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SPECIAL FEATURE

Ecosystem Responses and Behaviors Under Changing Pressures of Air Pollutants

Effects of climate and acidic deposition on interannual variations of stream water chemistry in forested watersheds in the Shimanto River Basin, southern Japan

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Abstract

Although the amount of acidic deposition has recently decreased in Japan, it has still deteriorated some forest ecosystems during the past several decades. Moreover, recent climate changes can affect stream water chemistry. We investigated the temporal trend and effects of climate conditions on stream water chemistry for more than 20 years in two areas (Yusuhara and Taisho) in the Shmanto River Basin, southern Japan, where the effects of acidic deposition are considered to be modest. Stream water samples were collected monthly from three forest watersheds selected at each site. The annual means of the stream chemistry were predicted by multiple regression analysis. The ammonium, nitrate, and sulfate concentrations in the bulk precipitation have decreased at Yusuhara, and the sodium, magnesium, calcium, chloride, nitrate, and sulfate concentrations in the stream water have decreased in both areas. The nitrate and sulfate concentrations apparently responded to the decreasing input of acidic deposition. The sunlight hours were positively related with the potassium, magnesium, calcium, nitrate, sulfate, and bicarbonate concentrations in stream water. The results suggest that long sunlight hours boost the photosynthetic activities, thus promoting soil respiration and decomposition of soil organic matter. Moreover, a higher carbonic acid concentration in the soil solution promotes cation weathering and carbonic acid dissociation to bicarbonate. Given the decreasing trends in magnesium and calcium concentration with no change in bicarbonate concentration, we inferred that previousinputs of acidic deposition enhanced the rate of rock weathering.

KEYWORDS

acidic deposition, forest watersheds, recovery, rock weathering, stream water

1 | INTRODUCTION

Atmospheric acidic deposition has harmed Japanese forest ecosystems since the 1960s (Takahashi et al., 2020). Some studies have reported decreased pH (Yamada et al., 2007) and changes of sulfur dynamics in fresh water ecosystems (Nakahara et al., 2010; Sase et al., 2019). In the 1980s, elevated nitrogen loss from stream waters in some forest ecosystems in Japan caused nitrogen-saturated conditions (Aber et al., 1989). Some forests in the suburbs of large cities have shown symptoms of nitrogen saturation (Chiwa et al., 2012; Itoh et al., 2021; Mitchell et al., 1997; Nishina et al., 2017; Ohrui & Mitchell, 1997).

Fresh water chemistry has been generally recovering since the input of acidic deposition was reduced in the United States and European countries (Likens et al., 1996; Lucas et al., 2013; Oulehle et al., 2017; Stoddard et al., 1999) and long-term changes of stream water chemistry in watersheds have been reported in Japan (Chiwa, 2021; Sase et al., 2019, 2021, 2023). The sulfate (SO_4^{2-}) concentration in Japanese watersheds has been decreasing since the 2000s (Sase et al., 2019, 2021). However, the nitrate (NO_3^-) concentration is more variable, being significantly decreased in some forests but not in others (Chiwa et al., 2019; Sase et al., 2023). Chiwa et al. (2019) suggested that the NO_3^- concentration in forest stream water has increased because deer browsing, which has reduced the understory vegetation. At the Sea of Japan side of the Kajikawa watershed, the stream NO_3^- concentration has not decreased despite the declining trend of nitrogen deposition (Sase et al., 2023). These results suggest that the recovery process from acidic deposition varies among forest ecosystems. Therefore, to understand the mechanisms of recovery from acidic deposition, we require long-term information from diverse climate, geological, and forest types. Acidic deposition in Japan is usually studied in forest watersheds which receive large amounts of acidic deposition (Nakahara et al., 2010; Sase et al., 2019, 2021; Yamada et al., 2007). However, information from rural and remote areas is required to understand the recovery processes in Japan.

Climate conditions also affect nutrient cycling and stream water chemistry in forest ecosystems (Campbell et al., 2009; Schlesinger et al., 2016). Freeze–thaw cycles in winter can affect NO_3^- leaching in spring (Mitchell et al., 1996; Shibata, 2016) and droughts and storms can affect concentration–discharge relationships (Murphy et al., 2018). In the Ijira area where acidic deposition is high, the NO_3^- and SO_4^{2-} runoff rates rapidly increased during the extremely hot and dry summer of 1994 (Nakahara et al., 2010; Sase et al., 2019). In Sweden, the base cation concentration is mainly affected by acidic deposition in the warmer southern area and by climate conditions in the colder northern area (Lucas et al., 2013). According to these findings, the effects of annual climate conditions are important for understanding the recovery of ecosystems from acidic deposition. Previous studies selected temperature, precipitation, and drought as the climatic conditions (Campbell et al., 2009; Schlesinger et al., 2016) but the relationship between solar radiation and stream water chemistry remains largely unknown. The annual variation of solar radiation is related to carbon cycling in forest ecosystems (Baldocchi et al., 2018). In moderately acidic soil, carbonic acid (H_2CO_3) dissociation to bicarbonate (HCO_3^-) promotes cation weathering from rocks (Fujii et al., 2012; van Breemen et al., 1984). Meanwhile, soil organic matter decomposition is a major proton-consumption process (Fujii et al., 2022). These findings imply possible links between solar radiation, carbon cycling, and rock weathering.

Two evergreen conifers—Japanese cedar (*Cryptomeria japonica*) and hinoki cypress (*Chamaecyparis obtusa*)—are widely planted in Japan. Nitrogen-saturated conditions have been reported in some Japanese cedar plantations located in the suburbs of large-city areas (Mitchell et al., 1997; Nishina et al., 2017). Japanese cedar and hinoki cypress form arbuscular mycorrhizal (AM) symbioses with a potential risk of nitrate leaching (Chiwa et al., 2019). However, comparisons between the stream waters of coniferous plantations and natural forests are limited (Takagi, 2015).

In this study, we investigated the temporal changes in stream water chemistry over more than 20 years in conifer plantations and natural forests in the Shimanto River Basin in two areas on Shikoku Island, southern Japan. The objectives of the study were to determine (1) whether the stream water chemistry differs between conifer plantation and natural forests; (2) whether the stream water chemistry is related to mean temperature, precipitation, and sunlight hours during the growing season; and (3) whether the NO_3^- and SO_4^{2-} concentrations in stream water have decreased in response to the reduced acidic deposition input. Based on the study findings, we discuss the recovery processes from acidic deposition and changes in water chemistry under recent climate changes. Finally, we compare the stream waters of the plantation and natural forests and discuss the effects of forest management on stream water chemistry.

