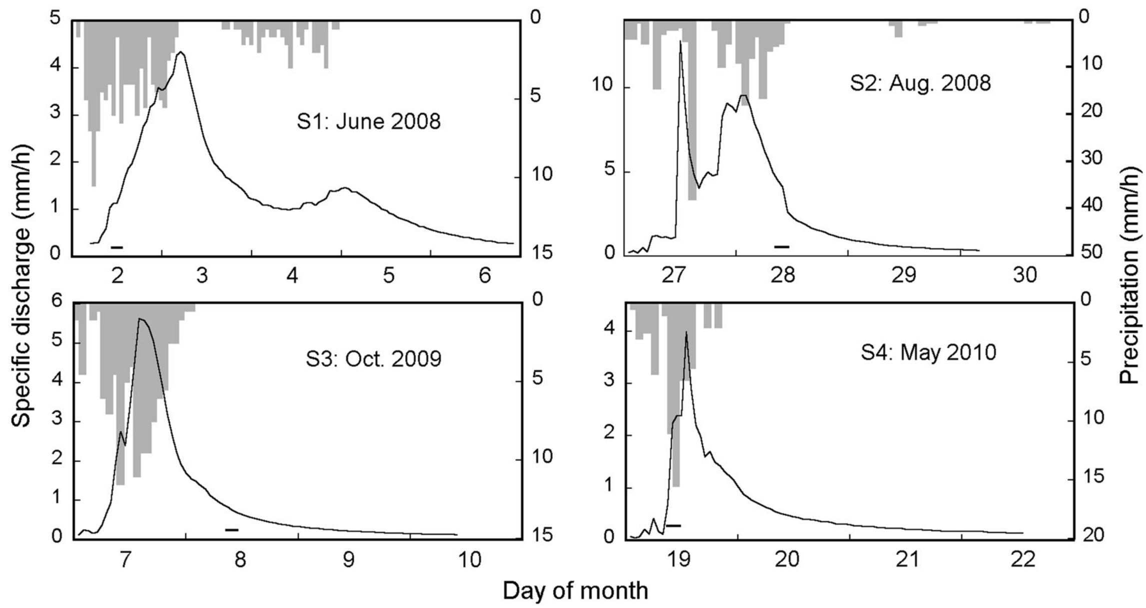

Fig. 2 Specific discharge measured at catchment E and precipitation of the stormflow samplings. The *horizontal bars* indicate the duration of sampling for 12 catchments (about 4 h)

The average concentrations of NO_3^- for baseflow stream water and precipitation measured at catchment E during the study period were 0.56 mg/l ($n = 46$) and 0.69 mg/l ($n = 63$), respectively.

The average water chemistry concentrations for the coniferous and broadleaved catchments for each sampling day are presented in Fig. 3. Only NO_3^- for sampling S2 varied significantly with forest type, with the coniferous catchments exhibiting higher concentrations. The two-way ANOVA using flow condition as the regressor revealed that the concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} varied significantly depending on the flow conditions in both forest types, and pH varied significantly in the broadleaved catchments (Table 4). These constituents (Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and pH) were lower under stormflow conditions (Fig. 3), independent of the phase of the hydrographs. The two-way ANOVA with forest type as the regressor revealed that the concentrations of Cl^- and DOC varied significantly between forest type only under stormflow conditions (Table 5): concentrations of Cl^- were higher in the coniferous catchments and DOC was higher in the broadleaved catchments (Fig. 3). There were no significant differences in concentrations between forest types under baseflow conditions.

For catchments with older forest (i.e., over 80 years old; coniferous catchments d, e, and f and broadleaved catchments D, E, and F) the concentrations of NO_3^- were higher in the coniferous catchments than in the broadleaved forest catchments under stormflow conditions (Fig. 4), based on the two-way ANOVA with forest type as the regressor conducted for only the older forest catchments (Table 6). No significant differences were observed for other constituents in the catchments with older forest.

