Dissolved nitrogen concentration in river water and its impacts on downstream brackish-estuary lakes in the Bekanbeushi River and Lake Akkeshi catchment, northern Japan

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Abstract

To clarify the effects of land use in a catchment on river water quality, its nutrient environment and primary production in downstream brackish-estuary lakes, we observed nutrient concentrations (nitrogen and phosphorus) in river and lake water and analyzed land use in the catchment. The concentration of nitrate-nitrogen tended to increase in river water associated with a high percentage of agricultural land (pastureland) in its catchment. It is suggested that nitrogen management in agricultural lands in the catchment area and the arrangement of forests and riparian wetlands and their nitrogen removal functions may have an important effect on the productivity of aquatic organisms and food webs in downstream lakes, especially near river estuaries.

Introduction

Biological productivity in terrestrial ecosystems, including forests and agricultural lands, is supported in part by nitrogen (N), an essential nutrient (e.g., Vitousek et al. 1997). In addition, N runoff from various terrestrial land uses reaches lakes and coastal areas through rivers and becomes an important nutrient for phytoplankton and other aquatic organisms (Howarth et al. 1988). Coastal ecosystems are rich in ecosystem services and are important habitats for a wide variety of phytoplankton, fish and other aquatic biota (Beck et al. 2001). When N export from land to water increases above a certain level, excess nutrients yield negative consequences for aquatic primary producers in coastal and estuary ecosystems (Paterson and Whitfield 2000). Excessive application of chemical fertilizers and manure to agricultural lands can lead to high N runoff into water bodies (Howarth et al. 1996; Boyer et al. 2002), leading to a variety of adverse effects, including water quality degradation in downstream lakes and coastal areas, harmful algal blooms, low dissolved oxygen levels in water, and a loss of aquatic biodiversity (e.g., Carpenter et al. 1998). The relationship between terrestrial N inputs and N concentrations in river water depends on the balance between how much N is retained and how much N is exported to the hydrosphere within each land use and land cover type in the catchment (Bellmore et al. 2018).

Many studies have been conducted on the relationship between land use and river water quality. In most cool-temperate forest ecosystems, N is a limiting factor for primary productivity, resulting in externally derived N (i.e., atmospheric N deposition and biological N fixation) being retained in forests through absorption by plants and soil microorganisms (e.g., Shibata and Fukuzawa 2010). In a clear-cutting experiment in a forested catchment in the northeastern United States of America, the concentration of nitrate N (NO$_3^-$) in river water increased after logging (Likens et al. 1970), indicating that a large amount of N is retained under natural conditions through biogeochemical cycling within the forest ecosystem. Okazawa et al. (2009) found that NO$_3^-$ concentrations in river water are lower in densely forested areas, indicating that forest ecosystems play a major role in maintaining low N concentrations in river water. Shibata et al. (2021) also showed that the presence of forest ecosystems in the upper catchment lowers the NO$_3^-$ concentration in river water in the lower reaches. Riparian forests and wetlands are also important for N cycling and river water quality. Interface zones between land and water, such as riparian
wetlands, are rich in soil moisture and possess anaerobic conditions, promoting denitrification by soil bacteria and archaea (Hill 1996). Since denitrification is the process of removing \( \text{NO}_3^- \) from soil and water, denitrification processes in riparian zones have the ability to reduce N pollution from terrestrial areas to rivers (Hill 1996; Yoh 2014). However, certain amounts of chemical fertilizers and compost are commonly applied to agricultural lands to grow crops. The nitrogen that is not absorbed by the crops and microorganisms in soil can be leached into the river. Therefore, it is known that the proportion of agricultural land in a catchment is positively correlated with the N concentration of river water downstream (e.g., Woli et al. 2002). In the coastal watershed of Chesapeake Bay in the United States of America, a strong positive correlation was shown between the percentage of agricultural land in the catchment and \( \text{NO}_3^- \) and total N concentrations in water discharged from the catchment to the river, with approximately 80% of the total N in water being \( \text{NO}_3^- \) (Jordan et al. 1997). Nitrogen concentrations leaving the catchment via river water are intricately controlled by many complex biotic and abiotic factors, including ecosystem N requirements and fertilizer N inputs in agricultural lands, and vary with land use distribution, soil type, topography, N uptake by plants and microbes, other external N inputs on land systems, and hydrological and biogeochemical N processes in the ground (e.g., Jiang et al. 2015).