2 | MATERIALS AND METHODS

2.1 | Study site

The study was conducted in the Yusuhara (N33°20′, E132°57′) and Taisho areas (N33°8′, E132°55′) of the Shimanto River Basin (Figure 1). The mean annual

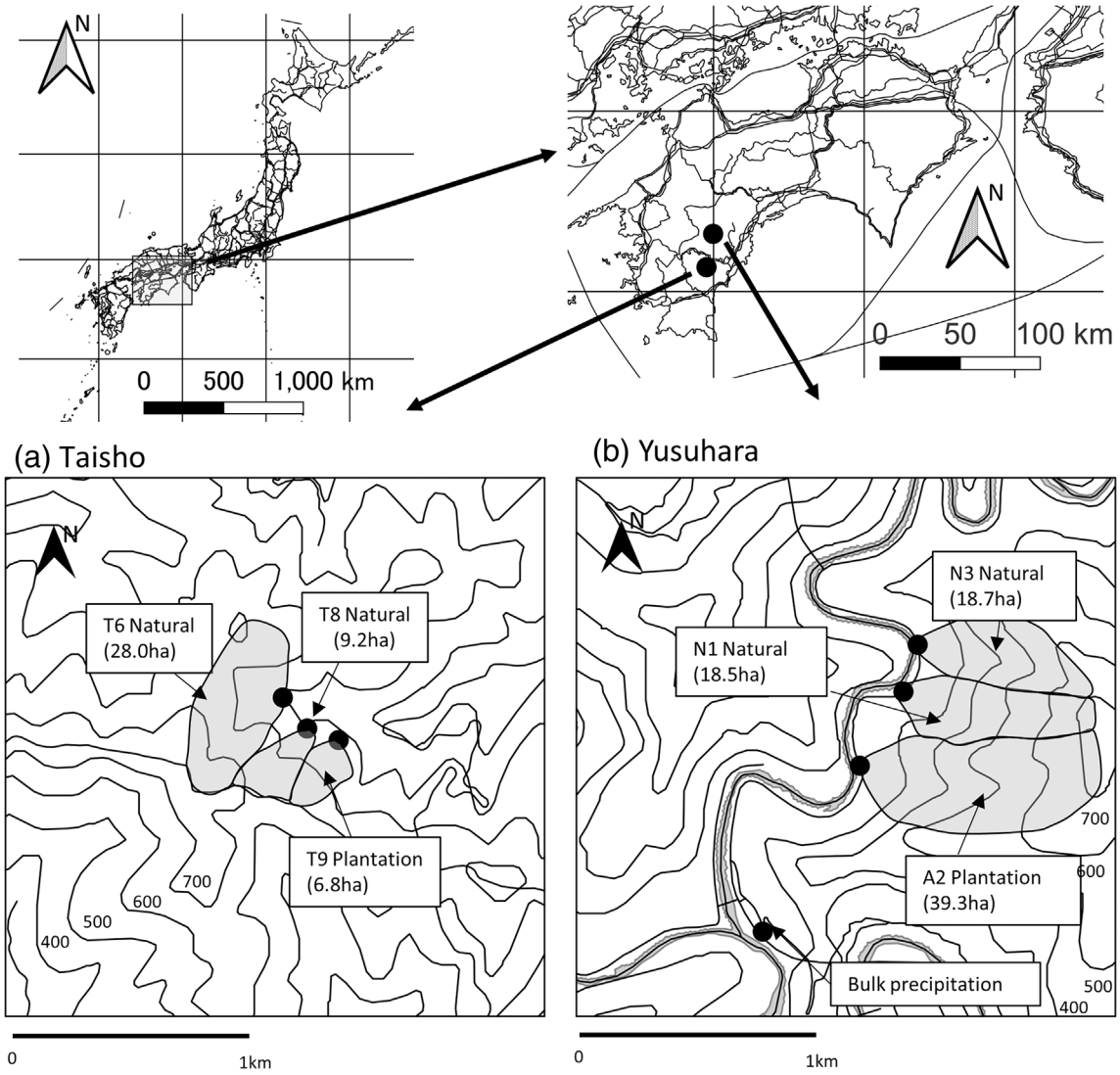

FIGURE 1 Location of the study areas in Taisho (a) and Yusuhara (b). Natural and plantation represents natural and plantation forests, respectively.

temperature (MAT) and mean annual precipitation (MAP) were extracted from 1-km mesh data in the Digital National Land Information database of the Ministry of Land, Infrastructure, and Transport, Japan (https://nlftp.mlit.go.jp/ksj/). To adjust for the altitude difference between the mesh and study-site data, the MAT was decreased by 0.6°C for each 100-m increase in altitude. In the Yusuhara and Taisho areas, the MAPs were 2960 and 2870 mm, respectively, and the MATs were 13.7 and 14.0°C, respectively. The study sites were two natural forest watersheds (N1, N3) and one plantation watershed (A2) in Yusuhara (Sakai et al., 2019) and two natural forest watersheds (T6, T8) and one plantation watershed (T9) in Taisho. The natural forests in Yusuhara are dominated by evergreen conifers (*Abies firma* and *Tsuga sieboldii*) and evergreen oak (*Quercus salicina*) (Ando et al., 1977), while the plantation forest is composed of Japanese cedar, hinoki cypress, and deciduous oak (*Quercus acutissima*) forests. In Taisho, the natural forests are dominated by evergreen conifers (*Abies firma*, *Tsuga sieboldii, and Chamaecyparis obtusa*) and evergreen oak (*Quercus salicina* and *Quercus acuta*) whereas the plantation forest consists of hinoki cypress. The mycorrhizal symbiosis types are AM on Japanese cedar and hinoki cypress and ectomycorrhizal on the other dominant tree species in natural forests (Chiwa et al., 2019). A study on the soil microbial community in a Yusuhara cedar forest identified minimal ectomycorrhizal fungi (Sawada et al., 2021). The stem basal area (BA) in the study area decreases in the order of Japanese cedar > natural forest > hinoki cypress (Inagaki et al., 2015, 2016; Table 1). The annual BA increment is lower in natural forests than in Japanese cedar and hinoki cypress, and (for the same forest type) it is higher in Yusuhara than in Taisho. Geologically, the Yusuhara area comprises alternating

TABLE 1 Stem basal areas (BAs) and annual BA increments in the natural forest and coniferous plantations in the study areas.

	Natural forest		Evergreen coniferous planation		
	Year	BA	Year	Cedar BA	Cypress BA
Yusuhara					
Initial (m^2 ha^{-1})	2000	56.3	2005	60.9	42.0
Final (m^2 ha^{-1})	2015	59.5	2015	80.3	56.6
Annual increment (m^2 ha^{-1} $year^{-1}$)		0.21		1.94	1.46
Taisho					
Initial (m^2 ha^{-1})	1997	55.9	2005	65.3	49.9
Final (m^2 ha^{-1})	2012	58.2	2015	81.0	59.9
Annual increment (m^2 ha^{-1} $year^{-1}$)		0.15		1.57	1.00

Note: Data from Inagaki et al. (2015, 2016) and the Ministry of the Environment Monitoring Sites 1000 Project (SIN01.zip, http://www.biodic.go.jp/moni1000/findings/data/index.html).

layers of sandstone and mudstone formed during the early Cretaceous Aptian and Late Cretaceous Turonian, whereas the Taisho area is marine sandstone formed during the Late Cretaceous Turonian and Maastrichtian (Geological Survey of Japan, 2023). The soil was classified as Dystrudept in Soil Taxonomy (Soil Survey Staff, 2014). The area has a warm climate and high precipitation. The parent materials are derived from sedimentary rocks and rock weathering is very rapid (Inagaki et al., 2019). The forest ecosystem has a high buffering capacity against the adverse effects of acidic deposition.

