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Evaluating Stream Water Quality through Land Use Analysis in Two Grassland Catchments: Impact of Wetlands on Stream Nitrogen Concentration

A. Hayakawa,* M. Shimizu, K. P. Woli, K. Kuramochi, and R. Hatano

ABSTRACT

We evaluated the impacts of natural wetlands and various land uses on stream nitrogen concentration in two grassland-dominated catchments in eastern Hokkaido, Japan. Analyzing land use types in drainage basins, measuring denitrification potential of its soil, and water sampling in all seasons of 2003 were performed. Results showed a highly significant positive correlation between the concentration of stream NO_3–N and the proportion of upland area in drainage basins in both catchments. The regression slope, which we assumed to reflect the impact on water quality, was 24% lower for the Akkeshi catchment (0.012 ± 0.001) than for the Shibetsu catchment (0.016 ± 0.001). In the Akkeshi catchment, there was a significant negative correlation between the proportion of wetlands in the drainage basins and stream NO_3–N concentration. Stream dissolved organic nitrogen (DON) and carbon (DOC) concentrations were significantly higher in the Akkeshi catchment. Upland and urban land uses were strongly linked to increases in in-stream N concentrations in both catchments, whereas wetlands and forests tended to mitigate water quality degradation. The denitrification potential of the soils was highest in wetlands, medium in riparian forests, and lowest in grasslands; and was significant in wetlands and riparian forests in the Akkeshi catchment. The solubility of soil organic carbon (SOC) and soil moisture tended to determine the denitrification potential. These results indicate that the water environment within the catchments, which influences denitrification potential and soil organic matter content, could have caused the difference in stream water quality between the two catchments.

Human activities associated with intensive agriculture, livestock farming, and sewage disposal from urban areas have been identified as a major contributor to riverine nitrogen loadings (Howarth et al., 1996; Carpenter et al., 1998; Boyer et al., 2002), which can lead to eutrophication of surface waters, causing degradation of aquatic ecosystems and problems such as toxic algal blooms, loss of oxygen, fish kills, and loss of biodiversity (Carpenter et al., 1998). Evaluating the impact of human activities on river water quality is required to conserve water quality and natural resources, and to adequately manage land uses in drainage basins. However, nonpoint sources of pollution are difficult to detect since they generally encompass large areas in drainage basins and involve complex biotic and abiotic interactions.

Agricultural land use within catchments has been linked to increased concentrations of inorganic N in drainage waters. The concentration of NO_3–N in stream water has been strongly correlated with the proportion of agricultural land associated with grassland and common upland crops in the catchment (Tabuchi et al., 1995; Woli et al., 2002). Woli et al. (2002) found that the regression slope of the relationship was largest for intensive livestock farming area, intermediate for mixed agriculture and livestock farming, and smallest for grazing-based horse farming area. The slopes indicated an impact intensity of upland field on stream water. Therefore, they defined the slope as impact factors of water quality. Woli et al. (2004a) further reported that the impact factors had a significant positive correlation with the cropland surplus N, which was estimated by using the N budget approach. This appears to indicate that by estimating the proportion of agricultural upland area in the catchment and calculating the surplus N in cropland we can predict the quality of river water with respect to NO_3–N concentration.

Natural biogeochemical processes can contribute to mitigation of river water quality. Terrestrial–aquatic interfaces, such as riparian forests and wetlands, have high denitrification potentials, because aerobic and anaerobic hot spots coexist in the soil profile, allowing both nitrification and denitrification to occur (McClain et al., 2003). Denitrification is the conversion of NO_3–N to gaseous N (N_2O or N_2). It is performed by particular groups of ubiquitous heterotrophic bacteria that have the ability to use NO_3–N as an electron acceptor during anaerobic respiration. Therefore, the factors controlling denitrification rates are the supply of C and NO_3–N and anoxia (Tiedje, 1994). Several studies have reported that ground water NO_3–N concentrations decrease in riparian forests adjacent to uplands where ground water is polluted by intensive agricultural management (Peterjohn and Correll, 1984; Lowrance, 1992; Hill, 1996). Wetlands also have N removal potential, mainly by denitrification (Jansson et al., 1994; Fisher and Acreman, 2004; Wigand et al., 2004). Hefting et al. (2004) reported that water table elevation was an important factor regulating N dynamics in riparian wetlands. However, attempts to scale up from these results (by relating the presence of riparian wetlands to NO_3–N removal by denitrification) have been largely unsuccessful, causing a significant impediment to the construction of N budgets and the modeling of biogeochemical cycles across different spatiotemporal scales (McClain et al., 2003).

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Abbreviations: DOC, dissolved organic carbon; DON, dissolved organic nitrogen; PON, particulate organic nitrogen; SOC, soil organic carbon; SON, soil organic nitrogen; TDN, total dissolved nitrogen; TN, total nitrogen; WESOC, water-extractable soil organic carbon; WESON, water-extractable soil organic nitrogen.

Compared to inorganic forms of N, relatively few data are available for dissolved organic nitrogen (DON), even though it has been reported to contribute significantly to total dissolved nitrogen (TDN) in stream water (Meybeck, 1982; Chapman et al., 2001; Perakis and Hedin, 2002). Recently, several reports showed that Histosol-dominated catchments or the proportion of wetland area in drainage basins could explain the variability in concentrations of DON in stream water (Clark et al., 2004; Pellerin et al., 2004; Willett et al., 2004). Seitzinger et al. (2002) reported that a higher proportion of anthropogenically derived DON was bioavailable to estuarine bacteria relative to forest-derived DON. Few studies, however, evaluated the impact of human development (i.e., urbanization and agricultural development) on DON concentrations in stream water.

The Akkeshi and Shibetsu catchments are located in eastern Hokkaido, Japan. More than 95% of the agricultural land in these catchments consists of grassland utilized for dairy farming. Woli et al. (2004a) analyzed the proportion of land uses such as grassland and common upland field, forest, urban area, wetland, and wasteland of drainage basins and found that the stream NO_3–N concentrations were positively correlated with the proportion of grassland and common upland field in both catchments. The regression slope of the relationship or the impact factor was lower in the Akkeshi catchment than in the Shibetsu catchment. They also found that the increase in proportion of forests and wetland in the drainage basins decreased NO_3–N concentration. However, they did not discuss the possible reasons of varied impact factors in those two similar catchments, nor did they discuss the role of wetlands and riparian forests as possible buffers for water quality.

