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Relationship of topography to surface water chemistry with particular focus on nitrogen and organic carbon solutes within a forested watershed in Hokkaido, Japan

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Abstract:

We studied the relationships between streamwater chemistry and the topography of subcatchments in the Dorokawa watershed in Hokkaido Island, northern Japan, to examine the use of topography as a predictor of streamwater chemistry in a watershed with relatively moderate terrain compared with other regions of Japan. Topographic characteristics of the Dorokawa watershed and its subcatchments were expressed as topographic index (TI) values, which ranged from 4·5 to 20·4 for individual grid cells (50×50 m^2), but averaged from 6·4 to 7·4 for the 20 subcatchments. Streamwater samples for chemical analyses were collected four times between June and October 2002 from 20 locations in the watershed. The pH of water that passed through the watershed increased from ~5·0 to 7·0, with major increases in Na^+ and Ca^{2+} and marked decreases in NO_3^- and SO_4^{2-}. Distinctive spatial patterns were observed for dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and NO_3^- concentrations of streamwater across the watershed. Statistical analyses indicated significant linear relationships between the average TI values of subcatchments and DOC, DON, and NO_3^- concentrations. Furthermore, the proportion of DOC in streamwaters in the wet season increased with TI values relative to other nitrogen species, whereas NO_3^- concentrations decreased with TI. The gradients of soil wetness and the presence of wetlands explained many of the observed spatial and temporal patterns of DOC, DON, and NO_3^- concentrations in the surface waters of the Dorokawa watershed. Our results suggest that the TI is especially useful for predicting the spatial distribution of DOC, DON and NO_3^- in the surface waters of Hokkaido, where topographical relief is moderate and wetlands more common than in other regions of Japan. Copyright © 2006 John Wiley & Sons, Ltd.

KEY WORDS Hokkaido; biogeochemistry; forested watershed; streamwater chemistry; topographic index; dissolved organic carbon; dissolved organic nitrogen; nitrate

INTRODUCTION

Topography is considered to be one of the major determinants of the chemistry of ground and surface waters because it influences the interactions between biogeochemistry and hydrology in watersheds (Childers and Gosselink, 1990; Dillon and Molot, 1997; Soranno *et al.*, 1999; Johnson *et al.*, 2000; Webster *et al.*, 2000). One of the early studies that analysed the relationships between watershed topography and streamwater chemistry was done by Vitousek (1977). He found negative relationships between the elevation of streamwater sampling points and the concentrations of Ca^{2+}, SiO_2, and Na^+ in streamwater.

Ohrui and Mitchell (1998) also evaluated the effects of the steep topography of forested watersheds near Tokyo on Honshu Island, Japan, in affecting the NO_3^- concentrations in streamwaters. They reported that due to the steep topography the near-stream zones of a forested watershed had higher nitrogen mineralization and nitrification rates than well-drained ridge areas did, and acted as a net source of nitrogen. This result is

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in contrast to other studies on watersheds with less-steep topography, where the near-stream zone often acts as a nitrogen sink due to denitrification (Hill, 1996; Cirmo and McDonnell, 1997).

Topography plays an important role in affecting soil moisture conditions. Various expressions of topographical characteristics of catchments have been used to explain the observed biogeochemical patterns. For example, catchment slope was used to predict dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations in lake water (D'Arcy and Carignan, 1997), and upslope versus downslope position was used to explain differences in soil DOC concentrations (Boyer *et al.*, 1997).

The topographic index (TI) is an indirect expression of catchment topography and was devised by Kirkby (1975) as an index of the propensity of soil for wetness. The TI is defined as $\ln(a/\tan\beta)$, where a is the contributing area per unit contour length and β is the local slope angle. TI is a topographically estimable indicator of potential wetness of a location depending on how much water the location can collect from its upslope area and how fast the groundwater can move through the area. TI has been used to explain topographic controls on various hydrological and biogeochemical behaviours of catchments. For example, Wolock *et al.* (1990) found a correlation between catchment average TI and H^+ concentrations of streamwater. Creed and Band (1998) used TI to derive soil saturation deficit as a hydrological control over the nitrogen export to streamwaters during snowmelt. They showed that the combination of topography and temporal moisture conditions provide a good predictor of NO_3^- flushing behaviour of a catchment during snowmelt events.

Most studies on hydrological and biogeochemical relationships in Japan have focused on Honshu, the largest island of Japan, where more than 80% of the Japanese population resides (Ohte *et al.*, 1995; Hobara *et al.*, 2001; Katsuyama *et al.*, 2001). However, more recently, studies on these subjects have begun in Hokkaido (Ozawa *et al.*, 2001; Shibata *et al.*, 2001). Hokkaido, the northernmost island of the four major islands of Japan, extends from about latitude 41 °N to 46 °N. Unlike Honshu, which has extremely steep slopes, Hokkaido has relatively moderate topography and has a cooler climate (e.g. average monthly temperature for 1971 to 2000 at six representative meteorological sites in Hokkaido ranges from $-5{\cdot}4$ to $20{\cdot}3$ °C versus $3{\cdot}7$ to $26{\cdot}2$ °C for the averages of 50 sites in Honshu). The climate of Hokkaido is classified as temperate to cool-temperate. Owing to its moderate slopes, Hokkaido has many freshwater wetlands that are characterized by the presence of constantly wet soils and wetland vegetation. This island contains 86% of all wetland areas in Japan (Geographical Survey Institute, 2001).

It is possible that the moderate topography of Hokkaido and the presence of wetlands exert unique biogeochemical signals in the streamwaters in Hokkaido compared with those in Honshu. Saturated soils in riparian areas throughout the world are known to be important in affecting the biogeochemistry of ground and surface waters (Naiman and Décamps, 1997; Shibata *et al.*, 2004). Similarly, many studies have shown the influence of wetlands on streamwater chemistry (Hansen *et al.*, 1994; Hill, 1996). Wetlands are also recognized as a significant source of DOC (Urban *et al.*, 1989) and DON (Marion and Brient, 1998). Bischoff *et al.* (2001) reported that the wetlands in a forested Adirondack watershed in New York, although a relatively small proportion of the water area, played a disproportionate influence on the storage of nitrogen.