The climate condition was based on data from the Meteorological Agency Station near the study site. The Yusuhara data were obtained from Yusuhara Station (N33°23.4′, E132°55.3′, elevation 415 m) located 7 km from the study area. The Taisho precipitation data were obtained from Taisho Station (N33°11.6′, E132°58.3′, elevation 150 m) located 7.5 km from the study area. The temperature and sunlight hours were obtained from Kubokawa Station (N33°12.4′, E133°7.7′, elevation 205 m) located 20.5 km from the study area. The temperature data were adjusted for elevation as described above. The mean temperature, precipitation, and sunlight hours were calculated during the growing season (March–October).

2.2 | Sampling, chemical analyses, and budgets

The sampling process is described in Sakai et al. (2019). In summary, stream water was collected biweekly or monthly. The bulk precipitation was sampled as described for the throughfall measurement. The electrical conductivity (EC) and pH values of the samples were measured using a conductivity cell (CV-40, CM25R, DKK-TOA Corporation, Tokyo, Japan) and a glass electrode (HM-26S; HM-30G; HM30, DKK-TOA Corporation), respectively. The water samples were filtered through a 0.45-μm membrane filter. The ion concentrations were measured using ion chromatography (IC-7000D, Yokogawa Analytical Systems Inc., Tokyo, Japan; DX-320, ICS-1600-cation/2100-anion, Thermo-Fisher Scientific Inc., Waltham, USA). During the 2009–2019 period, the HCO_3^- concentrations in the bulk precipitation were determined by titration (endpoint pH = 4.8). During the 2001–2008 period, they were calculated from the pH and inorganic carbon concentrations determined by a total organic carbon (TOC) analyzer (GCT-12 N, Shimadzu Corp., Kyoto, Japan, and TOC-2000, Hiranuma Corp., Mito, Japan) (Sakai et al., 2019). The HCO_3^- concentration in the stream water was calculated as:

$$\left[HCO_3^-\right]\left(\mathrm{mol_c\,L^{-1}}\right) = \left(\left[Na^+\right] + \left[K^+\right] + 2\left[Ca^{2+}\right] + 2\left[Mg^{2+}\right]\right) - \left(\left[Cl^-\right] + \left[NO_3^-\right] + 2\left[SO_4^{2-}\right]\right).$$

The calculated HCO_3^- concentrations in 2009–2019 were highly correlated with those determined by the titration method (Figure S1). Therefore, the above estimation was deemed suitable for analyzing the long-term trends in the study areas.

The proton budget of the N3 watershed in Yusuhara during the 2011–2015 period is reported in Inagaki et al. (2019). The Cl^- output far exceeds the Cl^- input, suggesting an important role of dry Cl^- deposition (Inagaki et al., 2019). Therefore, we additionally investigated the throughfall in the natural forest (N3) from March of 2020 to February of 2021 along with Japanese cedar and hinoki cypress forests (A2). A rain collector with a 210-mm-diameter funnel connected to a 10-L bottle was installed in each forest. The throughfall was collected biweekly or monthly and the water-sample volume was measured in a graduated cylinder. The collected samples were analyzed as described below. The non-sea salt Cl^-

and SO_4^{2-} were calculated using sodium (Na^+) as a sea salt index.

The proton budget was calculated using van Breemen et al.'s (1983) method.

To calculate the proton budget using throughfall data, we assume no exchange within the canopy and negligible plant uptake or leaching. This assumption was considered valid for the Na^+, Cl^-, and SO_4^{2-} concentrations in the present study. For each of these elements, the input reported by Inagaki et al. (2019) was multiplied by the ratio of the throughfall input to the bulk-precipitation input.

2.3 | Quality control

The quality of the chemical analyses of the bulk precipitation was controlled by the ion balances and theoretical ECs (EANET, 2000). Some samples violated the quality criteria under the field condition. We alleviated the standard for valid samples (no detection of phosphorous, $R1 < \pm 30\%$, $R2 < \pm 20\%$) (Sakai et al., 2019). The percentage of valid precipitation was low in 2000 and 2001, whereas the potassium (K^+) concentration was elevated when K^+ leached from a cherry tree growing near the collector in 2016 (Table S1). These 3 years were excluded from the trend analysis. The stream water data were controlled under the same criteria (EANET, 2000). Some data in 2004 and 2006 also failed the criteria, but these violations were likely attributable to uncertainty in the TOC analysis. Almost all samples during the remaining years of the study period met the criteria. Because the HCO_3^- concentration determined from the TOC analyzer was not used in our study, these anomalous samples were included in our stream water analysis.

2.4 | Statistical analysis

The weighted mean concentrations of the elements were calculated in the bulk-precipitation volume and predicted by year and precipitation through a multiple regression analysis. The element concentrations and precipitations were log-transformed before analysis. The annual rate of change was calculated from the partial regression coefficient with respect to year. The HCO_3^- concentrations were excluded from this analysis because they were determined by different analytical methods during different ranges of the study period.

The stream water chemistry was analyzed in terms of annual means. The ion concentrations in the stream water were regressed against the precipitation data, sunlight hours, mean temperatures, year, and watersheds in multiple regression analyses. The concentrations, precipitation data, and number of sunlight hours were log-transformed prior to analysis. Pairwise comparisons between the forest watersheds were analyzed by the Tukey method. All statistical analyses were performed using JMP software (ver. 11.0.0., SAS Institute).

TABLE 2 Element inputs and outputs during the 2011–2015 period (from Inagaki et al., 2019).

	Input	Output	Ratio of output/input
Water (mm)	3034	1829	0.6
pH	5.00	7.47	
H^+	0.31	0.00	0.0
NH_4^+	0.37	0.01	0.0
Na^+	*1.07*	3.17	3.0
K^+	0.06	0.28	4.9
Ca^{2+}	0.27	4.82	17.9
Mg^{2+}	0.14	1.50	10.6
Cl^-	*1.27*	1.44	1.1
NO_3^-	0.19	0.19	1.0
SO_4^{2-}	*0.59*	2.05	3.5
HCO_3^-	0.23	6.56	28.4

Note: Inputs modified by the throughfall measurement are italicized (see Table 3).