The objectives of this study were to compare the two catchments, one with and the other without wetlands, to evaluate the impact of land use on in-stream N concentrations in grassland areas and to evaluate the effect of wetlands within the catchment on water quality. In addition, to explain the difference of water quality between the catchments and within a catchment of each site, we measured denitrification potential of soils from the main land uses of grassland, riparian forest, and wetland.

MATERIALS AND METHODS

Site Description

We studied the Akkeshi (43°10′ N, 144°48′ E) and Shibetsu catchments (43°35′ N, 144°52′ E), which had been previously studied by Woli et al. (2004a) (Fig. 1). The Akkeshi catchment (1010 km^2) is composed of the drainage basins of the Bekanbeushi River, and includes the town of Akkeshi and part of the town of Shibecha. The Shibetsu catchment (1309 km^2) is composed of the drainage basins of the Shibetsu River, and includes the towns of Shibetsu and Nakashibetsu. Both catchments have almost the same annual mean precipitation (about 1140 mm) and temperature (5°C) (Table 1). Andisols are the main soil type in both catchments, with Histosols distributed in the lowland areas in the Akkeshi catchment. Grassland makes up more than 95% of the agricultural land in both catchments, with dairy farming the main farming system; livestock density is similar, at 1.6 and 1.7 animal units (AU) ha^{-1} of agricultural land in the Akkeshi and Shibetsu catchments, respectively. One AU is equivalent to 1 dairy or beef cow, 1.3 horses, or 100 head of poultry, calculated on the basis of the amount of excrement, as recommended by Nyukantori Editors (1976, p. 372–381). Therefore, the climate, soil type, and farming systems are almost the same in both catchments. The major difference between the Akkeshi and Shibetsu catchments is the existence of wetlands. In the Akkeshi catchment

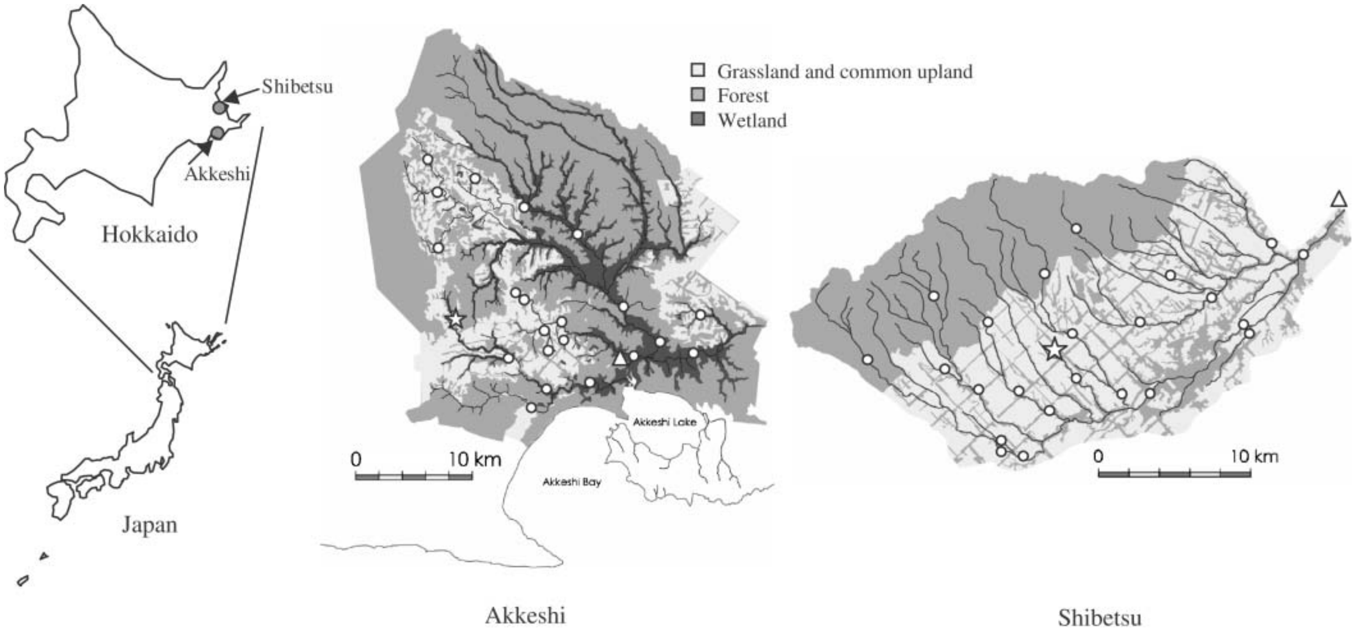

Fig. 1. **Location map of the study sites and distribution of sampling sites in the Akkeshi and Shibetsu catchments. ○ Denotes water sampling sites; ☆ denotes sites in riparian forest adjacent to grassland for measuring denitrification potentials; △ denotes sites of the wetland for measuring denitrification potentials.**

Table 1. Characteristics of the study sites.

Characteristic	Akkeshi	Shibetsu
Location	Akkeshi + Shibecha town	Nakashibetsu + Shibetsu town
Coordinates	43°10′ N, 144°48′ E	43°35′ N, 144°52′ E
Mean precipitation, mm	1 130	1 150
Mean temperature, °C	5	5
Area, km^2		
Total	1 010	1 309
Cropland	180	368
Common upland	2	19
Paddy field	0	0
Grassland	178	348
Wetland	83.2†	2‡
Cropland/total area	0.18	0.28
Grassland/cropland	0.99	0.95
Human population	16 318	28 970
Livestock, head		
Beef cattle	5 150	8 400
Dairy cattle	38 300	54 000
Horses	0	730
Livestock density, AU§ ha^{-1}	1.6	1.7

† Shinsho (2001).
‡ Tachibana et al. (1997).
§ Animal unit.

the Bekanbeushi wetland (83.2 km^2) stretches from the middle to lower reaches of the Bekanbeushi River (Shinsho, 2001). In contrast, almost all of the wetlands in the Shibetsu catchment have disappeared; the 2 km^2 that remain are the result of river improvement works that accompanied the change of land use from wetlands to grasslands (Tachibana et al., 1997; Nakamura, 2003).

Land Use Estimation

The area corresponding to each major land use type (e.g., upland fields, forests, urban areas, wetlands, and wastelands) in the drainage basins of each sampling site was estimated by dividing the respective drainage basins into a square mesh of 4 × 4 mm^2 on 1:25 000 topographic maps (one cell is thus equivalent to 1 ha). For sampling sites in the lower reaches of a stream, the drainage basins were determined by including the drainage basins of all upper streams and tributaries that flow into it (Woli et al., 2004a). The agricultural areas, cultivated with upland crops such as wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), sugar beet (*Saccharum officinarum* L.), and potato (*Solanum tuberosum* L.), including grasslands and excluding lowland paddy fields, are termed as ''upland field'' in this study.