The objectives of our study were to: (1) show overall changes in chemistry as precipitation is passed through the watershed and discharged into surface waters; (2) investigate the influence of topographical attributes of subcatchments on the streamwater DOC and nitrogen solute chemistry in a forested watershed of northern Hokkaido; (3) ascertain any seasonal differences in the spatial patterns of these solutes in this watershed. There have been no previous studies conducted in Hokkaido that focused on the relationships between topography of catchments and streamwater chemistry. Owing to the uniqueness of Hokkaido with respect to topography, wetland contributions, vegetation composition and climate compared with not only Japan, but also with other regions of the world, the evaluation of these relationships should provide further insight on the importance of topography in affecting water chemistry both within and among regions. Also, this information should provide a basis for future studies in Hokkaido that can address additional questions on hydrological and biogeochemical relationships in the region.

METHODS

Study site

The Dorokawa watershed is located in Hokkaido University's Uryu Experimental Forest (UREF), at 44°12′N, 142°11′E (Figure 1). The area of the entire watershed is 3165 ha. The elevation ranges from 284 to 681 m. The watershed has a gentle topography with an average slope of 9·2°. Average annual precipitation from 1996 to 2001 was 1255 mm, with the highest precipitation in late summer to late fall. This region has heavy snowfall: the annual maximum snow depth is 208 cm (the average of 1956–89 near the office of UREF located about 5 km east from the watershed) and 58% of precipitation comes as snow (Ishikawa *et al*., 1998). The dominant bedrock of Dorokawa watershed is Neogene andesite covering the majority of upland areas (Geological Survey of Japan, 1995). Quaternary sedimentary rock extends into some areas of the valley bottom. Vegetation cover is mostly cool-temperate natural mixed forests of hardwood and conifer species, mainly represented by Sakhalin fir (*Abies sachalinensis*), Mongolian oak (*Quercus crispula*), Japanese Manchurian ash (*Fraxinus mandshurica* var. *japonica*), Erman's birch (*Betula ermanii*), painted maple (*Acer mono*) and Amur cork-tree (*Phellodendron amurense*). The forest understory is almost exclusively dominated by Chishima dwarf bamboo (*Sasa kurilensis*), except for some wetland areas and riparian zones. The general pattern of vegetation distribution is such that the high-elevation ridge areas in the watershed are often devoid of trees and are only covered with dwarf bamboo. The high-elevation mountain sides have broadleaf forests as overstory vegetation. The most extensive middle-elevation areas and some low-elevation areas are covered with mixed forests. The low-elevation valley-bottom areas with wet soils are often covered with coniferous forests.

The Dorokawa watershed has several types of wetland. The most extensive type of wetland is classified as 'spruce–swamp forests', which contain sparse, but pure stands of Glehn's spruce (*Picea glehnii*) with dense thickets of dwarf bamboos (*Sasa* spp.) in the understory. These spruce–swamp forests extend near the lower reaches of the main stream draining the watershed. The groundwater level of this wetland type stays near, but not above, the surface during the growing season. Peat deposits of these spruce–swamp forests are typically ∼2·5 m deep. The second type of wetland, 'open mire', forms small patches of grasses and herbs without tree or dwarf bamboo cover. Alder shrubs (*Alnus* spp.) are often found in these wetlands. A third type of wetland is found in riparian areas that are dominated by ash, willows, sedges, and grasses. These 'riparian wetlands' are underlain by a mixture of peat and alluvial sediments.

Field sampling

Streamwater samples were collected four times, once in each early June, late June, late September, and mid October of 2002 from 20 sites in Dorokawa watershed. The sampling periods were planned so that seasonal patterns in streamwater chemistry might be detected to enable comparisons between early summer (June) and autumn, with the latter sampling including periods with substantial rain events (September and October). To minimize any temporal variation at each sampling time, streamwater samples from all sites were collected within 2 days. To facilitate sampling, most of the sampling points were in close proximity of logging roads crossing the streams. Owing to logistical limitations, samples could not be collected at all sites at all four sampling times.

We measured pH in the field with an Horiba B-212 glass electrode. Streamwater samples were filtered with aWhatman 0·7 μm GF/F filter within 24 h of collection, and further filtered with a TOA 0·2 μm membrane filter prior to ion chromatographic analysis. Samples were analysed in the laboratory of Hokkaido University. Concentrations of Cl^-, $NO_3{}^-$, SO_4^{2-}, Na^+, $NH_4{}^+$, K^+, Mg^{2+}, and Ca^{2+} were measured using ion chromatography (Dionex DX-500). Total DOC was analysed with a TOC analyser (Shimadzu TOC-5000). Total dissolved nitrogen (TDN) was determined with a TN analyser (Mitsubishi Chemical TN-100). The concentrations of total DON were calculated by subtracting the concentrations of NH_4-N and NO_3-N from that of TDN. Calculations that resulted in negative DON values were set to zero (only 5 of 61 samples).