3 | RESULTS

3.1 | Proton budget

Table 2 presents the input–output budget in the natural forest (area N3). The Na^+, K^+, calcium (Ca^{2+}), and magnesium (Mg^{2+}) outputs exceeded their inputs. The inputs and outputs of Cl^- were similar whereas the nitrogen (NH_4^+ plus NO_3^-) output was smaller than its input. The SO_4^{2-} output was 3.5-fold greater than its input. The throughfall inputs of Na^+, Cl^-, and SO_4^{2-} and the contribution of non-sea salt SO_4^{2-} were higher and lower, respectively, in the natural forest than in Japanese cedar and hinoki cypress forests. Whereas the contribution of nss-Cl^- was greater in the natural forest (15.9%) than in the bulk precipitation (0.4%) or throughfall in other forests (9.9%–10.6%) (Table 3). The nitrogen (NH_4^+ and NO_3^-) and K^+ were lower in the throughfall than in the bulk precipitation. Among the proton-generation processes, the main contributor to the proton budget was carbonic acid dissociation (60.1%), followed by anion mineralization and weathering (15.7%) and cation uptake by vegetation (13.0%) (Table 4). The proton-consumption

TABLE 3 Ion inputs to the bulk precipitation (BP) and throughfall ($cmol_c\ ha^{-1}$) in the natural fir forest (TF_{fir}), hinoki cypress (TF_{cyp}), and Japanese cedar planation (TF_{cedar}) from March 2020 to February 2021.

	BP	TF_{fir}	TF_{fir}/BP	TF_{cyp}	TF_{cyp}/BP	TF_{cedar}	TF_{cedar}/BP
Rain(mm)	2541	2140	0.8	2278	0.9	2240	0.9
pH	5.01	5.90	1.2	5.15	1.0	5.69	1.1
H^+	0.246	0.027	0.1	0.161	0.7	0.045	0.2
Na^+	0.758	1.351	1.8	0.836	1.1	0.669	0.9
K^+	0.025	1.370	55.0	0.353	14.2	0.492	19.7
NH_4^+	0.098	0.073	0.7	0.037	0.4	0.062	0.6
Mg^{2+}	0.183	0.555	3.0	0.307	1.7	0.271	1.5
Ca^{2+}	0.190	0.671	3.5	0.444	2.3	0.487	2.6
Cl^-	0.858	1.847	2.2	1.015	1.2	0.863	1.0
NO_3^-	0.148	0.131	0.9	0.049	0.3	0.075	0.5
SO_4^{2-}	0.391	0.459	1.2	0.333	0.9	0.320	0.8
$nssSO_4^{2-}/totalSO_4^{2-}$ (%)	76.7	64.7	—	69.8	—	74.9	—
$nssCl^-/totalCl^-$(%)	0.4	15.9	—	9.9	—	10.6	—

TABLE 4 Proton budget in the natural fir forest in the Yusuhara area (N3).

	$kmolc\ ha^{-1}\ year^{-1}$	(%)
Proton sources		
H^+ input	0.31	(2.9)
N transformation	0.86	(8.2)
Anion mineralization	1.65	(15.7)
H_2CO_3 dissociation	6.33	(60.1)
Cation uptake	1.37	(13.0)
Total	10.53	(100.0)
Proton sinks		
H^+ drainage	0.00	(0.0)
N transformation	0.35	(3.5)
Anion uptake	0.33	(3.2)
Cation weathering	9.45	(93.3)
Total	10.13	(100.0)

Note: The budget is modified from Inagaki et al. (2019). The contribution to total (%) is presented in parentheses.

process was dominated by weathering and mineralization of cations (93.3%).

3.2 | Control factors

Annual variation of water chemistry in bulk precipitation and stream water is presented in Figure 2 (Tables S1 and S2). Based on the results of multiple regression model in bulk precipitation, amount of precipitation exerted significant effects on the NH_4^+, NO_3^-, and SO_4^{2-} concentrations but no clear effects on the concentrations of other elements (Tables 5 and S3). The ECs and the Na^+, K^+, NH_4^+, Ca, NO_3^-, and SO_4^{2-} concentrations significantly decreased over time ($p < 0.05$), whereas the Cl^- concentration decreased marginally ($p = 0.06$). More specifically, the annual change rates of the Cl^-, NH_4^+, NO_3^-, and SO_4^{2-} concentrations were −2.4%, −7.6%, −2.3%, and −1.5%, respectively.

The climatic conditions during the growing season (March–October) (Figure 3) were highly correlated between Yusuhara and Taisho (Pearson correlation coefficient $r = 0.96$, $p < 0.001$ for temperature; $r = 0.90$, $p < 0.0001$ for precipitation; $r = 0.80$, $p < 0.0001$ for number of sunlight hours). In general, the results of the multiple regression for the stream water chemistry are very similar between the Yusurhara and Taisho areas (Tables 6 and S4). Greater precipitation decreased the stream Ca^{2+} and Mg^{2+} concentrations but did not significantly dilute the Cl^-, NO_3^-, and SO_4^{2-} concentrations. Surprisingly, a higher precipitation raised the Cl^- concentration in Yusuhara. Longer sunlight hours increased the concentrations of all elements except Cl^- and H^+. The significant relationship was observed between sunlight hours and stream water K^+ and HCO_3^- concentration (Figure 4). Higher temperatures decreased the K^+ concentration but did not affect the other elements. Watersheds significantly affected the concentrations of all elements except Cl^- in Taisho. In both areas, the K^+ and NO_3^- concentrations were lower in plantation forests than in natural forests (Table 7). The watershed effects on the Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, and HCO_3^- concentrations showed no obvious difference between natural and