Similar to river water quality, the proportion of agricultural land in a catchment has been shown to have a significant impact on N and phosphorus (P) concentrations in downstream lakes and coastal areas (Camargo et al. 2006; Paerl et al. 2011; Jordan et al. 2018; Chambers et al. 2012). However, few studies have been conducted to show how much N fertilizer input is ultimately allowed in terrestrial areas and how this affects water quality based on field observations of terrestrial and aquatic areas. As the impact of recent anthropogenic activities on ecosystems has become an issue, it is necessary to understand the changes in N dynamics patterns and processes in response to anthropogenic impacts to optimize N cycling at the catchment scale (e.g., Kimura et al. 2006) and to clarify the relationship between catchment land composition, including human activities, and the resulting river water quality (Hayakawa 2012). To test the impact of land use patterns on river water quality, it is useful to conduct research in catchments where multiple land uses are involved rather than in watersheds dominated by a single land use type.

The Bekanbeushi River and Lake Akkeshi catchment in eastern Hokkaido of northern Japan are the targets of this study; various studies have been conducted in them on the relationship between forests and agricultural lands and river water quality and on the response of primary producers in aquatic ecosystems to the nutrient environment in the lake (e.g., Woli et al. 2004; Hayakawa et al. 2006; Akabane et al. 2003; Kajiwara 2008; Isada et al. 2021). However, there have not been enough studies evaluating N dynamics in the entire catchment, taking into account the ecosystems of downstream lakes. Therefore, this study aimed to clarify the relationship between the N inflow from terrestrial to aquatic ecosystems of the entire catchment and land use distribution and the impact of terrestrial riverine N on the downstream brackish-estuary lake.

Therefore, in this study, we conducted a comparative analysis of nutrient concentrations in river water and land use distribution based on field observations in the Bekanbeushi River and Lake Akkeshi
catchment. To consider the dynamics and effects of N as a nutrient, we also analyzed and compared it to P, which is similarly important as a nutrient.

**Materials And Methods**

**Study site**

This study was conducted at the Bekanbeushi River and Lake Akkeshi catchment in eastern Hokkaido, northern Japan (Fig. 1). Bekanbeushi Marsh, the second largest in Japan, is located within the catchment (Nagao et al. 2016). The catchment has various land use patterns, with each tributary having a different percentage of forest, farmland, and wetlands, and more than 95% of the farmland is dairy grassland (pastureland). The dominant forest type is natural cool temperate mixed forest and larch plantation. The main soil type is Andosols (developed from volcanic rock and ash) and Histosol (peat soils) in the wetland. Lake Akkeshi, located downstream of the catchment, has a surface water area of 31.8 km² and an average water depth of 1.5 m. Lake Akkeshi is connected to Akkeshi Bay by an approximately 500 m-wide channel and is a brackish lake with seawater inflow. The cultivation of bivalve mollusks such as clams and oysters is active, and eelgrass is distributed in almost all areas of the lake except for the clam fishing grounds. In addition to the Bekanbeushi River, which is the main inflow river, Lake Akkeshi is joined by the Obetsu River and the Oboro River at its mouth (Abe 2016). The main stream of the Bekanbeushi River has a channel length of 69.9 km and a catchment area of 379 km² and is interspersed with forests, farmlands, wetlands, and other land uses. Woli et al. (2004) found a positive correlation between NO₃⁻ concentration and the area of farmland in this catchment. Hayakawa et al. (2006) reported that N in river water is strongly affected by the presence of wetlands and riparian forests, but the details of this effect have not been fully clarified. In addition, although Lake Akkeshi is not currently experiencing major water quality degradation or ecosystem disturbance, it has experienced a drastic decline in Pacific oysters (*Crassostrea gigas*) in the past, which has been argued to be due to the logging of forests in the upper reaches (Inukai and Nishio 1937).

**Sampling sites and methods for water quality analysis**

River waters were collected at 14 locations within the catchment in April, June, September, and October 2018. Sampling locations were selected to cover as much of the entire catchment as possible and to ensure that the tributaries terminating at each sampling site had different land use distributions (Fig. 1, Table 1). River water was collected directly from the river surface with a prewashed bucket from above a bridge. Where it was difficult to collect water from the bridge, surface water was collected directly from the riverbank using a prewashed bucket. Lake waters were collected monthly from April to November 2017 in Lake Akkeshi. Surface lake water was collected at eight sites to cover Lake Akkeshi (Fig. 1). The collected lake and river water was brought back to the laboratory and filtered using a preburned glass fiber filter (Whatman GF/F, 0.7 µm pore size, 47 mm diameter) within 24 hours of collection, and the filtrate was frozen and stored until further chemical analysis.
Table 1
Site name, site code, latitude (north latitude) and longitude (east longitude) at the river water sampling points.