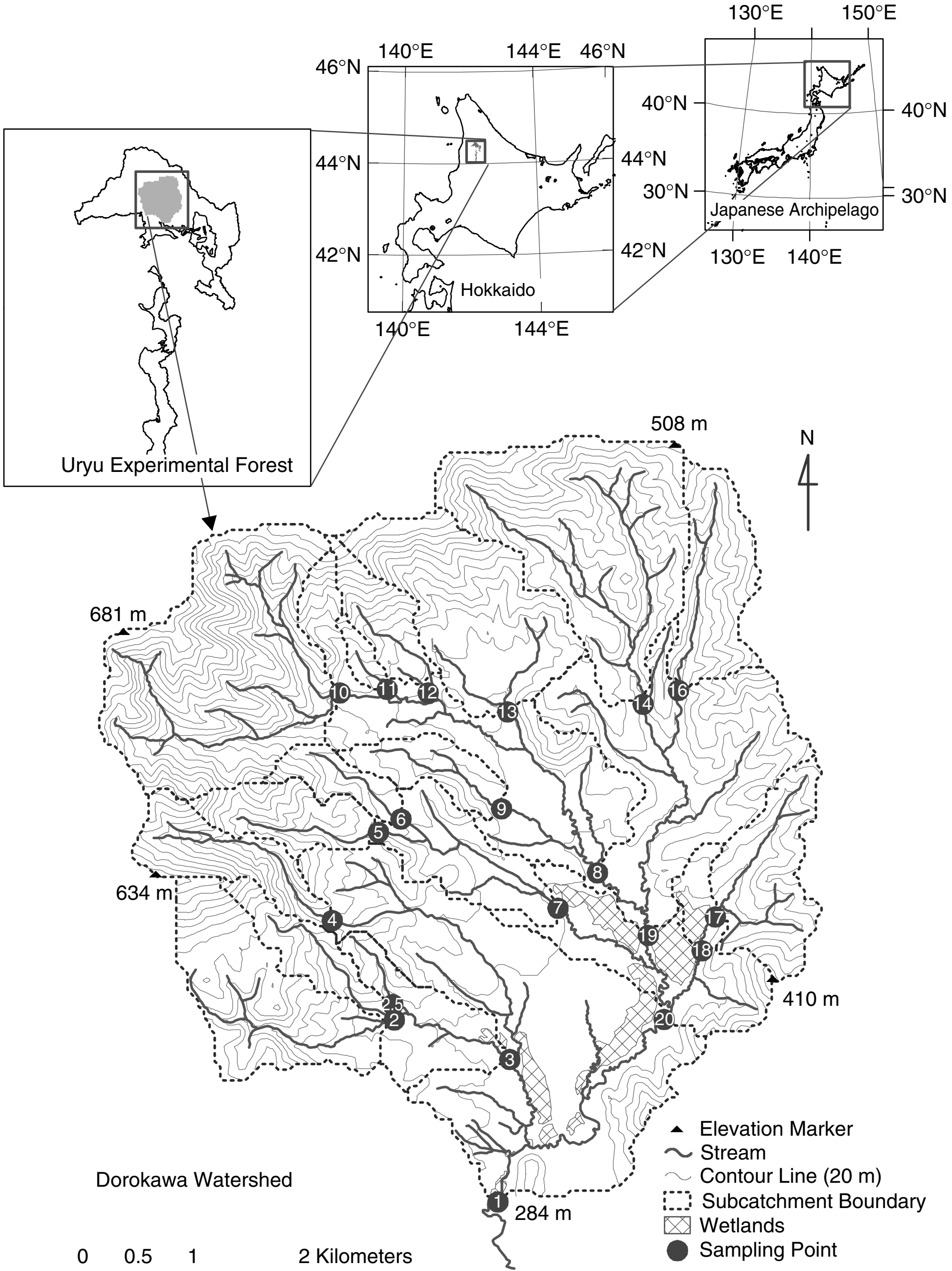

Figure 1. Maps of Dorokawa watershed and streamwater sampling sites

Wet-only deposition data collected at the research facility of UREF from April 2000 to March 2001 by Hokkaido University were obtained to compare the chemistry of precipitation and streamwater (Field Science Center for Northern Biosphere, Hokkaido University, 2000). The deposition-monitoring site is located approximately 5 km away from the nearest streamwater sampling point, both of which are at the same elevation.

Geographical information system data preparation

To compute the drainage area of each streamwater sampling point, subcatchments were delineated using the streamwater sampling points as outlets based on a digital elevation model (DEM) of 50 m × 50 m resolution (Geographic Survey Institute, 1999) using TauDEM, computer software developed by Tarboton (2001).

The raster geographical information system (GIS) layers of TI (Kirkby, 1975) were used as an indicator of wetness that can be estimated from the watershed's topography (Figure 2). The TI was defined as $\ln(a/\tan\beta)$, where a is the specific contributing area (an area that drains precipitation water through the particular point per unit contour length—in raster GIS, per the length of the side of a grid cell) and β is the local slope in degrees (Kirkby, 1975). The GIS layer of TI was generated in ArcGIS® software from the layers of slope (derived from the DEM in ArcGIS®) and specific contributing area (derived from the DEM in TauDEM). Since the TI value at a point in a catchment contains both the information about its upslope areas and its own location, there could be several ways to characterize the catchment using TI, such as: (1) the TI value at the sampling