Discussion

Nitrogen saturation of forest ecosystems due to excess atmospheric nitrogen deposition has been reported previously in Japan (Ohrui and Mitchell 1997; Ohte et al. 2001a; Zhang et al. 2008a; Tabayashi and Koba 2011). In the present study, the NO_3^- concentration of baseflow streamwater at catchment E was lower than that of precipitation. In addition, the annual average NO_3^- concentrations for streamwater and rainfall in the region surrounding the study site (Miyazaki Prefecture) were 0.61 and 0.70 mg/l (wet deposition only), respectively, representing the lowest levels found in Japan (Konohira et al. 2006; Japan Environmental Laboratories Association 2010). Therefore, the results of this study could be discussed without the effect of nitrogen saturation.

Under stormflow conditions, higher concentrations of DOC and lower concentrations of Cl^- were found in the broadleaved catchments, and higher concentrations of NO_3^- were found in the catchments with older coniferous forest. However, the concentration of these three constituents were not lower under stormflow conditions than under baseflow conditions. This suggests that these constituents were not diluted by a substantial contribution of

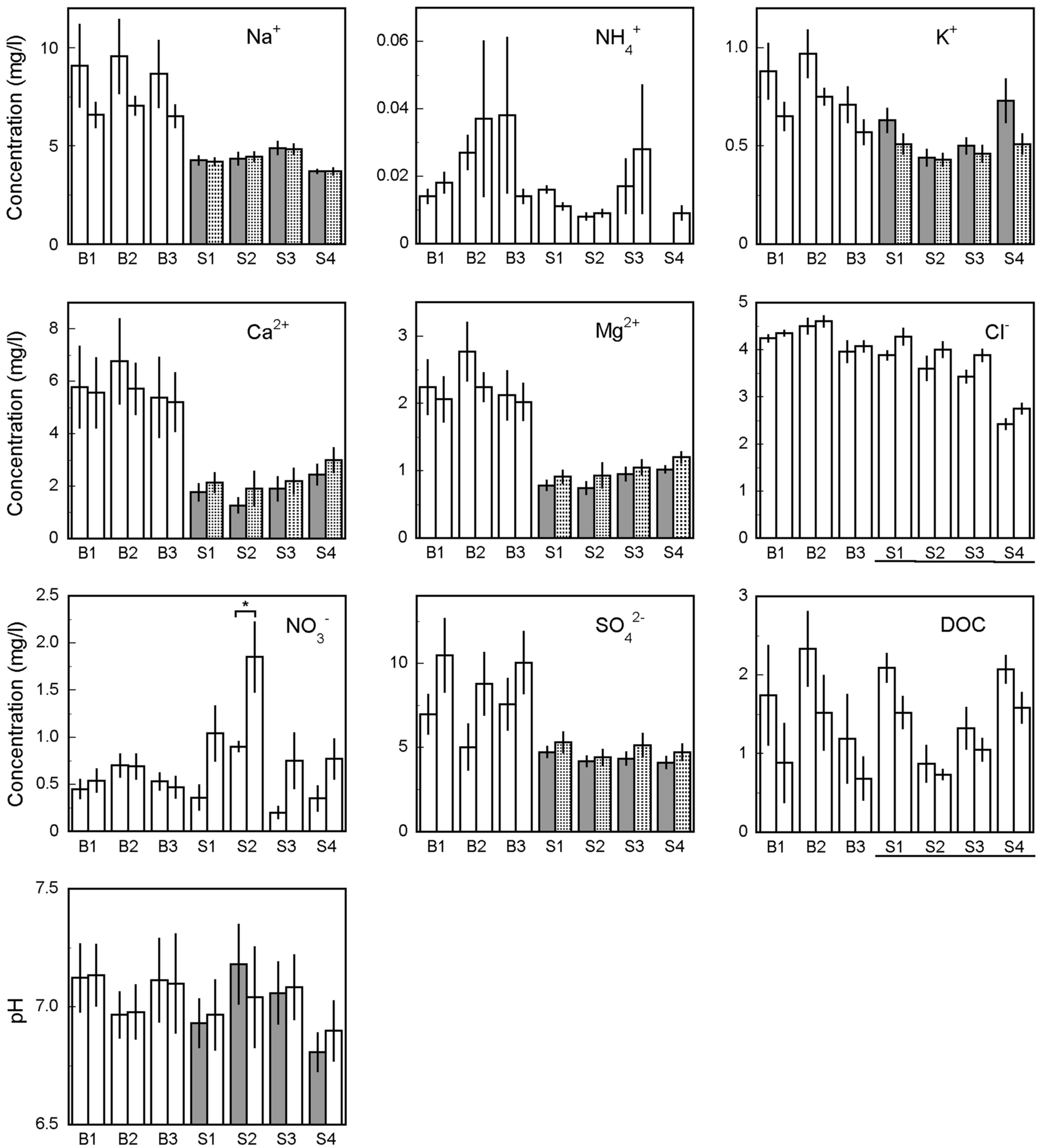

Fig. 3 Average concentration and pH of broadleaved (*left bar*) and coniferous (*right bar*) catchments for each sampling day. *B1–B3* and *S1–S4* indicate baseflow condition and stormflow condition, respectively. *Vertical lines* of the *bars* indicate standard errors. *Underbars* of the sampling days denote significant differences between forest types for each flow condition. *Colored bars* denote significant differences between the flow conditions for each forest type. An *asterisk* denotes statistically significant difference between broadleaved and coniferous catchments