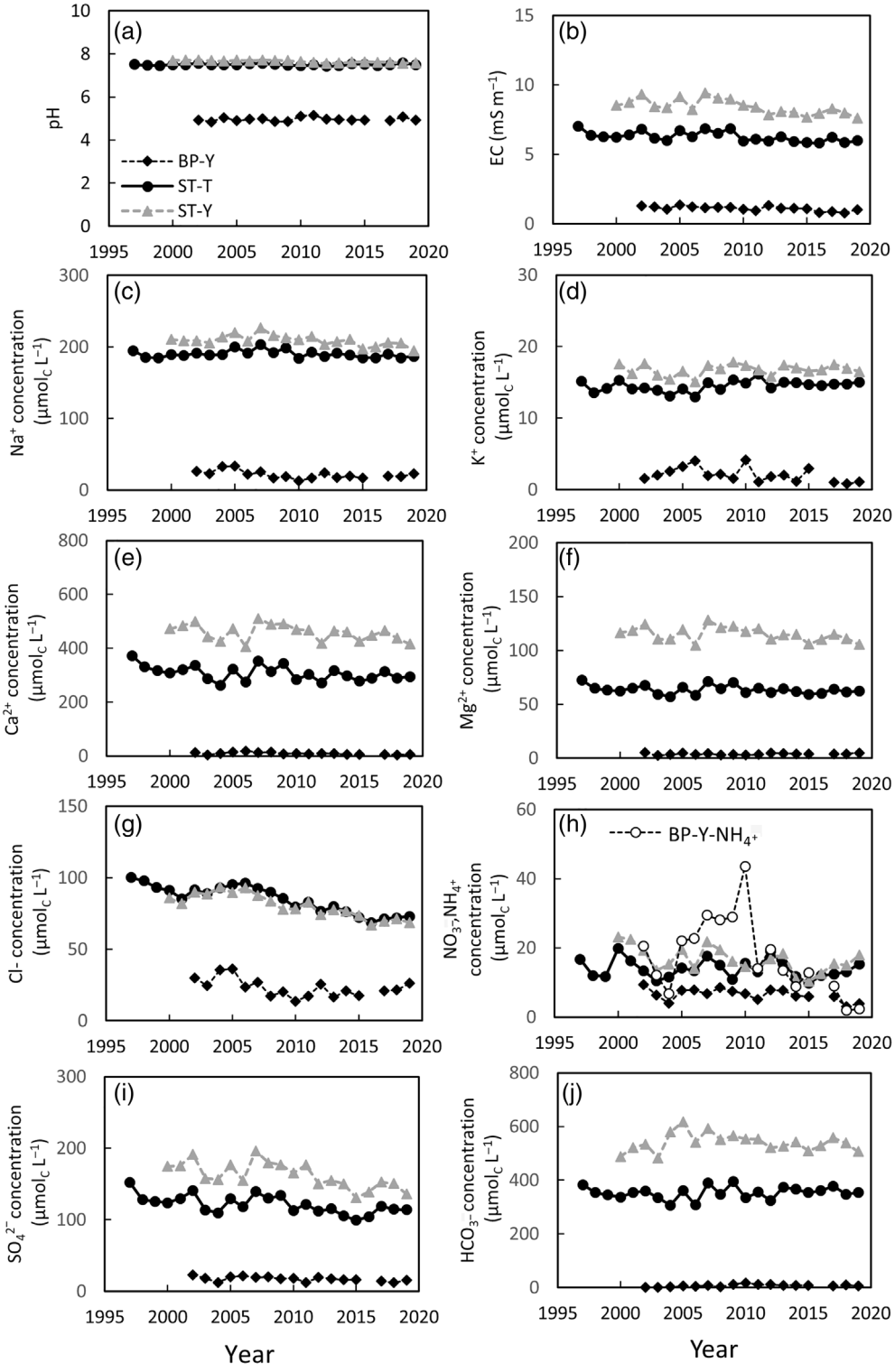

FIGURE 2 Annual variation in the chemical concentrations of bulk precipitation in Yusuhara (BP-Y), stream water in Yusuhara (ST-Y), and Taisho areas (ST-T). Mean values of pH (a), EC (b), and concentration of sodium (c), potassium (d), calcium (e), magnesium (f), chloride (g), nitrate and ammonium in bulk precipitation (h), sulfate (i), and bicarbonate (j) are presented.

plantation forests. Meanwhile, the ECs and the Na^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} concentrations in both areas significantly decreased over time ($p < 0.05$). The H^+ concentration showed an increasing trend in Yusuhara ($p < 0.0001$) but remained steady in Taisho ($p > 0.05$). The K^+ and HCO_3^- concentrations in stream water exhibited no temporal trend in either area ($p > 0.05$).

4 | DISCUSSION

4.1 | Na^+ and Cl^- concentrations

Judging from the similar amount of Cl^- input and output in the natural forest in Yusuhara (N3) (Table 2), production and accumulation of Cl^- in the forest ecosystems

	Annual precipitation		Year		
	β	*p*	*β*	*p*	Annual change (%)
EC	−0.522	0.002	−0.61	0.005	−1.7
H^+	−0.466	0.071	−0.06	0.792	−0.2
Na^+	0.220	0.358	−0.52	0.042	−2.4
K^+	−0.125	0.586	−0.53	0.032	−4.8
NH_4^+	−0.500	0.012	−0.50	0.012	−7.6
Mg^{2+}	−0.247	0.340	0.35	0.178	1.3
Ca^{2+}	−0.312	0.147	−0.53	0.020	−4.1
Cl^-	0.239	0.328	−0.48	0.059	−2.4
NO_3^-	−0.634	0.001	−0.41	0.022	−2.3
SO_4^{2-}	−0.548	0.009	−0.41	0.038	−1.5
HCO_3^-	—	—	—	—	—

TABLE 5 Multiple regression models to estimate electric conductivity (EC) and ion concentrations of bulk precipitation in Yusuhara.

should be negligible (Svensson et al., 2012). Cl^- deposition is typically derived from sea salt. Yoshinaga et al. (2021) found a significant relationship between distance from the sea and Cl^- concentration in stream water in the Simanto River Basin. In the present study, although Taisho was closer to the sea than Yusuhara, the stream water Cl^- concentrations were similar in both areas. During a typhoon event, the Cl^- input depends on the typhoon track and slope aspects (Torii, 2007). The Cl^- input in the natural forest throughfall (N3) was 2.2-fold higher than in the bulk precipitation (Table 3), suggesting that a large amount of Cl^- is dry-deposited and captured by the forest canopy. Meanwhile, the throughfall Cl^- was higher in the natural forest than in Japanese cedar and hinoki cypress. A natural forest can capture more dry deposition than plantation forests owing to its complex canopy structure, where tall conifers dominate the top layer and evergreens are included in the sub-canopy layers. Lovett et al. (2005) suggested that dry-deposition capture is greater in older natural forests than in young forests. In contrast, the stream water Cl^- concentrations did not significantly differ among the Taisho forest watersheds. These results suggest that the effects of forest types on throughfall Cl^- can vary between areas.

The Na^+ and Cl^- concentrations in the bulk precipitation and stream water decreased over time (Table 6), as previously reported for freshwater Cl^- concentration in some ecosystems (Evans et al., 2011; Lovett et al., 2005; Lucas et al., 2013; Sase et al., 2021). The Na^+ and Cl^- concentrations in the bulk precipitation peaked in 2004 and 2005, when the areas were hit by severe typhoons (Torii, 2007). The Na^+ and Cl^- concentrations in the stream water peaked a few years later, in 2007 and 2006, respectively (Figure 2c,e). The typhoon attacks early in the study period can explain the decreasing trend to some extent. However, whether the large input in 2004 and 2005 can explain the subsequent long-term (>10 years) decrease in Cl^- concentration is questionable. In the present study, dry deposition was an important contributor to Cl^- input but information on the Cl^- input via long-term throughfall is lacking. In the Kajikawa watershed, the throughfall Cl^-, nss-S and nss-Ca inputs decreased during the winter season (Sase et al., 2021), indicating that although dry-deposited Cl^- can be derived from sea salt, its dynamics are driven by substances related to anthropogenic activities (nss-S and nss-Ca). Sixteen percent of the throughfall Cl^- in the natural forest of our study was non-sea salt, which is partly derived from dry deposition of anthropogenic origin. Lovett et al. (2005) suggested that the Cl in HCl gas emitted from coal combustion reacts with alkaline particles in the atmosphere, producing particulate Cl. Recent studies of aerosols in China also suggest an anthropogenic origin (coal combustion or biomass burning) for aerosol Cl (Luo et al., 2019; Wang et al., 2020). Judging from these findings, the long-term decreasing trend of stream water Cl^- cannot be explained by storm events alone. Reduction of the anthropogenic Cl^- input is another potential cause of the long-term decreasing trend.