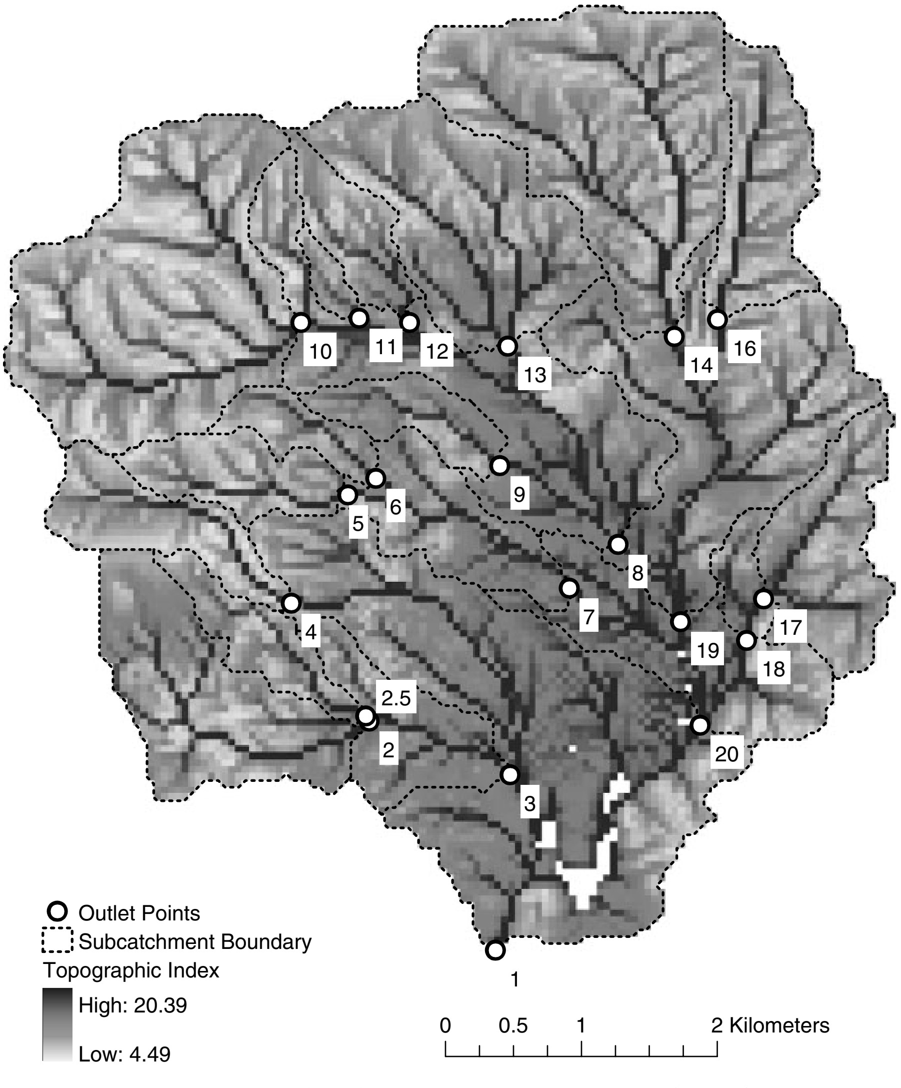

Figure 2. Grid map of TI of Dorokawa watershed. Cell size is 50 m × 50 *m*

point; (2) the average TI value for all cells upslope from the sampling point; (3) a distance-weighted average of all TI values of the cells upslope from the sampling point (Welsch *et al.*, 2001). We used the catchment average TI to make it comparable to other topographic parameters.

Mean values of spatial parameters for each subcatchment were calculated in ArcGIS® using previously delineated catchment boundaries. For the calculation of catchment mean TI values, all the cells in each catchment, including those delineated as stream network, were included.

Slope and TI values were not generated for a few grid cells clustered in the flat bottom valley areas of the largest catchment of Dorokawa watershed owing to computational limitations when there are little elevational gradients between adjacent cells. These cells, if not excluded, would potentially have had high TI values due to low slope and large contributing area per unit contour length. Exclusion of these cells, which account for only 0·5% of the catchment area, resulted in slight overestimation of mean slope value and slight underestimation of mean TI values for this catchment.

Statistical data analysis

We performed analysis of covariance (ANCOVA) using SAS® software to examine the relationships between the chemical constituents of streamwater and the spatial parameters of each subcatchment, including an evaluation of the effect of sampling periods. In this analysis, sampling period was treated as a categorical variable and geographic parameters as covariates. In these analyses, 13 sites (2, 2·5, 4, 5, 6, 9, 10, 11, 12, 13, 14, 16, and 17) out of the 20 sites were selected, eliminating seven sites that are nested within these 13 catchments to avoid the confounding effects of nested subcatchments, i.e. the effects of some extreme chemical concentrations at an upstream site appearing again at its downstream site.

RESULTS

Geographical characteristics of subcatchments

Hereafter, streamwater sampling points are referred to as 'outlets' in relationship to the subcatchments that contribute drainage water to these points. Subcatchments and their respective outlets are both identified by their respective sampling point numbers. Outlet 1 is the entire Dorokawa watershed.

The mean TIs of the Dorokawa watershed and its subcatchments fell within a narrow range from 6·4 to 7·4 (Table I). The index values for the individual 50 m × 50 m grid cells in the whole watershed ranged from 4·5 to 20·4. Subcatchments 10 and 4 had the lowest TI values, 6·4 and 6·5 respectively, mostly due to their steep slopes. The entire Dorokawa watershed has the highest mean TI (7·4), due not only to the large contributing area, but also to the large proportion of its flat bottom valley that was not included in any of the delimited subcatchments.

General chemical characteristics of Dorokawa streamwater

The sampling periods in early June and late June occurred as discharge was returning to base flow after snowmelt runoff subsided in mid May (Figure 3). Discharge during the late September sampling was slightly higher than the June sampling periods. October sampling was during high flow due to a 16 mm rain event the day before sampling.

To ascertain how the water chemistry changed as the precipitation passed through the terrestrial system until it joins the surface waters, the concentrations of major ions in streamwater from three sampling sites, each representative of upstream, middle-stream, and downstream in the watershed, were compared with that of wet deposition at UREF (Japan Environmental Laboratories Association, 2003) in Table II. Since we did not have any atmospheric deposition monitoring sites inside Dorokawa watershed, we used the deposition data collected at UREF research station 5 km away from the most downstream point (outlet 1) even though this distance between streamwater sampling points and the deposition monitoring site may be subject to some

Table I. TI for each subcatchment ranked in high to low order

Catchment no.	Catchment area (ha)	TI	
		Mean	STD[a]
1	3165	7·4	2·17
9	57	7·3	1·52
7	224	7·3	1·99
3	336	7·3	1·92
20	2233	7·2	2·12
18	152	7·2	1·81
13	224	7·1	1·88
8	974	7·1	2·07
19	1718	7·1	2·08
2	188	7·1	1·82
17	123	7·0	1·67
12	58	7·0	1·74
2·5	60	7·0	1·77
6	41	6·9	1·67
11	15	6·9	1·40
14	333	6·8	1·80
16	114	6·7	1·73
5	75	6·6	1·73
4	89	6·5	1·78
10	376	6·4	1·71

[a] Standard deviation.

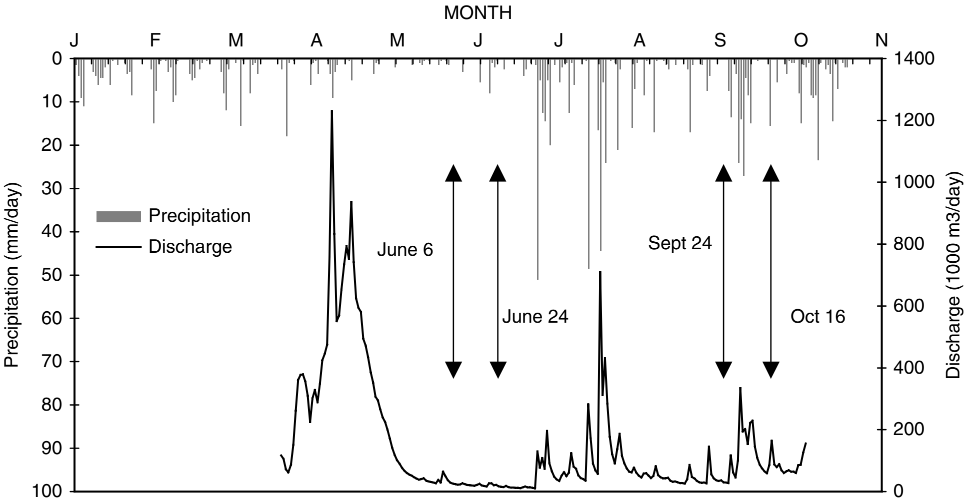

Figure 3. Precipitation and discharge at UREF during the study period. Precipitation was recorded at the UREF research station from January to November 2002. Solid curve is the daily discharge calculated from the streamwater level recorded at outlet 20 by a datalogger every hour from 26 March to 31 October 2002