Sampling

Woli et al. (2004a) conducted intensive water sampling in 74 drainage basins in the Akkeshi catchment and 57 drainage basins in the Shibetsu catchment and analyzed the impacts of different land uses on stream NO_3–N concentration. In this study, more frequent monitoring was undertaken by reducing the number of sampling sites to 21 and 23 in Akkeshi and Shibetsu catchments, respectively (Fig. 1). Representative sites were chosen from among the sites with similar values of stream NO_3–N concentration and drainage basin area ensuring that the subcatchments of varied characteristics are incorporated. Water sampling was performed once in all seasons in 2003: spring (April), summer (July), fall (September), and winter (November). Water samples were collected in 1-L polypropylene bottles separately from each site in both catchments. At the same time of water sampling, stream water discharge rates from the drainage basins were also measured at each sampling site with a flow velocity meter (TK-105; Toho Dentan, Tokyo). The water discharge rate was calculated by multiplying the sectional area of the stream by flow velocity at 60% depth at 8 to 10 points along a transect across the stream.

Chemical Analysis of Water Samples

After water sampling was conducted, water samples were stored on ice until transported to the laboratory, filtered through 0.2-μm membrane filters within a few days, and analyzed for dissolved nutrients within a month. Nonfiltered samples were used for total nitrogen (TN) analysis. Samples were stored at 4°C until analysis. We checked whether NO_3–N concentrations in stream water could change or not during the preservation. The NO_3–N concentrations of seven samples were analyzed over 8 d (1, 2, 5, and 8 d after filtration) with three replications. The NO_3–N concentrations (average ± SD) at the first day were 0.03 ± 0.003, 0.24 ± 0.004, 0.40 ± 0.003, 0.56 ± 0.004, 0.59 ± 0.007, 1.16 ± 0.005, and 1.85 ± 0.014 mg N L^{-1}. After 8 d, the concentrations were 0.04 ± 0.025, 0.25 ± 0.004, 0.41 ± 0.003, 0.55 ± 0.005, 0.58 ± 0.011, 1.20 ± 0.003, and 1.89 ± 0.014 mg N L^{-1}, respectively. The differences of the concentrations during 8 d were between −0.013 and 0.047 mg N L^{-1}. It explained from −2.3 to 4.3% of NO_3–N concentrations measured in the first day. The results of a *t* test did not show significant difference ($P = 0.12$) between NO_3–N concentrations of the first and eighth day, although NO_3–N concentrations tended to increase slightly. The results of a *t* test among the concentrations of all measurement day combinations also did not show any significant difference ($P > 0.05$). This indicated that NO_3–N concentrations would not significantly change until analysis.

Total N and total dissolved nitrogen (TDN) were determined by the method of alkaline persulfate digestion and HCl-acidified UV detection; NO_3–N was determined by ion chromatography (QIC Analyzer; Dionex, Sunnyvale, CA); and NH_4–N was determined by colorimetry using the indophenol blue method. Particulate organic nitrogen (PON) and DON were calculated by subtracting the concentration of TDN from TN, and inorganic N (NO_3–N, NH_4–N) from TDN, respectively. Total dissolved C and inorganic C were determined by TOC analyzer (TOC-5000A; Shimadzu, Kyoto, Japan) and dissolved organic carbon (DOC) was calculated by subtracting inorganic C from total dissolved C.

Measurement of Denitrification Potential

The denitrification potential of soil was measured in wetlands, riparian forests, and grassland adjacent to riparian forests in both the Akkeshi and Shibetsu catchments (Fig. 1). Denitrification potential was determined by using the acetylene block technique, which inhibits the final conversion of N_2O to N_2 gas (Tiedje, 1994). Soil samples were taken from both catchments once in July 2004. Samples were taken in triplicate with an auger from depths of 0 to 15, 15 to 30, 30 to 60, and 60 to 90 cm (except the wetland sample of 60 to 90 cm in the Akkeshi catchment). The triplicate samples from each depth were mixed before analysis. To determine the difference among the sites in the amount of organic C available to denitrifying organisms, we defined denitrification potential as the denitrification rate that occurred under anaerobic conditions with abundant NO_3–N at 25°C. Samples of fresh, homogenized soil (15 g) were placed into 100-mL serum bottles. An aliquot of 15 mL solution treated with NO_3–N (200 mg N L^{-1} as KNO_3) and chloramphenicol (1 g L^{-1}) was added to the bottles. The serum bottles were evacuated and flushed four times with N_2 to ensure anaerobic conditions, and acetylene

(C_2H_2) gas was added to a final concentration of 10% (10 kPa) in the headspace. Headspace gas was sampled by syringe at 2 and 4 h and denitrification rates were calculated from the linear portion of N_2O produced over time. Nitrous oxide was determined using a gas chromatograph with an electron capture detector (GC-14B; Shimadzu). Soil organic carbon (SOC) and nitrogen (SON) were determined by NC analyzer (NC-1000; Sumigraph, Niihama, Japan). Water-extractable soil organic carbon (WESOC) and nitrogen (WESON) were determined by analyzing a 1:5 water-extracted solution (1:20 for wetland soil). The DOC and DON concentrations of the solution were determined by the above mentioned method.

Stream and ground water table levels were monitored using a water table sensor (MC-1100W; STS, Sirnach, Switzerland) in the wetland and riparian forest, near where denitrification potentials were measured in the Akkeshi catchment. The water table sensors were installed 10 m from the edge of the stream.

Statistical Analysis

The Kruskal–Wallis test was used to determine whether there was a significant difference among the concentrations in four seasons within the catchments. We also compared the regression slopes of the relation between the proportion of upland area and stream NO_3–N concentration (log scale) in each of the catchments.

A redundancy analysis was also performed using the CANOCO 4 computer application (Braak and Smilauer, 1998) to evaluate the correlation between the land use types and the variables related to concentrations of N species. This technique, which is commonly used for determining relations between biological communities and environment, has been applied recently for determining the relationship between land use types and water quality variables (Sliva and Williams, 2001; Woli et al., 2004b). CANOCO (CANOnical Community Ordination) is a technique for relating explanatory variables to response variables. Data analysis using this technique leads to an ordination diagram of samples, species, and environmental variables, which optimally describes how community composition (water quality variables or N species in our study) varies with the environment or land use variables (Braak and Smilauer, 1998).