4.2 | K^+, Mg^{2+}, Ca^{2+}, and HCO_3^- concentrations

The stream water K^+, Mg^{2+}, Ca^{2+}, and HCO_3^- concentrations increased during the longer sunlight hours of the growing season. To our knowledge, this relationship has not been previously reported. The underlying mechanism is unclear but can be speculated as follows (Figure 5). Longer sunlight hours promote photosynthesis and soil

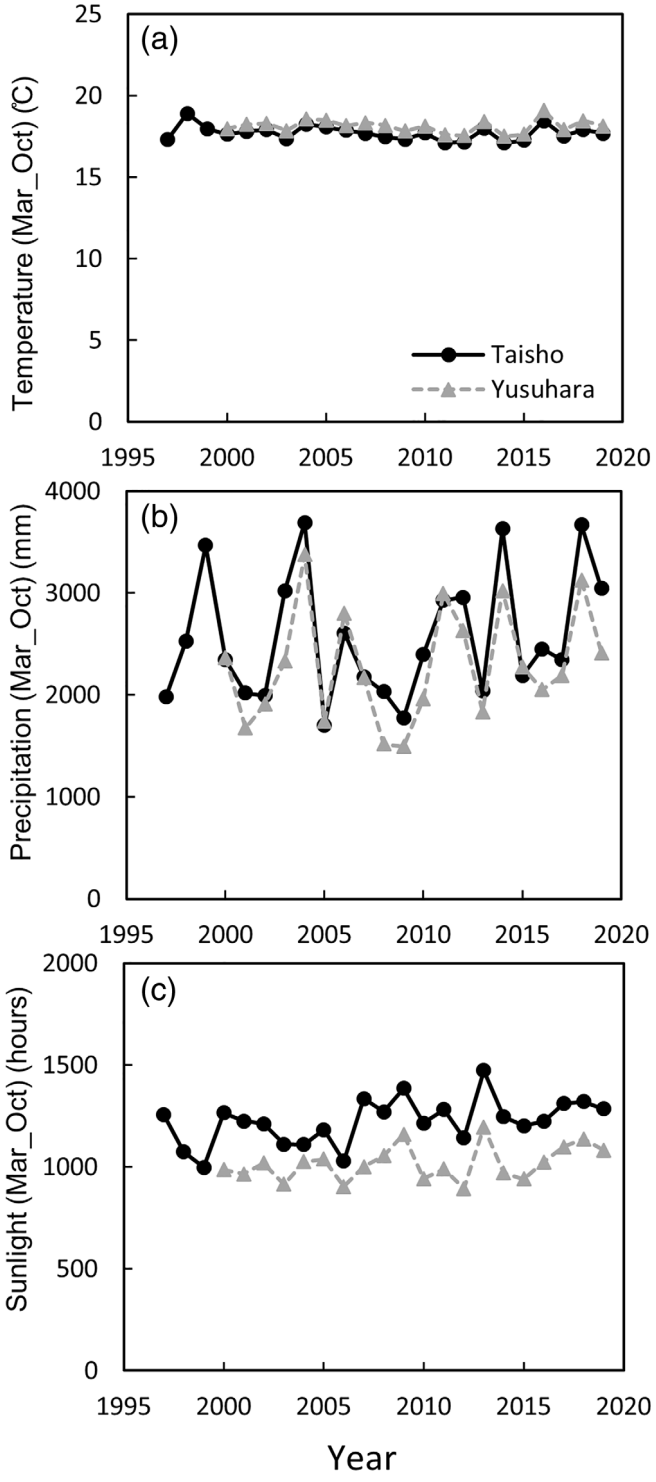

FIGURE 3 Mean temperatures (a), precipitations (b), and sunlight hours (c) during the growing season (March to October) in the study areas.

respiration. Some studies have associated solar radiation with the net carbon exchange or ecosystem respiration (Baldocchi et al., 2018; Froelich et al., 2015; Saigusa et al., 2005). The carbon fixed by photosynthesis is rapidly transported underground (within 5 days) and respired as CO_2 (Ekblad & Högberg, 2001; Högberg et al., 2001; Kuzyakov & Cheng, 2001). Solar radiation also promotes carbon exudation from roots (Nakayama & Tateno, 2018). Therefore, solar radiation is expected to increase the carbonic acid concentration in soil solutions. Subsequently, the carbonic acid dissociates to HCO_3^-. Another pathway increases the carbon supply to soil microbes via the root exudates, promoting organic matter decomposition and the release of base cations and SO_4^{2-} from organic matter.

The stream water Ca^{2+} concentration decreased during the study period, while the HCO_3^- concentration remained steady (Table 6). Long-term monitoring of fresh water chemistry has revealed a decreasing Ca^{2+} trend in some ecosystems. Moreover, the alkalinity or HCO_3^- content varies among ecosystems (Likens et al., 1996; Oulehle et al., 2017; Sase et al., 2021; Stoddard et al., 1999; Weyhenmeyer et al., 2019). The decreasing trend of Ca^{2+} concentration has been attributed to reduced Ca^{2+} deposition (Oulehle et al., 2017) or vegetation uptake (Likens et al., 1996; Stoddard et al., 1999). In the present study, the Ca^{2+} deposition decreased, but the above-mentioned processes cannot be the primary drivers because the Ca^{2+} input was much lower than the Ca^{2+} output. Moreover, as the rate of Ca^{2+} accumulation in the aboveground biomass (0.78 $kmol_c\ ha^{-1}\ year^{-1}$) is much lower than the rock weathering rate (5.3 $kmol_c\ ha^{-1}\ year^{-1}$) (Inagaki, Fujii, & Urakawa, 2022), the Ca^{2+} concentration is unlikely to limit plant production in our study. Because Ca^{2+} weathering is very rapid and the stream HCO_3^- concentration showed no decline over time, the Ca^{2+} weathering rate was likely enhanced by acidic deposition in the past and has subsequently decreased toward its pre-industrialization level. This process can dominantly explain the decreasing trend of stream water Ca^{2+} concentration. Similar patterns have been reported in some freshwater ecosystems (Weyhenmeyer et al., 2019). Soil-exchangeable Ca has declined in natural Japanese cedar forests on Shikoku Island (Yamada et al., 2013). Tanikawa et al. (2014) inferred that directional changes in soil-exchangeable Ca are related to tree species and soil-buffering capacity. In the first-time collected samples, the soil Ca could have been elevated due to accelerated weathering triggered by acidic deposition.

The stream water K^+ concentration was lower in the plantation than in natural forests (Table 7). This finding can be explained by the higher stem-growth rate in plantations than in natural forests and the higher uptake of K^+ by plantation trees. The throughfall K^+ was also lower in the plantation than in natural forests (Table 3), suggesting greater retranslocation of K^+ before senescence in plantation trees than in natural forest trees (Sardans & Penuelas, 2015).

TABLE 6 Multiple regression models to estimate electric conductivity (EC) and ion concentrations of stream water.