heterogeneity in climatic conditions. Overall ion concentrations increased in streamwater due to water losses through evapotranspiration, as well as by addition of ions from other ion sources, including dry deposition, loss from soil exchange sites, microbial mineralization, and mineral weathering. The major inorganic solutes of streamwater in Dorokawa watershed were Cl^-, Na^+, Ca^{2+}, Si, and Mg^{2+}. The contribution to the charge

Table II. Comparison of chemistry between wet deposition at Uryu Experimental Forest (average of monthly concentrations of year 2000) and streamwater (average of four sampling times at three representative sites)

	Wet Deposition (μeq l^{-1})	Site 1 (μeq l^{-1})	Site 10 (μeq l^{-1})	Site 19 (μeq l^{-1})
Na^+	63·17	297·71	265·94	275·93
Ca^{2+}	8·07	171·93	183·25	181·36
Mg^{2+}	16·64	126·02	127·55	133·88
K^+	7·74	21·24	16·42	19·93
H^+	7·81	0·13	0·08	0·04
$NH_4{}^+$	27·12	21·48	2·72	0
Cl^-	68·83	259·79	168·39	193·50
SO_4^{2-}	30·36	27·36	23·63	23·73
$NO_3{}^-$	13·55	39·52	11·61	7·65
Sum of cations[a]	130·55	638·51	595·95	611·14
Sum of anions[a]	112·75	326·67	203·64	224·87

[a] Sum of cations (anions) in this table.

balance by measured anions in streamwater was much less than that of the cations. Since the streamwater generally has a high pH (~7), the majority of this imbalance was likely due to $HCO_3{}^-$, which was not directly measured in this study.

The major ion concentrations changed significantly after precipitation entered the terrestrial systems and appears as streamwater. The concentrations of H^+ at all streamwater sampling points (pH ~7) were much lower than that of precipitation water (pH ~5). The ratio of Na^+ to Cl^- was much higher in streamwater than in precipitation, suggesting an additional source of Na^+ in the terrestrial environment to the streamwater, such as mineral weathering.

Among major cations, the concentration of Ca^{2+} exhibited a major increase in streamwater, also suggesting an additional mineral source within the watershed. The decreases in the concentrations of $NH_4{}^+$ and $NO_3{}^-$ suggest the loss of these ions through biotic uptake of nitrogen, which is often a limiting element in terrestrial ecosystems (Aber *et al.*, 2003). The decrease in SO_4^{2-} in streamwater may have been partly due to biotic demand, but abiotic sulphate adsorption could also have contributed to this decrease (Mitchell *et al.*, 1992).

Spatial and temporal patterns of streamwater DOC and nitrogen solutes within Dorokawa watershed

Spatial patterns of streamwater DOC and nitrogen solutes are shown with respect to approximate geographical positions and relative positions in the stream network in Figures 4 and 5. Concentrations of $NO_3{}^-$ were extremely high at outlet 1 in early June and late June, even though its immediate upstream sites did not have high $NO_3{}^-$ concentrations (Figure 4a). Concentrations of $NO_3{}^-$ were also high at outlets 4 and 10, and moderately high at outlets 5 and 16, all of which are located in the upper reaches of the watershed. As found for $NO_3{}^-$, $NH_4{}^+$ concentrations in early June and late June were relatively high at outlet 1, the outlet of the entire watershed (Figure 4b). It is unknown what contributed to these exceptionally high $NO_3{}^-$ and $NH_4{}^+$ concentrations at outlet 1. Outlet 2 also showed relatively high $NH_4{}^+$ concentrations in early June and late June compared with the other outlets. Concentrations of DON were generally high in the southeastern region of the watershed at outlets 1, 17, 18, 19, and 20 (Figure 5a). DON concentrations at outlets 18 and 19 were higher than those of their upstream catchments, suggesting the presence of additional sources of DON in these lower subcatchments. Similarly, concentrations of DOC were generally high in the southeastern part of the watershed at the same outlets for which DON concentrations were high (Figure 5b). The highest DOC concentrations were most evident in late June, late September, and mid October. At all the outlets, mid-October samples showed the highest DOC concentrations among the four sampling periods.