RESULTS

Stream Nitrogen and Carbon Concentrations

Mean stream NO_3–N concentrations in the Akkeshi and Shibetsu catchments were 0.63 ± 0.61 and 0.62 ± 0.51 mg N L^{-1}, respectively (Table 2). The distribution pattern of the mean NO_3–N concentrations was different between the Akkeshi and Shibetsu catchments (Fig. 2). In the Akkeshi catchment, the upper reaches of some streams and tributaries had high concentrations reaching up to 1.0 mg N L^{-1} and the concentration decreased to as low as 0.41 mg N L^{-1} further downstream. On the other hand, in the Shibetsu catchment, NO_3–N concentrations were low in the upper reaches but increased in the middle to lower reaches, with five sites exceeding 1.0 mg N L^{-1}. The mean stream TN concentration in the Akkeshi and Shibetsu catchments was 1.34 ± 0.79 and 0.95 ± 0.72 mg L^{-1}, respectively. Mean stream NH_4–N and PON concentrations were relatively small (5–9% of TN concentration) in both the Akkeshi and Shibetsu catchments, but were slightly higher in the Akkeshi catchment than in the Shibetsu catchment (Table 2). Stream DON dominated TN in both the Akkeshi and Shibetsu catchments, accounting for 37 and 34% of TN concentration, respectively. Both stream DOC and DON concentrations were significantly higher in the Akkeshi catchment (Fig. 3). The mean value of DOC was more than 1.8 times higher in the Akkeshi catchment than in the Shibetsu catchment, and DON was more than 1.6 times higher (Table 2).

The water discharge rate per unit area of drainage basin and the variability in the rate were of similar magnitude in the Akkeshi and Shibetsu catchments (Table 2).

Relation between Land Use Type and Concentrations of Stream Nitrogen and Carbon

Linear regression analysis showed a positive correlation between the concentration of NO_3–N and the proportion of upland area in the drainage basins. This correlation was highly significant in all seasons with no significant difference between seasonal NO_3–N concentrations in either catchment ($P = 0.95$ in Akkeshi; $P = 0.48$ in Shibetsu). One sampling site in the Akkeshi catchment had a remarkably high NO_3–N concentration (2.73 ± 0.58 mg N L^{-1}) and was excluded for some statistical analyses on the assumption that it was possibly

Table 2. Mean, standard deviation, median, maximum, and minimum values of the proportion of land use type in each drainage basin, and the water discharge rate and concentrations of chemicals† in streams sampled in the Akkeshi and Shibetsu catchments.

	Watershed area	Upland	Forest	Urban	Wetland	Wasteland	Discharge	Discharge per unit area	TN	NO_3–N	NH_4–N	DON	PON	DOC
	km²	%					$m^3\ s^{-1}$	$m^3\ s^{-1}\ km^{-2}$	mg L^{-1}					
						Akkeshi ($n = 21$)								
Mean	55	51.7	37.1	1.2	6.0	4.1	2.36	0.030	1.34	0.63	0.12	0.50	0.10	4.65
SD	100	26.7	21.6	1.0	6.8	3.5	5.04	0.017	0.79	0.61	0.16	0.13	0.04	0.73
Median	13	51.0	36.5	1.1	3.6	3.4	0.30	0.025	1.07	0.50	0.04	0.46	0.09	4.59
Maximum	360	98.1	71.6	4.3	18.5	14.7	18.13	0.078	3.47	2.73	0.67	0.88	0.17	6.20
Minimum	1	7.4	0.0	0.2	0.0	0.0	0.01	0.005	0.50	0.06	0.00	0.37	0.04	3.33
						Shibetsu ($n = 23$)								
Mean	84	40.2	54.2	0.5	–	0.8	3.23	0.031	0.95	0.62	0.05	0.32	0.03	2.55
SD	134	28.7	30.4	0.8	–	0.7	5.85	0.012	0.72	0.51	0.07	0.18	0.03	0.74
Median	29	44.0	52.7	0.1	–	0.8	0.97	0.031	1.03	0.58	0.02	0.33	0.04	2.74
Maximum	543	90.3	100.0	3.4	–	1.9	22.78	0.051	2.54	1.66	0.30	0.64	0.09	4.01
Minimum	3	0.0	0.0	0.0	–	0.0	0.02	0.003	0.00	0.00	0.00	0.03	0.00	1.38

† DOC, dissolved organic carbon; DON, dissolved organic nitrogen; PON, particulate organic nitrogen; TN, total nitrogen.