<table>
<thead>
<tr>
<th>Site name</th>
<th>Site code</th>
<th>Latitude (north)</th>
<th>Longitude (east)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bekanbeushi upper</td>
<td>BK-up</td>
<td>43° 16’ 49”</td>
<td>144° 43’ 09”</td>
</tr>
<tr>
<td>Takkaruushi</td>
<td>TK</td>
<td>43° 15’ 02”</td>
<td>144° 43’ 24”</td>
</tr>
<tr>
<td>Bekanbeushi middle</td>
<td>BK-mid</td>
<td>43° 13’ 10”</td>
<td>144° 45’ 03”</td>
</tr>
<tr>
<td>Katanashi</td>
<td>KT</td>
<td>43° 11’ 23”</td>
<td>144° 43’ 38”</td>
</tr>
<tr>
<td>Bekanbeushi lower</td>
<td>BK-down</td>
<td>43° 08’ 00”</td>
<td>144° 51’ 15”</td>
</tr>
<tr>
<td>Chiraikaribetsu upper</td>
<td>IT</td>
<td>43° 06’ 54”</td>
<td>144° 58’ 06”</td>
</tr>
<tr>
<td>Ohbetsu upper</td>
<td>OG</td>
<td>43° 06’ 41”</td>
<td>144° 46’ 20”</td>
</tr>
<tr>
<td>Toraibetsu</td>
<td>TR</td>
<td>43° 13’ 11”</td>
<td>144° 54’ 53”</td>
</tr>
<tr>
<td>Sattebetsu</td>
<td>ST</td>
<td>43° 08’ 21”</td>
<td>144° 48’ 52”</td>
</tr>
<tr>
<td>Homakai</td>
<td>HM</td>
<td>43° 05’ 50”</td>
<td>144° 44’ 06”</td>
</tr>
<tr>
<td>Chiraikaribetsu mouth</td>
<td>RC</td>
<td>43° 05’ 56”</td>
<td>144° 55’ 39”</td>
</tr>
<tr>
<td>Ohbetsu mouth</td>
<td>RO</td>
<td>43° 05’ 46”</td>
<td>144° 51’ 44”</td>
</tr>
<tr>
<td>Oboro mouth</td>
<td>RQ</td>
<td>43° 04’ 31”</td>
<td>144° 49’ 02”</td>
</tr>
<tr>
<td>Bekanbeushi mouth</td>
<td>RB</td>
<td>43° 06’ 27”</td>
<td>144° 53’ 30”</td>
</tr>
</tbody>
</table>

Water quality analysis methods

The analysis items were dissolved total nitrogen (TN), dissolved total phosphorus (TP), dissolved organic nitrogen (DON), NO$_3^-$, ammonium nitrogen (NH$_4^+$), dissolved inorganic nitrogen (DIN) and phosphorus (PO$_4^{3-}$). The DIN is the sum of NO$_3^-$ and NH$_4^+$. DON was obtained by subtracting the DIN from TN. Because nitrite nitrogen (NO$_2^-$) was at very low concentrations in this study, approximately 0.4-5.0% of NO$_3^-$, the sum of NO$_3^-$ and NO$_2^-$ was used for NO$_3^-$.

Nutrient concentrations were analyzed using an autoanalyzer (AACS4, BL-Tech, Co Ltd.). The units of mg L$^{-1}$ for N and P species are mg N L$^{-1}$ and mg P L$^{-1}$, respectively.

Analysis of land use
The land use distribution, elevation (maximum, minimum and average) and slope (maximum, minimum and average) in the tributary catchment at each water sampling site were analyzed using Arc-GIS (Table 2). The analysis was conducted using the 2014 editions of the National Land Use Data Land Use Subdivision Mesh Data provided by the Ministry of Land, Infrastructure, Transport and Tourism (MLIT). The land use types classified in these data were rice paddy fields, other agricultural land (cultivated land for crops other than paddy fields, including pastureland), forests, wastelands (wastelands, wetlands, mining land, etc.), building sites, roads, railroads, other sites, river land and lakes, beaches, seawater areas, and golf courses. Rice paddies, roads, beaches, saltwater areas, and golf courses were omitted because they did not exist in any watershed of the sampling points in this study. Considering the land use characteristics of the studied catchment, other agricultural lands were analyzed as pasturelands and wastelands as wetlands (Fig. 2).