soil water, i.e., water flowing through soil, which would contain an abundance of these constituents. In particular, DOC and NO_3^- are strongly associated with biological processes in soil, including the decomposition of plant litter and interaction with microbes (Konohira and Yoshioka 2005; van Verseveld et al. 2009).

Table 4 Probabilities of two-way ANOVA for effects on constituent concentration, with flow condition and catchment as regressors and catchment was a repeated measure, for both forest types

Constituents	Broadleaved			Coniferous		
	Flow condition	Catchment	Flow × catchment	Flow condition	Catchment	Flow × catchment
Na^+	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
K^+	**0.04**	**<0.01**	**<0.01**	**0.01**	**<0.01**	**<0.01**
NH_4^+	0.10	**<0.01**	0.39	0.37	0.37	0.20
Ca^{2+}	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
Mg^{2+}	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
Cl^-	0.07	**0.03**	0.49	0.20	0.09	0.12
NO_3^-	0.60	**<0.01**	**<0.01**	0.14	**<0.01**	**<0.01**
SO_4^{2-}	**0.02**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**
pH	**0.03**	**<0.01**	**<0.01**	0.08	**<0.01**	**0.04**
DOC	0.73	**<0.01**	**<0.01**	0.56	0.06	**<0.01**

Level of significance at 0.05 are indicated in bold

Table 5 Probabilities of two-way ANOVA for effects on constituent concentration, with forest type and sampling day as regressor and sampling day as repeated measure, for both flow conditions

Constituents	Stormflow			Baseflow		
	Forest type	Sampling day	Forest type × sampling day	Forest type	Sampling day	Forest type × sampling day
Na^+	0.99	**<0.01**	0.89	0.29	**0.03**	0.73
K^+	0.25	**<0.01**	**0.01**	0.21	**<0.01**	0.32
NH_4^+	0.80	**0.01**	0.78	0.82	0.50	0.41
Ca^{2+}	0.48	**<0.01**	0.76	0.82	**0.03**	0.35
Mg^{2+}	0.32	**<0.01**	0.88	0.62	**<0.01**	0.10
Cl^-	**0.01**	**<0.01**	0.98	0.51	**<0.01**	1.00
NO_3^-	0.06	**<0.01**	0.16	0.97	**<0.01**	0.36
SO_4^{2-}	0.44	**<0.01**	0.30	0.22	**<0.01**	0.53
pH	0.82	**<0.01**	0.69	0.86	0.93	0.46
DOC	**0.04**	**<0.01**	0.31	0.16	**<0.01**	0.58