	Precipitation (March–October)		Sunlight (March–October)		Temperature (March–October)		Year			Watersheds ($n = 3$)
	β	p	β	p	β	p	β	p	Annual change (%)	p
Yusuhara										
EC	−0.142	0.002	0.113	0.028	0.001	0.974	−0.333	0.0001	−0.75	0.0001
H^+	0.158	0.003	0.031	0.588	−0.033	0.517	0.400	0.0001	1.55	0.0001
Na^+	0.026	0.625	0.139	0.024	−0.024	0.638	−0.278	0.0001	−0.40	0.0001
K^+	−0.210	0.004	0.300	0.0004	−0.161	0.022	0.014	0.851	0.02	0.0001
Mg^{2+}	−0.175	0.011	0.212	0.007	−0.108	0.101	−0.267	0.0003	−0.46	0.0001
Ca^{2+}	−0.157	0.001	0.128	0.005	−0.054	0.157	−0.145	0.001	−0.46	0.0001
Cl^-	0.152	0.001	0.063	0.207	−0.004	0.916	−0.562	0.0001	−1.66	0.0001
NO_3^-	−0.095	0.160	0.209	0.008	0.044	0.507	−0.372	0.0001	−2.55	0.0001
SO_4^{2-}	−0.106	0.152	0.251	0.004	−0.108	0.133	−0.576	0.0001	−1.48	0.0001
HCO_3^-	−0.150	0.001	0.085	0.041	−0.045	0.210	0.043	0.263	0.13	0.0001
Taisho										
EC	−0.198	0.001	0.120	0.010	−0.044	0.196	−0.290	0.0001	−0.54	0.0001
H^+	−0.056	0.551	−0.084	0.432	0.054	0.491	0.055	0.573	0.16	0.0001
Na^+	−0.197	0.008	0.192	0.022	−0.103	0.094	−0.194	0.013	−0.14	0.0001
K^+	0.047	0.196	0.238	0.0001	−0.103	0.001	−0.030	0.428	−0.07	0.0001
Mg^{2+}	−0.163	0.018	0.389	0.0001	−0.060	0.290	−0.357	0.0001	−0.51	0.0001
Ca^{2+}	−0.083	0.026	0.214	0.0001	0.009	0.762	−0.238	0.0001	−0.86	0.0001
Cl^-	−0.050	0.533	0.002	0.983	−0.009	0.890	−0.847	0.0001	−1.52	0.073
NO_3^-	0.001	0.988	0.225	0.014	−0.019	0.770	−0.168	0.045	−0.95	0.0001
SO_4^{2-}	−0.134	0.056	0.298	0.0003	−0.031	0.592	−0.570	0.0001	−1.22	0.0001
HCO_3^-	−0.077	0.050	0.201	0.0001	0.000	0.996	−0.029	0.477	−0.09	0.0001

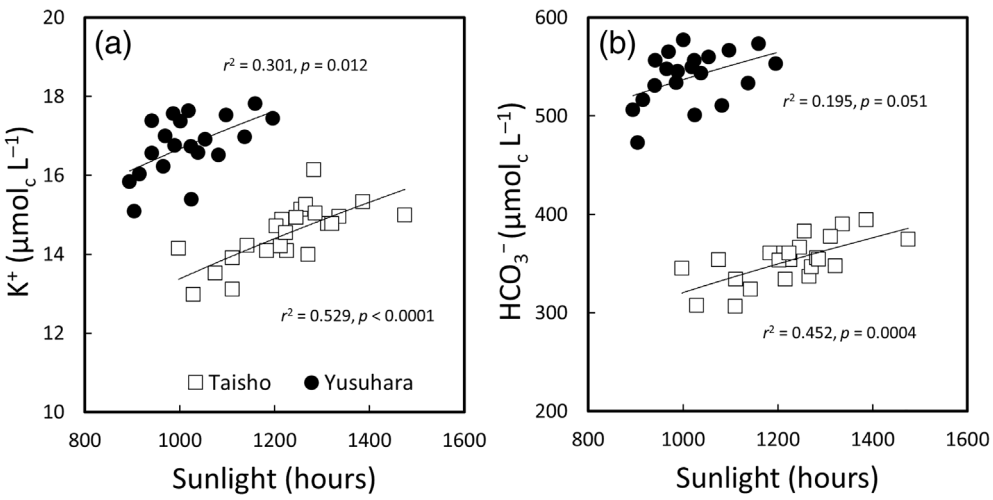

FIGURE 4 Relationships between stream water concentrations of potassium (a) and bicarbonate (b) and sunlight hours. Regression lines were obtained through linear regression analysis with log transformation.

The higher mean temperatures during the growing season would have led to lowered the stream water K^+ concentration and raised the retention of K^+. According to these findings, K is among the most limiting nutrients in the area. K^+ limitation has been recognized in forest ecosystems worldwide (Sardans & Penuelas, 2015).

TABLE 7 Mean ion concentrations ($\mu mol_c\ L^{-1}$) of the stream water in forest watersheds.

	Yusuhara						Taisho					
	N1 (Natural)		N3 (Natural)		A2 (Plantation)		T6 (Natural)		T8 (Natural)		T9 (Plantation)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
EC ($mS\ m^{-1}$)	9.61	0.57a	7.27	0.46c	8.40	0.59b	7.16	0.44a	5.46	0.31c	6.23	0.36b
pH	7.74	0.05c	7.55	0.07a	7.66	0.05b	7.57	0.05c	7.41	0.05a	7.52	0.05b
Na^+	231.6	8.8a	194.9	6.5c	200.7	7.4b	186.8	4.8b	183.4	5.1c	200.2	5.9a
K^+	18.1	0.8a	16.8	0.9b	15.5	0.8c	13.8	0.7b	17.4	1.0a	12.3	0.6c
Mg^{2+}	128.6	6.3a	106.8	6.0b	109.6	7.4b	68.2	4.0a	57.5	4.0c	64.9	4.2b
Ca^{2+}	542.7	32.9a	359.8	22.0c	472.3	35.3b	396.1	36.3a	228.9	20.9c	298.3	27.3b
Cl^-	89.6	8.8a	86.3	9.8a	65.6	6.5b	85.4	12.4a	83.0	10.5a	86.2	6.5a
NO_3^-	16.7	3.7b	22.4	4.6a	10.6	3.3c	12.8	2.5b	19.9	4.3a	9.1	2.0c
SO_4^{2-}	173.8	18.0a	140.2	16.0b	173.1	20.6a	139.1	15.1a	114.1	11.9b	111.2	11.7b
HCO_3^-	640.1	42.6a	430.6	28.5c	550.5	31.3b	424.7	27.5a	267.8	20.3c	366.8	24.7b

Note: Different letters indicate significant difference among forest watersheds (Tukey test).

4.3 | SO_4^{2-}, NH_4^+, and NO_3^- concentrations

In the natural forest (N3), the stream SO_4^{2-} runoff was 3.5-fold larger than the SO_4^{2-} input (Table 2), suggesting that a sizable portion of SO_4^{2-} was derived from weathering of sedimentary rocks. The SO_4^{2-} concentrations in both the bulk precipitation and stream water decreased over time. In previous studies, the decreasing trend of fresh water SO_4^{2-} was interpreted as a response to reduced SO_4^{2-} input (Likens et al., 1996; Oulehle et al., 2017; Sase et al., 2019, 2021; Stoddard et al., 1999). Based on the stable isotope ratio of sulfur in soil and rainfall, Sase et al. (2019) suggested that stream SO_4^{2-} originates from rock weathering rather than from precipitation. Furthermore, measurements of the stable isotope ratio in tree rings suggest that trees can absorb acidic S deposits. Moreover, a large amount of sulfate accumulates in soil (Tanikawa et al., 2022). These findings suggest that sulfur deposited in forest ecosystems is accumulated and retained over the long term. In the present study, the sunlight hours and stream water SO_4^{2-} concentration were positively correlated (Table 6), suggesting that SO_4^{2-} release from organic matter decomposition largely regulates the stream water SO_4^{2-} concentration.