Table 2
Catchment area, mean elevation, mean slope, and percentage of land area (forest, pastureland, and wetland) for each sub-watershed. See Table 1 for site codes.

<table>
<thead>
<tr>
<th>Code</th>
<th>Area (km²)</th>
<th>Elevation (m a.s.l.)</th>
<th>Slope (degree)</th>
<th>Forest (%)</th>
<th>Pastureland (%)</th>
<th>Wetland (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK-up</td>
<td>20.4</td>
<td>92.1</td>
<td>6.3</td>
<td>95.5</td>
<td>0.1</td>
<td>4.4</td>
</tr>
<tr>
<td>TK</td>
<td>20.7</td>
<td>63.0</td>
<td>6.9</td>
<td>67.8</td>
<td>22.6</td>
<td>9.3</td>
</tr>
<tr>
<td>BK-mid</td>
<td>36.4</td>
<td>75.6</td>
<td>6.5</td>
<td>89.4</td>
<td>0.0</td>
<td>9.6</td>
</tr>
<tr>
<td>KT</td>
<td>29.0</td>
<td>52.3</td>
<td>6.3</td>
<td>64.1</td>
<td>23.1</td>
<td>12.6</td>
</tr>
<tr>
<td>BK-down</td>
<td>351.8</td>
<td>53.3</td>
<td>5.9</td>
<td>60.4</td>
<td>17.8</td>
<td>16.7</td>
</tr>
<tr>
<td>IT</td>
<td>15.6</td>
<td>44.9</td>
<td>4.5</td>
<td>50.8</td>
<td>41.8</td>
<td>6.6</td>
</tr>
<tr>
<td>OG</td>
<td>1.5</td>
<td>71.7</td>
<td>1.9</td>
<td>24.0</td>
<td>72.1</td>
<td>1.6</td>
</tr>
<tr>
<td>TR</td>
<td>10.5</td>
<td>71.1</td>
<td>3.0</td>
<td>36.7</td>
<td>15.7</td>
<td>5.4</td>
</tr>
<tr>
<td>ST</td>
<td>4.1</td>
<td>47.4</td>
<td>5.7</td>
<td>76.5</td>
<td>23.5</td>
<td>0.0</td>
</tr>
<tr>
<td>HM</td>
<td>27.0</td>
<td>72.7</td>
<td>3.4</td>
<td>21.6</td>
<td>63.7</td>
<td>13.1</td>
</tr>
<tr>
<td>RC</td>
<td>40.4</td>
<td>36.1</td>
<td>4.7</td>
<td>62.1</td>
<td>21.2</td>
<td>15.8</td>
</tr>
<tr>
<td>RO</td>
<td>36.5</td>
<td>53.0</td>
<td>4.4</td>
<td>41.8</td>
<td>44.7</td>
<td>11.1</td>
</tr>
<tr>
<td>RQ</td>
<td>85.8</td>
<td>55.9</td>
<td>4.8</td>
<td>49.0</td>
<td>40.8</td>
<td>7.8</td>
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<tr>
<td>RB</td>
<td>379.0</td>
<td>52.4</td>
<td>5.8</td>
<td>60.3</td>
<td>17.9</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Statistical analysis
Since the number of samples for nutrient concentration data differed from one sampling site to another due to various technical limitations, a one-year average was used in the following multiple regression analysis. To analyze the influence of the land use distribution in the tributaries on nutrient concentrations, multiple regression analysis was conducted with forest area percentage and wetland area percentage as explanatory variables and nutrient concentrations as the objective variable. Because a preliminary analysis showed a statistically significant negative correlation ($r = -0.86$, $p < 0.05$) between the percentage of forest area and pastureland areas (Appendix Table 1), the pastureland area was excluded from the explanatory variables in the multiple regression analysis in consideration of multicollinearity issues. To further investigate whether nutrient concentrations were affected by the elevation and slope of the watershed, multiple regression analysis was conducted with the maximum elevation (m), minimum elevation (m), maximum slope angle (degrees), and minimum slope angle (degrees) for each watershed as explanatory variables and nutrient concentrations as objective variables. Preliminary analysis showed that mean elevation had a statistically significant positive correlation with minimum elevation ($r = 0.72$, $p < 0.05$) and mean slope angle with maximum elevation ($r = 0.60$, $p < 0.05$), so these variables were excluded from the multiple regression analysis due to multicollinearity issues. Pearson correlation analysis was performed between forestland area and nutrient concentration in river water collected each month. If there were significant correlations in multiple months, we performed ANCOVA to test differences in the correlations among months. Statistical analysis was performed using the statistical analysis software R (v.4.0.5; R Core Team 2020). A P value of less than 0.05 was considered statistically significant.