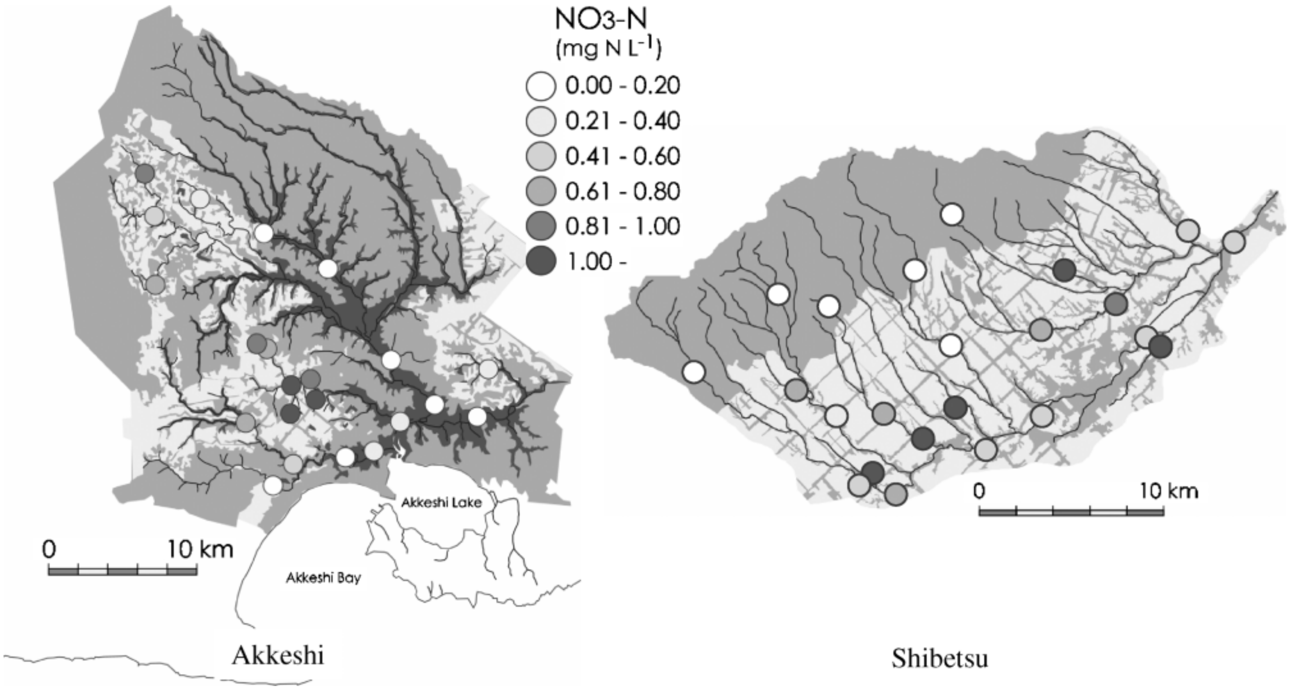

Fig. 2. Distribution of mean NO_3–N concentrations in the Akkeshi and Shibetsu catchments.

affected by a point source (Fig. 4). The regression slope, which is defined as the impact factor of river water quality, was lower in the Akkeshi catchment (0.012 ± 0.001) than in the Shibetsu catchment (0.016 ± 0.001) in all seasons. Comparison of the two regression slopes for each season showed a significant difference ($P < 0.05$) between the Akkeshi and Shibetsu catchments in all seasons other than spring (April), when snowmelt occurs. In the Akkeshi catchment, the average NO_3–N concentrations correlated negatively with the proportion of wetland ($r = -0.545$, $P < 0.05$) (Table 3). On the other hand, the proportion of upland and urban areas significantly explained the concentrations of TN and NO_3–N in both the Akkeshi and Shibetsu catchments.

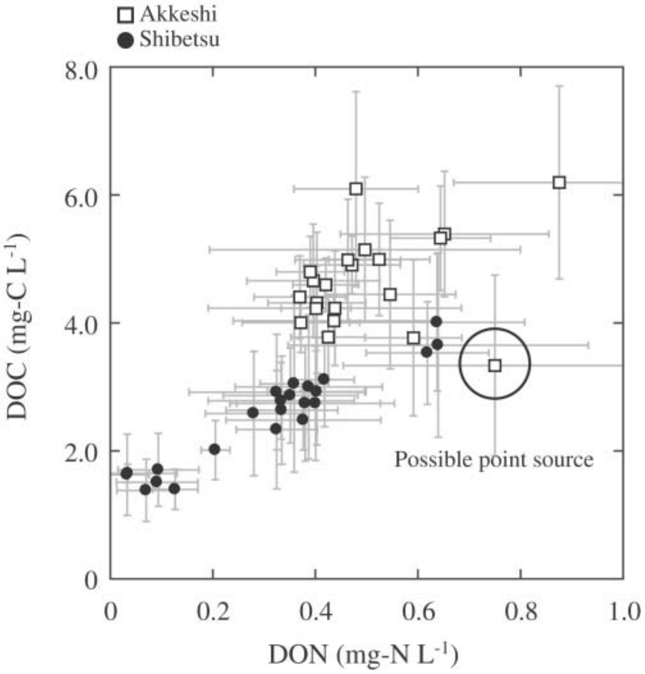

Fig. 3. Relationship between the mean dissolved organic nitrogen (DON) and carbon (DOC) concentrations in the Akkeshi and Shibetsu catchments. Error bars represent standard deviations for data from four seasons.

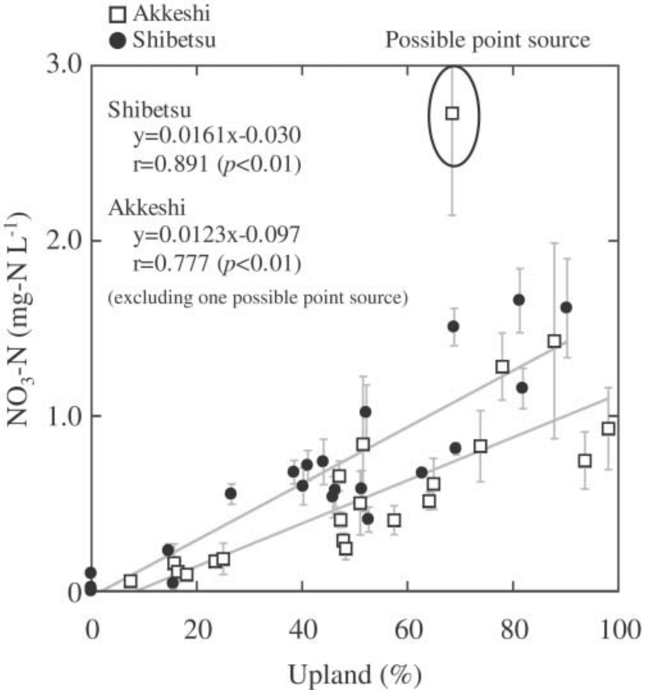

Fig. 4. Relationship between the proportion of upland in drainage basins and NO_3–N concentration in stream water in the Akkeshi and Shibetsu catchments. Error bars represent standard deviations for data from four seasons.

Table 3. Relationship among water quality variables and land use proportions in drainage basins in the Akkeshi catchment (upper triangle of the table, $n = 20$; one point source excluded) and Shibetsu catchment (lower triangle of the table, $n = 23$) expressed as Pearson's correlation coefficients.†

	Upland	Forest	Urban	Wetland	Wasteland	TN	NH_4–N	NO_3–N	DON	PON	DOC
Upland		−0.967**	0.492*	−0.708**	−0.423	0.691**	0.522*	0.634**	0.616**	0.092	0.310
Forest	−0.758**		−0.492*	0.543*	0.291	−0.656**	−0.491*	−0.608**	−0.540*	−0.137	−0.366
Urban	0.397	−0.322		−0.487*	−0.045	0.772**	0.285	0.858**	0.520*	−0.210	−0.189
Wetland	–	–	–		0.234	−0.589**	−0.467*	−0.545*	−0.538*	0.111	−0.006
Wasteland	0.492*	−0.323	0.361	–		−0.287	−0.124	−0.264	−0.466*	−0.013	−0.043
TN	0.910**	−0.688**	0.570**	–	0.400		0.706**	0.947**	0.869**	0.103	0.119
NH_4–N	0.509*	−0.432*	0.829**	–	0.365	0.718**		0.463	0.714**	0.478*	0.501*
NO_3–N	0.912**	−0.705**	0.444*	–	0.316	0.985**	0.632**		0.731**	−0.125	−0.102
DON	0.918**	−0.661**	0.571**	–	0.462*	0.977**	0.656**	0.952**		0.264	0.326
PON	0.230	−0.060	0.455*	–	0.611**	0.248	0.202	0.127	0.308		0.365
DOC	0.934**	−0.729**	0.574**	–	0.550**	0.962**	0.698**	0.932**	0.959**	0.318	

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

† DOC, dissolved organic carbon; DON, dissolved organic nitrogen; PON, particulate organic nitrogen; TN, total nitrogen.