Level of significance at 0.05 are indicated in bold

The results demonstrating higher NO_3^- concentrations for the older coniferous catchments under stormflow conditions suggest that, despite limited sampling frequency, forest type is one of the factors controlling the NO_3^- concentration of stream water. The NO_3^- concentration has been shown to increase under stormflow conditions (Takagi et al. 2004; Chiwa et al. 2010a; Oda et al. 2011), although the level of this increase depends on the rising phase (i.e., before peak flow) or the recession phase (i.e., after peak flow) of hydrograph (Rusjan et al. 2008). Sampling was performed once per storm under the stormflow conditions of the present study. The stormflow conditions (i.e., hydrographs) of the 11 other catchments would not have been exactly the same as those of catchment E. However, regardless of the timing of sampling (i.e., before or after the peak), the degree of discharge, and the season and year of the storms, the NO_3^- concentration was always higher in the older coniferous catchments under stormflow conditions. Zhang et al. (2008b) reported that, under baseflow conditions, the NO_3^- concentration and total dissolved nitrogen were higher in coniferous forests than deciduous broadleaved forests in four areas in Japan. In addition to forest type, forest age is also known to affect the NO_3^- concentration of stream water (Vitousek 1977; Reynolds et al. 1994; Stevens et al. 1994; Ohrui and Mitchell 1998; Goodale et al. 2003). Various other factors might affect these NO_3^- concentrations, including catchment aspect, soil depth, and the area of the riparian zone; all of these factors likely varied between the older coniferous and broadleaved catchments. However, the NO_3^- concentrations of the three older coniferous catchments were always higher than those of the broadleaved catchments, for all four stormflow conditions. In order to clarify the effects of these other factors, an additional sampling design stratifying these factors will be required in a future study.

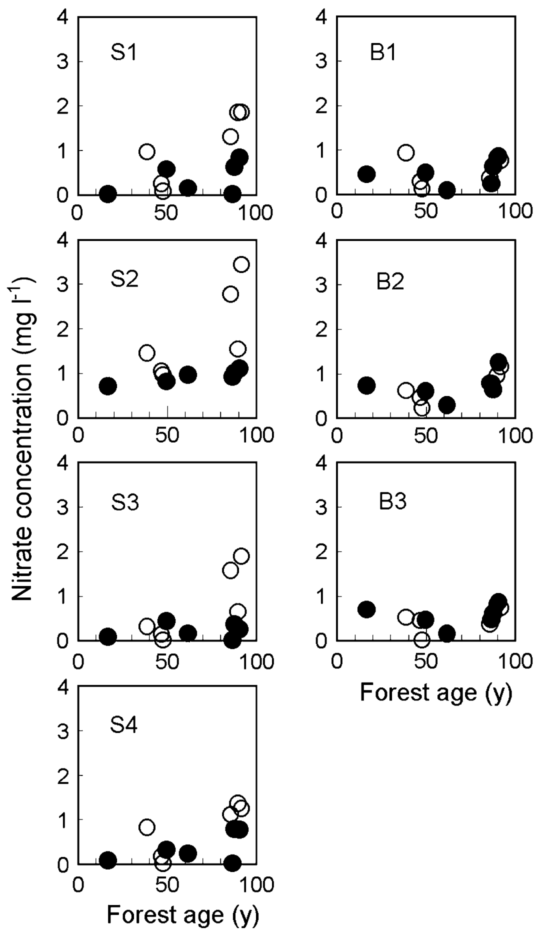

Fig. 4 Correlation between forest age and nitrate concentration of catchments for each sampling day. *B1–B3* and *S1–S4* indicate baseflow condition and stormflow condition, respectively. *Open* and *solid circles* denote coniferous and broadleaved catchments, respectively