**Results**

**Nutrient concentrations in river water**

Nutrient (N and P) concentrations in river water at each site are shown in Table 3. The sites located upstream of the catchment, such as BK_up, TK, BK_mid, and TR, tended to have lower concentrations overall. Looking at the catchment as a whole, the annual mean TN concentrations ranged from 0.21–2.58 mg L$^{-1}$, DIN concentrations ranged from 0.12–2.45 mg L$^{-1}$, TP concentrations ranged from 0.01–0.07 mg L$^{-1}$, and PO$_4^{3-}$ concentrations ranged from 0.01–0.06 mg L$^{-1}$. The annual mean NO$_3^-$ concentrations (± standard deviation (SD)) at the RB, RO, and RQ (the mouths of the Bekenbeushi River, Obetsu, and Oboro Rivers), the main rivers flowing into Lake Akkeshi, were 0.16 (± 0.02 SD), 0.32 (± 0.25 SD), and 0.35 (± 0.09 SD) mg L$^{-1}$; RO and RQ were almost twice as high as RB. Regarding seasonal variations (Fig. 3), all concentrations in RO increased significantly in September and were higher than those in RB and RQ. In other months, no remarkable differences were observed in each nutrient concentration. As a whole, NO$_3^-$ and PO$_4^{3-}$ concentrations had a similar pattern of seasonal variation, with RO and RQ values increasing only in September and not in RB (Fig. 3).
Table 3
Mean values and standard deviations (SD) of river water quality at each site. The analyzed parameters were nitrate nitrogen (NO$_3^-$), ammonium nitrogen (NH$_4^+$), dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), dissolved total nitrogen (TN), dissolved inorganic phosphorus (PO$_4^{3-}$), and dissolved total phosphorus (TP). The n indicates number of samples. See Table 1 for site codes. The SD is indicated in the parenthesis (not shown in case of the sample number is 2).