The NH_4–N concentration was strongly correlated with the proportion of upland area in the Akkeshi catchment and with urban area in the Shibetsu catchment. There was a strong positive correlation between DON and DOC concentrations in Shibetsu ($r = 0.959$, $P < 0.01$), whereas the correlation was weak in Akkeshi ($r = 0.326$) (Table 3).

Redundancy Analysis

The ordination diagram of the redundancy analysis (Fig. 5) displays explanatory variables (proportion of major land use types: uplands, urban areas, wastelands, wetlands, and forests), and response variables (concentrations of TN, NO_3–N, NH_4–N, and DON). The arrows indicate the directions of the gradients, and the distance between the species (points) and the gradients (arrows) indicates the correlation between the species and the physical gradient represented by the arrows. The length of each gradient arrow indicates the importance of the gradient in explaining the variation in water quality. One sample in Akkeshi was possibly affected by a point source and was excluded from the analysis. The TN and NO_3–N arrows almost overlap the arrow of proportion of upland area, indicating a close relationship between them (Fig. 5). The NH_4–N concentration was positively correlated with the proportion of upland area in the Akkeshi catchment, and positively correlated with the proportion of urban area in Shibetsu. On the other hand, the arrows of the forested land use variable and the N species concentration variables are almost opposing, reflecting the negative correlations between them. Furthermore, in the Akkeshi catchment, the concentration of each N species was also negatively correlated with the proportion of wetlands. There was a strong positive correlation between the DON arrow in the Shibetsu catchment and the proportion of upland area, but only a weak correlation in the Akkeshi catchment.

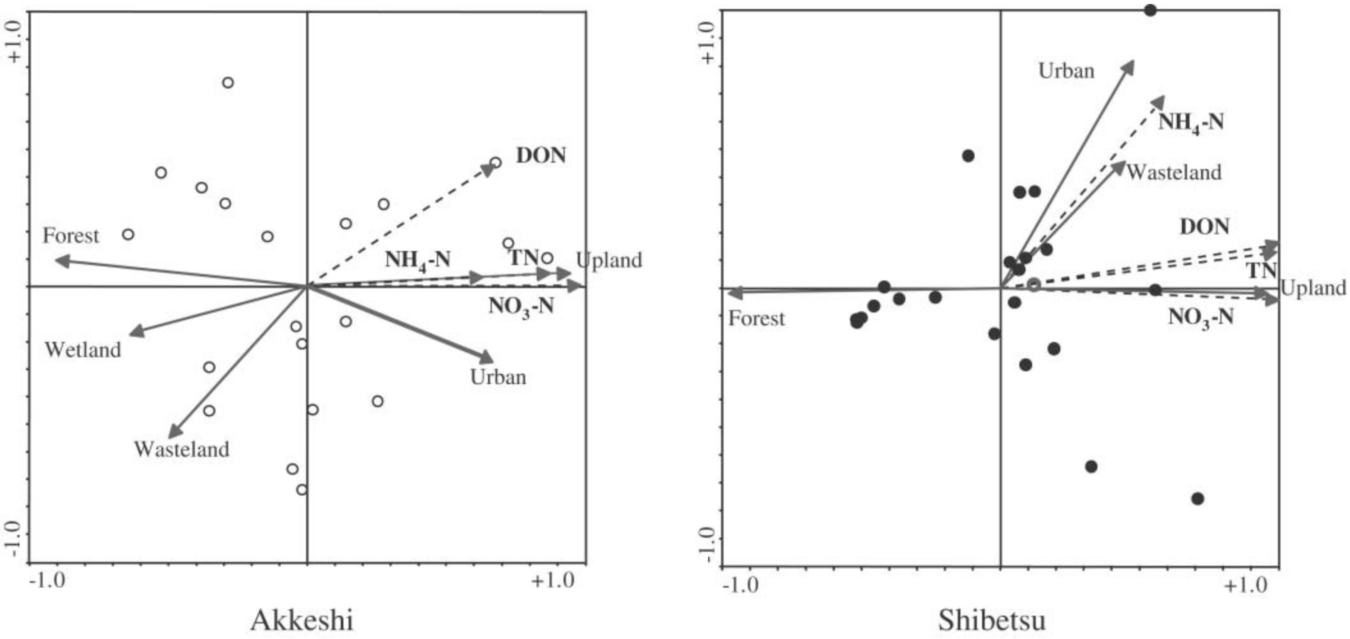

Fig. 5. Results of redundancy analysis. Solid lines denote explanatory variables (proportion of major land use types: uplands, forests, urban areas, wetlands, wastelands); dotted lines denote the response variables (concentrations of total nitrogen [TN], NO_3–N, NH_4–N, and dissolved organic nitrogen [DON]); ○ denotes sampling sites in the Akkeshi catchment; and ● denotes sampling sites in the Shibetsu catchment.

Soil Organic Matter

Soil moisture was highest in wetlands, and of similar magnitude in riparian forests and grassland; it tended to be higher in the Akkeshi catchment than in Shibetsu (Table 4). Soil organic carbon (SOC) ranged from 29.1 to 330.6 g C kg^{-1}, and water-extractable soil organic carbon (WESOC) ranged from 34.7 to 509.8 mg C kg^{-1}. All soil organic fractions (C and N) were highest in wetland soil, and were of similar magnitude in riparian forests and grasslands. In the Akkeshi catchment, grassland SOC was considerably higher (121.3 g C kg^{-1}) than that of riparian forest (50.1 g C kg^{-1}), while WESOC of grassland and riparian forest was of the same magnitude (Table 4).