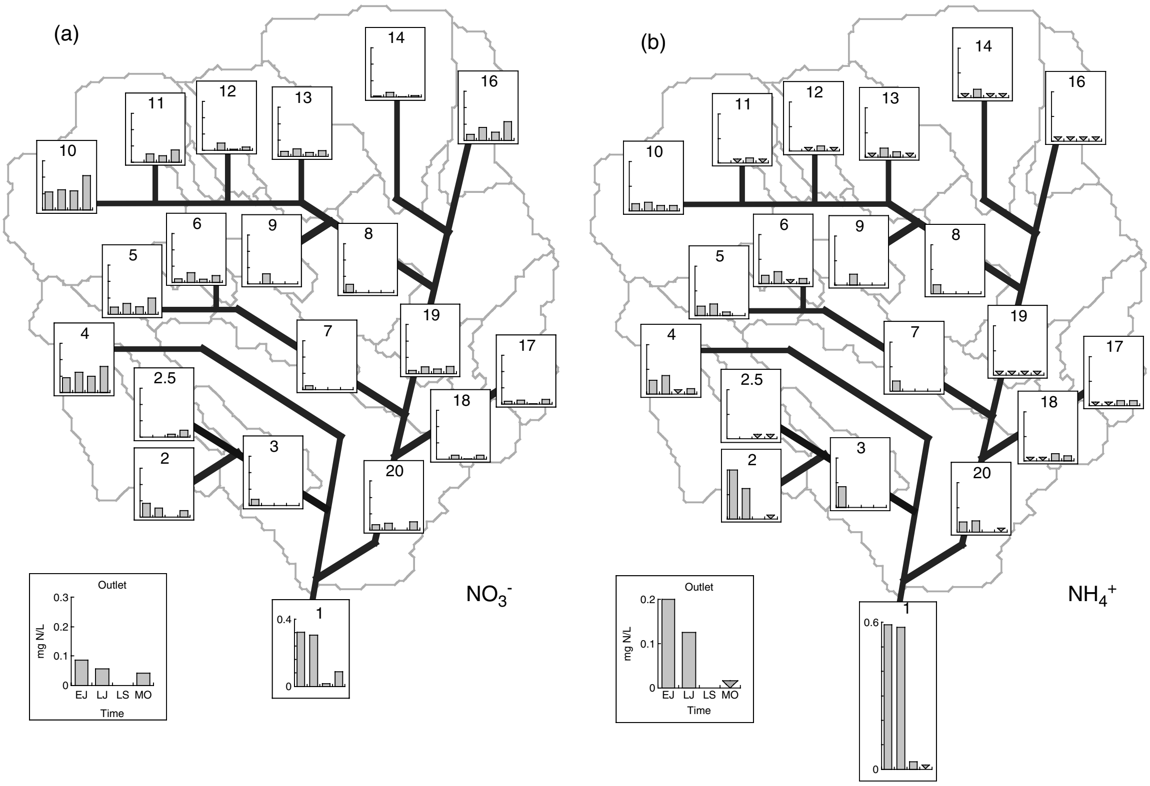

Figure 4. Spatial patterns of streamwater (a) NO_3^- and (b) NH_4^+ solute concentrations at each sampling point. The scale and axis label of each graph are the same as the sample graph at the left bottom unless stated otherwise. EJ: early June; LJ: late June; LS: late September; MO: mid-October. The inverted triangle indicates a value under the detection limits or calculation results less than zero

Relationships between TI and streamwater DOC and nitrogen solute chemistry

There were positive relationships between TI and both DOC and DON concentrations (Figure 6a and b). For both DOC and DON, the slopes of the regression curves were steepest for mid October. On the other hand, negative relationships were found between TI and NO_3^- (Figure 6c). The regression slope for NO_3^- was also steepest in mid October. ANCOVA on the 13 subcatchments found that DOC, DON, and NO_3^- concentrations have statistically significant linear relationships with TI values (Table III). For DOC and NO_3^- concentrations there were statistically significant differences in regression intercepts (time effects) between sampling times. Significant interactions between TI and sampling time were found for NO_3^- (i.e. at least one of the four regression slopes for each sampling season was different from the others).

A distinctive temporal pattern was also seen when the proportions of nitrogen species in total nitrogen were compared between sampling periods (Figure 7). Among mid-October samples, there was a clear trend of increasing proportion of DON along with the sites with higher TI, with a concomitant decrease in the proportion of NO_3-N.

DISCUSSION

DOC concentrations in Dorokawa streamwater had distinctive positive relationships with subcatchment TI values (Figure 6a). Concentrations were generally higher and the spatial patterns were most prominent in mid October. Wetlands are often found in the areas with high TI values and are known to be important

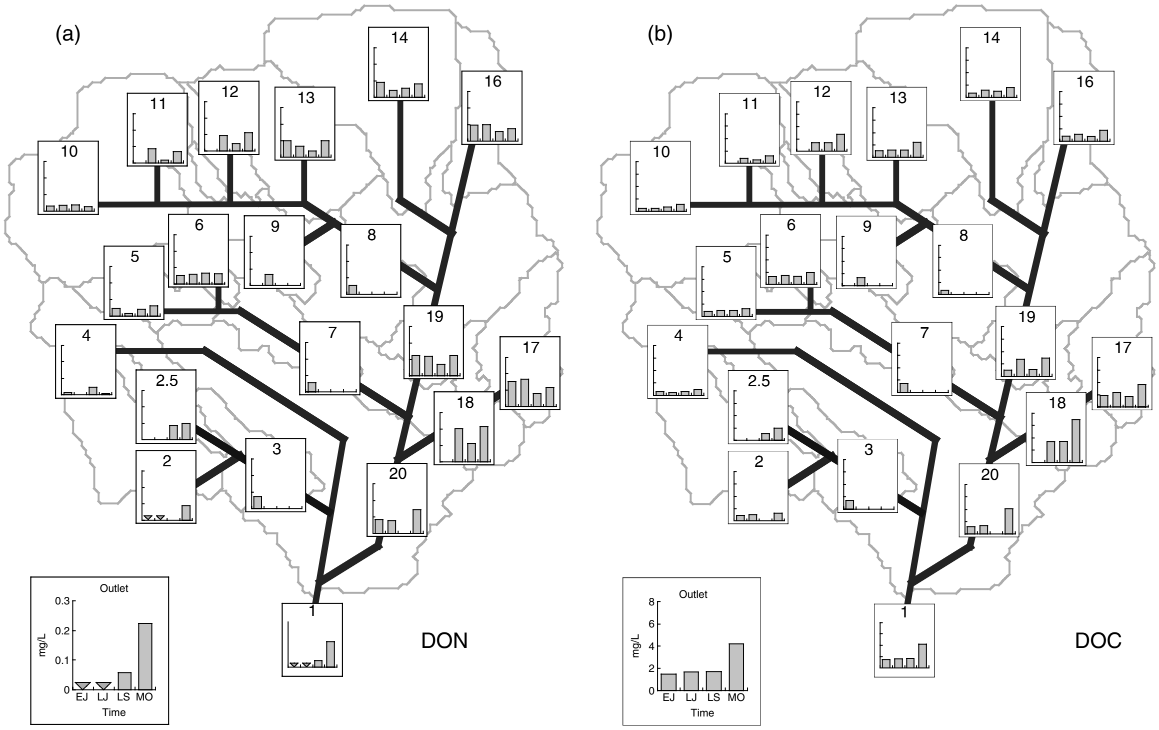

Figure 5. Spatial patterns of streamwater (a) DON and (b) DOC solute concentrations at each sampling point. The scale and axis label of each graph are the same as the sample graph at the left bottom corner unless stated otherwise. EJ: early June; LJ: late June; LS: late September; MO: mid-October. The inverted triangle indicates a value under the detection limits or calculation results less than zero

sources of DOC to streams (Hinton *et al.*, 1998). In the Dorokawa watershed, pure coniferous stands are strongly associated with most extensive types of wetland in the valley bottom. Coniferous tree litter is known to produce organic acids that can accumulate, especially in cold, wet climates (Schlesinger, 1997), such as that of Hokkaido. Therefore, the presence of Glehn's spruce in bottom wetland areas may be an important contributor of DOC to these surface waters.