<table>
<thead>
<tr>
<th>Code</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>DIN</th>
<th>DON</th>
<th>TN</th>
<th>PO$_4^{3-}$</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK-up</td>
<td>0.18 (0.03)</td>
<td>0.02 (0.00)</td>
<td>0.20 (0.03)</td>
<td>0.09 (0.06)</td>
<td>0.29 (0.04)</td>
<td>0.02 (0.00)</td>
<td>0.02 (0.00)</td>
</tr>
<tr>
<td>TK</td>
<td>0.21 (0.02)</td>
<td>0.02 (0.00)</td>
<td>0.23 (0.03)</td>
<td>0.13 (0.07)</td>
<td>0.37 (0.05)</td>
<td>0.02 (0.01)</td>
<td>0.02 (0.01)</td>
</tr>
<tr>
<td>BK-mid</td>
<td>0.11</td>
<td>0.02</td>
<td>0.13 (0.00)</td>
<td>0.08 (0.02)</td>
<td>0.21 (0.03)</td>
<td>0.01 (0.00)</td>
<td>0.02 (0.00)</td>
</tr>
<tr>
<td>KT</td>
<td>0.14</td>
<td>0.03</td>
<td>0.17 (0.00)</td>
<td>0.15 (0.05)</td>
<td>0.32 (0.05)</td>
<td>0.02 (0.01)</td>
<td>0.02 (0.01)</td>
</tr>
<tr>
<td>BK-down</td>
<td>0.17 (0.02)</td>
<td>0.02 (0.00)</td>
<td>0.19 (0.02)</td>
<td>0.13 (0.07)</td>
<td>0.32 (0.05)</td>
<td>0.02 (0.01)</td>
<td>0.02 (0.01)</td>
</tr>
<tr>
<td>IT</td>
<td>0.44 (0.08)</td>
<td>0.03 (0.01)</td>
<td>0.47 (0.07)</td>
<td>0.21 (0.05)</td>
<td>0.68 (0.10)</td>
<td>0.02 (0.01)</td>
<td>0.02 (0.01)</td>
</tr>
<tr>
<td>OG</td>
<td>2.35 (0.67)</td>
<td>0.10 (0.05)</td>
<td>2.45 (0.67)</td>
<td>0.13 (0.23)</td>
<td>2.58 (0.56)</td>
<td>0.06 (0.01)</td>
<td>0.07 (0.01)</td>
</tr>
<tr>
<td>TR</td>
<td>0.12 (0.00)</td>
<td>0.02 (0.00)</td>
<td>0.14 (0.00)</td>
<td>0.08 (0.02)</td>
<td>0.21 (0.03)</td>
<td>0.01 (0.00)</td>
<td>0.01 (0.00)</td>
</tr>
<tr>
<td>ST</td>
<td>0.10</td>
<td>0.02</td>
<td>0.12</td>
<td>0.13</td>
<td>0.25</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>HM</td>
<td>0.54 (0.11)</td>
<td>0.02 (0.00)</td>
<td>0.57 (0.11)</td>
<td>0.17 (0.13)</td>
<td>0.74 (0.06)</td>
<td>0.02 (0.00)</td>
<td>0.02 (0.01)</td>
</tr>
<tr>
<td>RC</td>
<td>0.21 (0.08)</td>
<td>0.03 (0.00)</td>
<td>0.24 (0.08)</td>
<td>0.21 (0.05)</td>
<td>0.45 (0.07)</td>
<td>0.01 (0.00)</td>
<td>0.02 (0.00)</td>
</tr>
<tr>
<td>RO</td>
<td>0.33 (0.22)</td>
<td>0.08 (0.07)</td>
<td>0.41 (0.29)</td>
<td>0.26 (0.14)</td>
<td>0.67 (0.42)</td>
<td>0.03 (0.03)</td>
<td>0.05 (0.03)</td>
</tr>
<tr>
<td>RQ</td>
<td>0.36 (0.08)</td>
<td>0.05 (0.02)</td>
<td>0.41 (0.07)</td>
<td>0.19 (0.07)</td>
<td>0.60 (0.11)</td>
<td>0.03 (0.01)</td>
<td>0.04 (0.01)</td>
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<td>RB</td>
<td>0.16 (0.01)</td>
<td>0.03 (0.01)</td>
<td>0.19 (0.01)</td>
<td>0.12 (0.06)</td>
<td>0.31 (0.04)</td>
<td>0.02 (0.00)</td>
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</tr>
</tbody>
</table>

Relationship between river water nutrient concentrations and land use distribution
Multiple regression analysis between nutrient concentrations and land use distribution showed that the multiple regression model with NO$_3^-$, DIN, and TN concentrations as objective variables was statistically significant. In addition, a statistically significant negative effect was found between the forest area percentage and those concentrations (Table 4). No statistically significant effect was detected for wetland area percentage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Forest area</th>
<th>Wetland area</th>
<th>p-value of regression model</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>-2.62 *</td>
<td>-1.82</td>
<td>0.030</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-2.37 *</td>
<td>-1.28</td>
<td>0.065</td>
</tr>
<tr>
<td>DIN</td>
<td>-2.28 *</td>
<td>-1.11</td>
<td>0.029</td>
</tr>
<tr>
<td>DON</td>
<td>-1.47</td>
<td>1.02</td>
<td>0.236</td>
</tr>
<tr>
<td>TN</td>
<td>-2.82 *</td>
<td>-1.72</td>
<td>0.025</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>-2.07</td>
<td>-1.42</td>
<td>0.088</td>
</tr>
<tr>
<td>TP</td>
<td>-2.28 *</td>
<td>-1.11</td>
<td>0.084</td>
</tr>
</tbody>
</table>

When the seasonal changes in nutrient concentrations of NO$_3^-$, NH$_4^+$, DIN, TN, and TP were compared with the forest area percentage, statistically significant negative correlations were found only in April and September for NO$_3^-$, DIN, TN, and TP concentrations and in April for NH$_4^+$ concentrations (Fig. 4). There was no significant difference in the slopes of those significant correlations between April and September. As noted in the Methods, significant negative correlations were found between forest area and pastureland area (Supplemental Table 1). No significant correlations were found between elevation or slope angle and nutrient concentrations, except for a significant negative correlation with the highest elevation and DON concentrations (data not shown).