Similar to the K^+ concentration, the stream water NO_3^- concentration was lower in the plantation forest than in natural forests (Table 7). This pattern can be largely explained by plant uptake. Some Japanese cedar forests in the suburban areas of large cities are nitrogen-saturated and produce elevated NO_3^- runoff (Chiwa et al., 2012; Itoh et al., 2021; Nishina et al., 2017; Ohrui & Mitchell, 1997). The organic horizon of Japanese cedar and hinoki cypress is very thin and decomposition is very rapid (Takahashi, 2021). These findings suggest a potential risk of nitrogen loss in conifer plantation species. In contrast, the nitrogen mineralization and nitrification rates in conifer plantations and natural forests are similar (Urakawa et al., 2015, 2016), and the base-flow NO_3^-

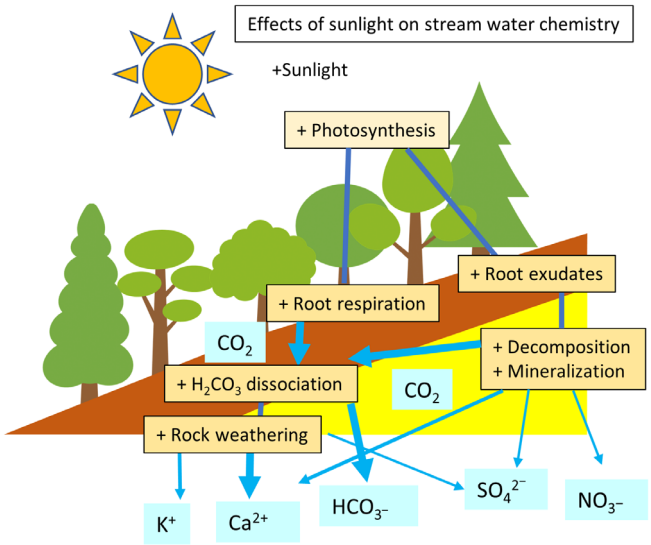

FIGURE 5 Conceptualized effects of sunlight on stream water chemistry. Arrow thickness represents approximate amount of ion flux. Longer sunlight hours promote photosynthesis, soil respiration, and carbon exudation from roots. Therefore, longer sunlight hours are expected to increase the carbonic acid concentration in soil solutions and increase the carbonic acid dissociates to HCO_3^-. Another pathway increases the carbon supply to soil microbes via the root exudates, promoting organic matter decomposition and the release of base cations and SO_4^{2-} from organic matter.

concentrations show no significant differences (Takagi, 2015). In a chronosequence study of a Japanese cedar plantation, the stream NO_3^- concentration increased after clear cutting but decreased sharply and reached very low level at the 20-year forests (Tokuchi & Fukushima, 2009). Therefore, the stream NO_3^- concentrations in Japanese cedar and hinoki cypress plantations are elevated under specific conditions (i.e., at clear cutting or high-nitrogen-deposition sites) but are generally low in other forests. Similar results were found in the present study.

The NO_3^- and NH_4^+ concentrations in the bulk precipitation decreased over time, consistent with previous studies (Chiwa, 2021; Sase et al., 2021). In their report on the national nitrogen budget of Japan, Hayashi et al. (2021) revealed that nitrogen emissions from transportation decreased after 2000 whereas the NH_3 emission from agricultural activity remained constant. The reduction of NO_3^- concentration in the bulk precipitation agrees with the national budget, but the reduction of NH_4^+ concentration deviates. However, Chiwa (2021) also reported a decreasing trend of NH_4^+ input in bulk precipitation. The temporal trend of NH_4^+ deposition strongly would depend on local agricultural activities.

The stream water NO_3^- concentrations decreased at annual rates of 2.55% and 0.95% in Yusuhara and Taisho, respectively. Previous studies reported similar decreasing trends (Chiwa, 2021; Groffman et al., 2018; Lucas et al., 2016; Urakawa et al., 2012) but others found no clear trends (Chiwa, 2021; Sase et al., 2021; Stoddard et al., 1999). Mechanisms by which the stream NO_3^- concentration declines with reducing nitrogen deposition have been proposed. Groffman et al. (2018) suggested that soil nitrogen mineralization decreased when the nitrogen input by litterfall is reduced. A study in Sweden suggested that the aboveground biomass increases after reducing clear cutting in the area, thus lowering the nitrogen loss from stream water (Lucas et al., 2016). The nitrogen concentration in the leaf litter of a hinoki cypress plantation decreases with increasing severity of competition with understory vegetation (Inagaki, Miyamoto, & Sakai, 2022). In another study, loss of understory vegetation by deer browsing increased the NO_3^- loss from stream water (Chiwa, 2021). Fukushima et al. (2011) found no relation between soil nitrogen mineralization and age of conifer plantations but Inagaki et al. (2004) reported greater nitrogen mineralization in middle-aged forests than in young forests. These finding suggest that although reducing the N deposition can lower NO_3^- loss from stream water, the degree of the reduction depends on the forest productivity and understory vegetation.

4.4 | Implications for forest management

The stream water SO_4^{2-}, NO_3^-, and Ca^{2+} concentrations decreased over time. Although acidic deposition was not obviously detrimental, the stream water chemistry showed an obvious temporal trend. It appears that the previously deposited sulfur and nitrogen were retained in forest ecosystems over a certain period and then gradually released. The rapid weathering rate of base cations imparts a high buffering capacity to ecosystems. The base cation concentration is thought to be decreasing toward its pre-industrialization level. The decreasing trend in base cation is likely to cause the nutrient limitation in forest ecosystems and aquatic environments in the future. It is expected that the rock weathering is approaching to pre-industrialization level, but the stream water chemistry is also affected by recent climate changes. Long-term monitoring is required to understand future changes and primary factors regulating stream water chemistry.

Within the study area, the temperature indicated obvious trends, but the precipitation and solar radiation showed no clear trends. The results suggest that higher temperatures lower the stream water K levels. Therefore, K limitation is expected to increase in warmer climates but could be alleviated if the K weathering rate increases with longer sunlight hours in future. As the coniferous plantations in this study showed no symptoms of nitrogen saturation, we suggest that nitrogen saturation is not a significant problem in the rural area of this study.

The results suggest that photosynthesis is strongly linked to stream water chemistry. Weathering of base cations is accelerated by warm climate, modestly acidic soil, and high plant productivity. Therefore, management practices that maintain forest productivity should be selected to maintain high-quality stream water.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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