The O horizon soil in the Glehn's spruce wetland, which mostly consisted of dwarf bamboo litter, as reported by Nagata (2002), had a very high C/N ratio of 52. The accumulated peat made of high C/N litter may be the major source of high DOC in soil water. In mid-October the high DOC concentrations in surface waters in areas adjacent to wetlands were probably the result of flushing of DOC that had accumulated during drier antecedent periods. Hinton *et al.* (1998) reported that flushing and surface runoff during a storm was the dominant mechanism of DOC export from wetlands in a forested watershed in Canada. DON concentrations showed a spatial pattern very similar to that of DOC concentrations, and thus also showed a positive relationship to the TI values for the subcatchments (Figure 6b). As for DOC, areas of organic matter accumulation in wetland areas, which were common in the bottom valley, were the likely sources of DON.

Concentrations of NO_3^- showed negative relationships with mean TI values (Figure 6c). High-TI subcatchments were also associated with low elevation and moderate slopes in the Dorokawa watershed. Wet areas are known to have high rates of denitrification, and hence gaseous nitrogen losses (Groffman *et al.*, 1996). In addition, the wetlands may also be storing nitrogen in organic forms as accumulating peat. Another potential cause for the decrease of nitrate concentration with increase of TI might be within-stream processes, including denitrification and nitrogen immobilization (Peterson *et al.* 2001), although these processes were not quantified in our study.

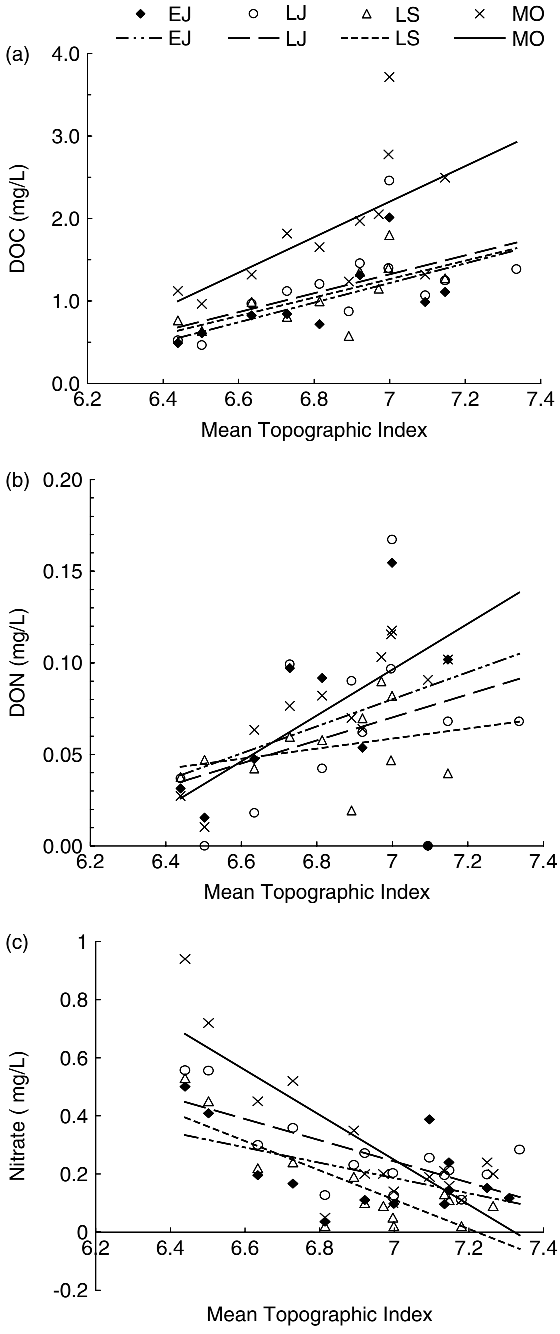

Figure 6. Regression of DOC, DON, NO_3^- concentrations and TIs at 13 subcatchment outlets of Dorokawa watershed: (a) DOC, (b)DON, and (c) NO_3^-. EJ: early June; LJ: late June; LS: late September; MO: mid October

In addition to the differences in terrain characteristics, the vegetation may have some influence on the spatial variability of nitrogen concentrations in streams in Dorokawa watershed. Numerous studies have shown that tree species composition may exert strong control on nitrogen cycling in forest ecosystems (e.g. Lovett *et al.*,

Table III. The results of ANCOVA analysis on TI against DOC and nitrogen solutes

Variable	*n*	R^2	Main effect (regression slope)		Time effect (intercept)		Main × Time (interaction)	
			F	Pr > *F*	*F*	Pr > *F*	*F*	Pr > F
DOC	44	0·57	21·54	<0·0001*	7·82	0·0004*	0·64	0·592
DON	44	0·29	9·87	0·0034*	0·81	0·496	0·70	0·560
NH_4^+	44	0·18	0·20	0·6609	2·30	0·093	0·35	0·787
NO_3^-	44	0·68	49·24	<0·0001*	4·59	0·008*	4·41	0·010*

* Statistically significant ($p = 0{\cdot}05$).

2004). The Dorokawa subcatchments are different not only in the terrain characteristics, but also in the tree type compositions. In Dorokawa watershed, the forest type distributions generally follow the gradient of elevation and the slope, such that deciduous-dominant forests are at high elevation and steep areas and conifer-dominant forests are at low elevation and flat areas with wet soils, and there are mixed forests in between. The catchments with low TI values, such as catchments 4 and 10, have a higher representation by deciduous broadleaf forests than in other subcatchments. Therefore, the vegetation types may also contribute to the spatial pattern in NO_3^- concentrations. (Campbell *et al.*, 2000; Lovett *et al.*, 2000; Piatek and Allen, 2001).