**Nutrient concentrations in blackish-estuary lake water**

In Lake Akkeshi, DIN concentrations decreased after April but increased in the summer months (July or August), decreased again after the summer season, and increased again in November when the winter season was near (Fig. 5). In addition, an increase in NH$_4^+$ concentrations were common at sites where DIN concentrations increased during the summer months. The increase in DIN concentrations in the spring and winter was mainly due to higher NO$_3^-$ concentrations than at other times of the year. The DIN
concentrations in lake water were generally lower than those in river water except for a few sites and periods (Figs. 3 & 5).

The PO$_4^{3-}$ concentrations in the lake water increased from July to September. The maximum PO$_4^{3-}$ concentration at L6 was 0.11 mg L$^{-1}$ in August, while the maximum PO$_4^{3-}$ concentrations at L1 and L2 were 0.03 and 0.04 mg L$^{-1}$, respectively, in September, which were lower than those at the other sites in the lake. The PO$_4^{3-}$ concentrations in the lake water were generally similar to those in the river water (Figs. 3 and 5). The DIN/DIP ratios of the lake water (Fig. 6) were high in April at all sites, decreased sharply after April, and then increased again around September.

**Discussion**

**Effect of land use on nutrient concentrations in river water**

Among the 14 tributaries observed, the OG, HM, and RQ sites with high percentages of farmland (pastureland) tended to have higher NO$_3^-$ concentrations in the river water than the other sites with low percentages of farmland (Fig. 2, Table 3). However, there was little difference in phosphorus concentrations among sites. These findings suggest that the distribution of pastureland in the catchment area contributes to increased NO$_3^-$ runoff from the terrestrial area to the river. The lower observed runoff of phosphorus may be due to the effect of the high phosphate adsorption capacity of volcanic ash soils (Saigusa et al. 1990), which are widely distributed in the catchment.

Nutrient concentrations in river water showed a statistically significant negative correlation with the percentage of forest area, which had a significant negative correlation with the percentage of farmland, but not with the percentage of wetland area (Tables 3 and 4). Van Beek et al. (2004) and Hayakawa et al. (2006) reported a significant influence of microbial denitrification in peat soils. In this study, differences in N concentrations in river water were detected depending on the percentage of pastureland area, though there were slight differences in N concentrations among sites in catchments with a large percentage of pastureland area (Supplemental Figs. 1 and 2). For example, the annual average TN and DIN concentrations in OG exceeded 2 mg L$^{-1}$, while those in HM, where more than half of the watershed area is pastureland, did not reach even 1 mg L$^{-1}$, as in OG. It was suggested that this difference was largely due to N removal via denitrification in the wetlands. Seventy-two percent of OG is pastureland and 1.6% is wetland, while 64% of HM is pastureland and 13% is wetland; hence, the wetland area in HM being 3.5 km$^2$ larger than that in OG. This difference in the size of the riparian wetlands may have affected the concentration of nitrogen in river water.

In another catchment located in eastern Hokkaido, the increased growth of phytoplankton due to excess nutrient loading from the land and the associated inputs of organic manure have damaged the benthic habitat and adversely affected the aquatic ecosystem in the Lake Furen catchment, where agricultural land dominates the entire catchment (Montani et al. 2011). Mikami and Igarashi (2014) showed that TN
concentrations in the Furen River (which flows into Lake Furen) have varied between 0.5 and 1.2 mg N L$^{-1}$ over the past 10 years. However, the annual average TN concentration in this studied catchment was less than 0.8 mg N L$^{-1}$ except in the OG, where the pastureland area ratio was more than 70% (Tables 2 and 3). In Lake Furen, most of the catchment area is used for dairy farming (Mikami et al., 2008), and the percentage of pastureland area in the Furen River catchment is approximately 70% (Muneoka et al. 2000). In contrast, the catchment area of this studied catchment has 24% pastureland, 57% forest, and 15% wetland, which means that there is less pastureland and more forest and wetland than in the catchment of Lake Furen. In eastern Hokkaido, large-scale pastureland development since the 1960s has decreased forest and wetland areas. In addition, recent changes in land use management, such as the expansion of management scale and cattle breeding, are believed to have greatly affected the water quality environment in the catchment (Nakamura et al. 2010). Our results suggest that changes in pastureland can alter the N concentration in downstream rivers. The negative effect of forestland and wetland on the N concentration in the river (Table 4) suggests that river water with a low N concentration from forested areas and N removal via denitrification in riparian wetlands has a dilution effect that plays an important role in the N concentration in river water in the downstream area, especially as a response to the high concentration of N discharged from pastureland lands in the Bekanbeushi River and Lake Akkeshi catchment. A significant relationship between several nutrient concentrations (i.e., TN, TP, DINS and NO$_3^-$) and forestland was observed in April and September, whereas it was insignificant in other months. Generally, in these areas, April has higher river discharge due to snowmelt; September also has high discharge as a result of the decrease in evapotranspiration during the late growing season (Maruya et al. 2019). It has been suggested that higher discharge amplifies the impact of land use on nutrient concentrations, as it leads to an increase in lower-concentration water from forests (as discussed above) and higher leaching of nutrients from pastureland along with hydrological flow in the ground.