Denitrification Potential

The denitrification potential was highest in wetlands, medium in riparian forests, and lowest in grasslands (Fig. 6). The maximum value at each site was observed between 0 and 30 cm depth and the values of wetland and riparian forest in the Akkeshi catchment were 10 to 100 times higher than those in the Shibetsu catchment. Denitrification potential tended to be positively correlated with the ratio between WESOC and SOC (Fig. 7). In particular, data from the Akkeshi catchment showed a significant positive correlation ($r = 0.849$, $P < 0.01$) (Table 5). Soil moisture also showed a positive correlation with SOC, SON, and denitrification potentials in both catchments (Table 5).

Ground Water Table in Riparian Forests and Wetlands

The level of the ground water table was always higher than the water level of the stream in the riparian forest. It fluctuated by 10 cm underground, peaking during rainfall events and rose to the surface of the ground (Fig. 8). On the other hand, in the wetland, the water level of the stream fluctuated by about 80 cm affected by the rise and fall of tides, causing the ground water table to fluctuate by about 40 cm (Fig. 8c). The level of the stream water was also distinctly higher than that of ground water table during high tides, with the result that stream water flowed into the wetland through the site of highest denitrification potential.

DISCUSSION

There was a highly significant positive correlation between NO_3–N concentration and the proportion of upland area in the drainage basins of both the Akkeshi and Shibetsu catchments (Fig. 4), and the redundancy analysis showed that the arrows for proportion of upland area and concentration of NO_3–N overlap (Fig. 5). These results indicate that the area of uplands was the most dominant factor for determining NO_3–N concentration, which is consistent with previous results (Woli et al., 2004a). In the Akkeshi catchment, the average concentration of NO_3–N in the streams in the drainage basins was negatively correlated with the proportion of wetland area, and each of the other N species also was negatively correlated with the proportion of wetland (Table 3). Woli et al. (2004b) reported that although the concentration of NO_3–N in the streams was weakly related to the proportion of paddy fields, there was a high positive correlation between TON (PON + DON) concentration in the streams and the proportion of paddy fields. This indicates that the effect of wetlands on stream TON concentration was different from the effect of paddy fields. The concentration of NH_4–N in streams in the Shibetsu catchment was correlated with the proportion of urban area (Table 3). This indicates that it might be affected by water discharged from sewage treatment plants and sewers. Sliva and Williams (2001) also reported that urban areas had a great influence on NH_4–N concentration, especially during spring and summer.

The concentrations of DOC and DON in streams were considerably higher in the Akkeshi catchment than in the Shibetsu catchment (Fig. 3, Table 2). In the Shibetsu catchment, there was a significant positive correlation between concentrations of both DOC and DON in streams and the proportion of upland area, but in the Akkeshi catchment, the relationship was weak (Table 3). The redundancy analysis also showed that the effect of upland area on stream DON concentration was stronger in the Shibetsu catchment than in the Akkeshi catchment (Fig. 5). McTiernan et al. (2001) found that there was a significant positive correlation between the amount of DOC leaching and the rate of N application in a grassland field without artificial drainage due to the increased production of dry matter caused by the increased input of fertilizer N. Probably this is the

Table 4. Soil moisture, soil organic carbon (SOC) and nitrogen (SON), C to N ratio, and water-extractable soil organic carbon (WESOC) and nitrogen (WESON) in the soils of three land use types in the Akkeshi and Shibetsu catchments. Data are the mean values (standard deviation) of soil in each land use type.

Site	*n*	Soil moisture	SON	SOC	C to N ratio	WESON	WESOC
		g g^{-1}	g N kg^{-1}	g C kg^{-1}		mg N kg^{-1}	mg C kg^{-1}
				Akkeshi			
Wetland	3	0.81 (0.06)	12.0 (2.6)	187.0 (62.0)	15.4 (1.6)	30.4 (6.9)	175.0 (40.6)
Riparian forest	4	0.52 (0.04)	3.5 (0.91)	50.1 (12.8)	14.4 (0.29)	7.1 (1.2)	46.7 (14.3)
Grassland	4	0.55 (0.05)	8.3 (1.1)	121.3 (15.5)	14.6 (0.85)	10.2 (0.87)	51.9 (8.1)
				Shibetsu			
Wetland	4	0.76 (0.06)	20.0 (3.2)	330.6 (59.1)	16.5 (0.88)	46.7 (9.6)	509.8 (181.4)
Riparian forest	4	0.39 (0.06)	2.4 (1.5)	29.1 (16.6)	12.5 (0.71)	7.8 (2.9)	35.0 (7.5)
Grassland	4	0.39 (0.02)	3.0 (0.73)	42.1 (9.5)	13.9 (0.25)	8.2 (2.4)	34.7 (11.4)