The trend of streamwater NO_3^- concentrations along the gradient of average TI for subcatchments was more pronounced in mid October than in the other sampling periods, with a steeper regression slope (Figure 6c). The increase of NO_3^- concentrations in mid October was most evident in those subcatchments with low TI values. The increase in NO_3^- concentrations may have been influenced by the flushing of upper soil layers by the rain event of the previous day. This flushing mechanism has been reported in various studies (Konohira *et al.*, 1997; Creed and Band, 1998; Inamdar *et al.*, 2000; McHale *et al.*, 2000). During dry periods, when base flow dominates, NO_3^- is produced and stored in upper organic soil horizons. The stored NO_3^- is flushed during storm events by the rising water table from the upper soil horizons into surface waters. Therefore, the amount of NO_3^- flushed during storm events is thought to be greater in subcatchments with high nitrification rates in upper soil horizons.

The temporal patterns of DON and NO_3^- observed in Figure 7 suggest that, during periods of high discharge, NO_3^- is the dominant nitrogen solute flushed by storm events from subcatchments with low TI values, whereas DON is the dominant nitrogen solute flushed from those with higher TI values. Although less prominent, similar patterns in the relative proportions of nitrogen solutes were seen in the late-September period. The proportions of nitrogen species in early-June and late-June periods did not show any clear trends with TI values. The distinct pattern of increasing DON proportion in dissolved nitrogen species along with the subcatchment mean TI gradient in fall suggest that soil wetness regime controlled by topography may have a significant influence on streamwater nitrogen chemistry during wet periods.

The differences in tree species composition, and hence litterfall patterns in fall, may also be contributing to the apparent trend of nitrogen species proportions along the TI gradient, since the forest composition among the subcatchments varies. Further study is required to separate the effects of vegetation on the spatial patterns of surface water solutes in the Dorokawa watershed.

CONCLUSIONS

The comparison of major solute concentrations between precipitation water and streamwater in the Dorokawa watershed provided information about changes in solute chemistry as water passed through the watershed. As water passed through the watershed there were marked increases Na^+, Ca^{2+}, and Mg^{2+} concentrations, which

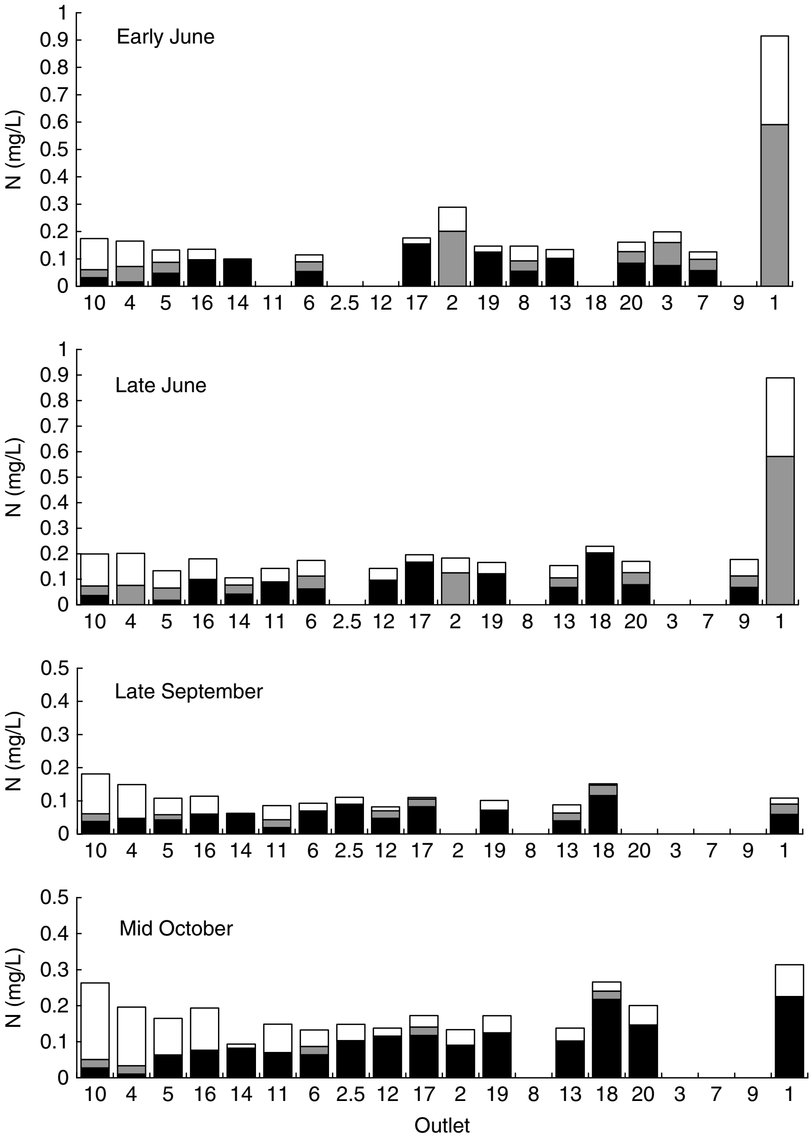

Figure 7. Proportion of nitrogen species in streamwater sample for each sampling event. DON was calculated as the balance of [TDN - (NO_3-N + NH_4-N)]. The sites are arranged in the order of low to high TI. White bar: NO_3-N; grey bar: NH_4-N; dark bar: DON

were likely to be added by mineral weathering and/or cation exchange. The decrease in nitrogen solutes as water passed through the Dorokawa watershed suggests that this watershed was a strong sink of inorganic nitrogen solutes.

Concentrations of NO_3^-, DOC, and DON showed distinctive spatial patterns in the Dorokawa watershed. The TI, as an indicator of wetness, was a significant predictor of the spatial variability of NO_3^-, DOC, and DON concentrations in subcatchments of the watershed. This relationship was linked to the contribution of wetlands in those areas with high TI values. The Dorokawa watershed has a relatively low elevational gradient compared with forested watersheds in many other regions of Japan. Thus, the large areas of wetland in Hokkaido will likely have a strong influence on the streamwater chemistry of other watersheds in this region.

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