**Nutrient environment in Brackish-estuary Lake Akkeshi**

Comparing nutrient concentrations in river and lake water, N concentrations in lake water were much lower than those in river water, but similar P concentrations were observed between lake and river water (Table 3, Fig. 5). This suggests that primary producers are more actively taking up N among the nutrients (N and P) flowing in from the river. Higher concentrations of NH$_4^+$ and PO$_4^{3-}$ might leach from lake sediments, as reported by Hasegawa et al. (2008) and Isada et al. (2021). They suggested that the combined effects of increased water temperature, reduced water mass exchange due to eelgrass growth, and oyster cultivation leach NH$_4^+$ and PO$_4^{3-}$ from the bottom of the lake sediments in summer. The composition ratio of microalgae in aquatic ecosystems, known as the Redfield ratio, is generally known to be close to C:N:P = 106:16:1 (Redfield et al. 1963). Since N in lake water remains at most sites and seasons in Lake Akkeshi (Fig. 5), it is unlikely that the growth of primary producers is strongly suppressed by N limitation. In terms of the Redfield ratio and DIN/DIP ratio, P is considered to be relatively more in surplus than N (Fig. 6), suggesting that the inflow of N through rivers from terrestrial catchments has the potential to further increase phytoplankton and/or primary production in the lake water of Lake Akkeshi.
Conclusion

The land use distribution in the Bekanbeushi River and Lake Akkeshi catchment influences the spatial distribution of NO$_3^-$ concentrations in river water. The NO$_3^-$ in river water tends to increase in tributaries with a high percentage of pastureland area. Nitrogen dynamics in river and downstream brackish-estuary lakes are affected by the land use patterns of the catchment and the biological and biogeochemical conditions in the lake. For sustainable catchment management in the future, it is important to take N balance and water quality changes into account when determining land use policies.

Declarations

Acknowledgments

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Competing interests

The authors confirm they do not have any conflict of interest.

References


**Figures**
Figure 1

Location of the sampling sites for water quality monitoring for river water (yellow balloon) and lake water (white open circle) at Bekanbeushi River and Lake Akkeshi catchment. See the Table 1 for the site codes. The L1, L3 and L5 is the sampling site for incubation experiments using lake water. Background image was copied from Google Earth.
Figure 2

Distribution of land use and water sampling points in the Bekenbeushi River and Lake Akkeshi catchment.
Figure 3

Seasonal changes of nutrient concentrations in river water at RB (estuary of BetsukanbeushiRiver), RO (estuary of ObetsuRiver) and RQ (estuary of OhoroRiver).
Figure 4

Seasonal changes in the correlation between the concentrations of $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{PO}_4^{3-}$, DIN, TN, and TP in the river water at each site and the percentage of forested area (%) in the watershed. Only seasons with statistically significant negative correlations are shown as line in the same color as the legend.
Figure 5

Seasonal changes in NO$_3^-$, NH$_4^+$, and PO$_4^{3-}$ concentrations at each site in Lake Akkeshi. The vertical axis indicates nutrient concentrations (mg/L) and the horizontal axis indicates the time of sampling (month). Periods when no sampling was conducted are shown as NA.
Figure 6

Seasonal changes in DIN/DIP ratio of lake water at each site in Lake Atkkeshi. The vertical axis indicates the DIN/DIP ratio, and the horizontal axis indicates the time when the samples were taken. Periods when no sampling was conducted are shown as NA and connected by dashed lines.

Supplementary Files

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