The higher NO_3^- concentrations in older coniferous catchments can likely be attributed to hydro-biological processes in both the canopy and soil, as suggested in previous studies. Knops et al. (2002) insisted that plant species impact the nitrogen cycle of forest ecosystems through two processes: control of inputs and losses, and interaction with organic matter and microbes in soil. Thus, plant species could affect soil nitrogen dynamics, although any effects would require a considerable period of time to be incorporated into soil. Inputs (deposition) and losses (soil seepage) of nitrogen have been reported to be higher in coniferous forests than deciduous broadleaved forests in Europe (Rothe and Mellert 2004; De Schrijver et al. 2007); this has been attributed to the crowns of coniferous trees exhibiting higher interception capacities for atmospheric deposition (De Schrijver et al. 2007). In terms of the interactions, Staelens et al. (2012) reported higher gross nitrification in coniferous forest soil than deciduous broadleaved forest soil. In contrast, in Japan, Inagaki et al.

Table 6 Probabilities of two-way ANOVA for effects on nitrate concentration of catchments with older forest, with forest type and sampling day as regressor and sampling day as repeated measure, for both flow conditions

Constituents	Stormflow			Baseflow		
	Forest type	Sampling day	Forest type × sampling day	Forest type	Sampling day	Forest type × sampling day
Na^+	0.62	**<0.01**	0.89	0.43	0.17	0.43
K^+	0.26	**<0.01**	0.24	0.32	**<0.01**	0.32
NH_4^+	0.30	0.52	0.27	0.34	0.47	0.38
Ca^{2+}	0.59	**0.04**	0.33	0.58	0.16	0.26
Mg^{2+}	0.43	0.13	0.54	0.49	**0.04**	0.16
Cl^-	0.36	**<0.01**	0.91	0.64	**<0.01**	0.88
NO_3^-	**<0.01**	**<0.01**	0.38	0.81	**<0.01**	0.79
SO_4^{2-}	0.98	0.09	0.73	0.51	**0.02**	0.24
pH	0.64	**<0.01**	0.41	0.82	0.52	0.71
DOC	0.08	**<0.01**	0.39	0.23	**0.02**	0.34

Level of significance at 0.05 are indicated in bold

(2004) reported lower soil nitrogen mineralization in coniferous forests than deciduous hardwood forests. Inagaki et al. (2004) also reported higher soil nitrogen mineralization in older forests compared to younger forests. Nitrate released from soil could contribute to that in stream water, as determined using the oxygen isotope ratio of NO_3^- (Piatek et al. 2005; Tobari et al. 2010). These previous studies indicated that coniferous forests tend to exhibit greater nitrate fluxes (inputs and release) and that these processes would be remarkable in older forests, although the inconsistent results had been reported. Thus, the higher NO_3^- concentrations in older coniferous catchments may reflect the nitrogen dynamics of these forests.

The NO_3^- concentrations in coniferous catchments were found to be higher than in the broadleaved catchments under stormflow conditions, especially in the older forests, but DOC concentrations were lower in the coniferous catchments. One of the probable reasons for this may be the inverse correlation between the concentration of DOC and NO_3^- in stream water: Konohira and Yoshioka (2005) insisted that excess nitrogen availability, together with a carbon deficit in the soil environment, could explain this inverse relationship. Higher Cl^- concentrations in coniferous catchments were also reported for 25 headwater catchments in the northern Kanto area in Japan by Ohuri and Mitchell (1998), who attributed these higher Cl^- concentrations to the condensation of wet-deposited Cl^- due to increased evaporation in coniferous forests. Similarly, Peters et al. (1998) also indicated that Cl^- resulted from atmospheric deposition and was affected only by evapotranspiration from soil.

The present study demonstrates that the catchments with older coniferous forest exhibited a higher NO_3^- concentration than the broadleaved catchments under stormflow conditions. Stormflows with a higher concentration cause increased loading downstream (Chiwa et al. 2010b). In recent years in Japan, the aging of coniferous plantations has become inevitable owing to postponement of harvest. An increase in the area of older coniferous plantation would result in more streams with increased NO_3^- loading downstream. Further studies are required to document the relationship between forest type and the water chemistry of streams under various stormflow conditions.

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