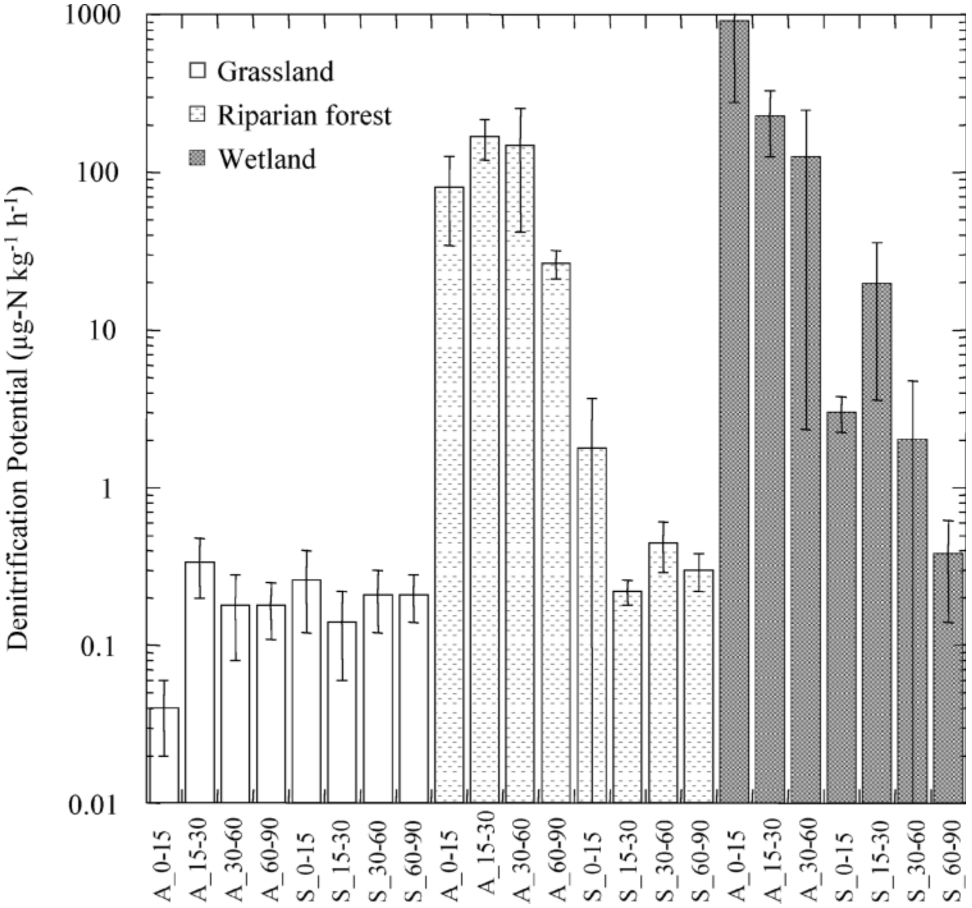

Fig. 6. Denitrification potentials of soils of three land use types. A_ denotes drainage basins in the Akkeshi catchment and S_ denotes drainage basins in the Shibetsu catchment. The values along the *x* axis show the depths of the soil samples analyzed.

reason for the effect of upland area on the concentrations of DON and DOC in streams in drainage basins in agricultural areas. On the other hand, Histosol-dominated catchments and the proportion of wetlands in the drainage basins were expected to explain the variability in the stream DON concentration (Clark et al., 2004; Pellerin et al., 2004; Willett et al., 2004) and stream DOC concentration (Hope et al., 1994; Chapman et al., 2001; Clark et al., 2004). However, because this study showed that the proportion of wetlands in the Akkeshi catchment did not correlate with stream DOC concentration and only showed a weak negative correlation with stream DON concentration (Table 3), upland areas might be a significant source of DOC and DON loadings in streams. The mean stream DOC and DON concentrations in the Akkeshi catchment were 1.8 and 1.6 times higher than those in the Shibetsu catchment, respectively (Table 2, Fig. 3); therefore, the whole Akkeshi catchment appears to be a source of DOC and DON. Soil moisture was significantly and positively correlated with SOC and SON and with WESOC and WESON in both the Akkeshi and Shibetsu catchments (Table 5), which indicates that the water environment in the catchment may influence the C and N biogeochemical cycles. This would account for the difference in stream DOC and DON concentrations between the two catchments.

In both the Akkeshi and Shibetsu catchments the denitrification potentials in the riparian forests and wetlands were higher than those in the grasslands (Fig. 6). Since wetlands in the Akkeshi catchment occupy about 15% of the total catchment area, the whole-catchment denitrification potential is estimated to be higher in the Akkeshi catchment than in the Shibetsu catchment. Furthermore, the denitrification potential as a function of SOC solubility (WESOC to SOC ratio) was higher in the Akkeshi catchment than in the Shibetsu catchment (Fig. 7). This suggests that the quality of SOC also influences denitrification rate. Van Beek et al. (2004) reported a high denitrification rate (87 kg N ha^{-1} yr^{-1}) in a peat soil under grassland; since there was an ample source of energy available throughout the soil profile, the denitrification rate was not limited by organic C. On the other hand, Murray et al. (2004) showed that low-molecular-weight C limited the denitrification potential in the subsoil of a gravelly loamy soil under grassland. Hill and Cardaci (2004) reported that the quantity and quality of soil organic C influenced denitrification potential. The high solubility of SOC, as well as the high SOC content in the wetlands in the Akkeshi catchment, might be a reason why concentrations of NO_3–N in the streams in the drainage basins of the Akkeshi catchment decreased downstream.

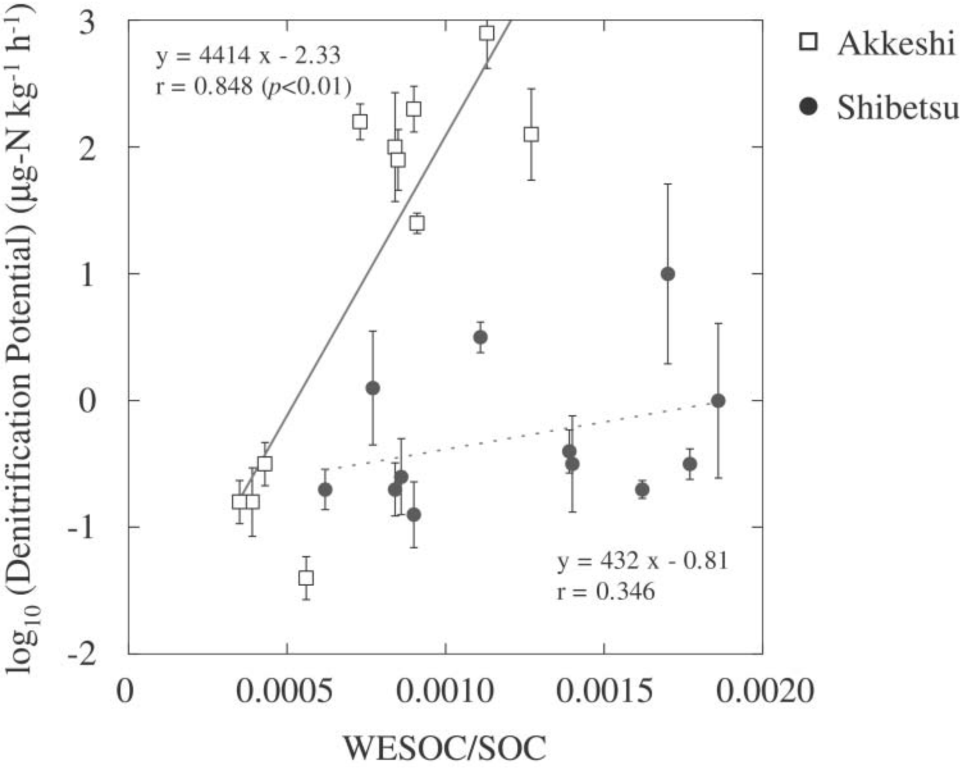

Fig. 7. Relationship between the ratio of water-extractable soil organic carbon (WESOC) to soil organic carbon (SOC) and $\log_{10}$ (denitrification potential) in the Akkeshi and Shibetsu catchments. Error bars represent standard deviations of three replications.

The level of the ground water table in the riparian forest and the wetland in the Akkeshi catchment fluctuated between 0 and 40 cm at the point near the ground surface where we observed high denitrification potentials (Fig. 8). Hefting et al. (2004) reported that the level of ground water table fluctuation regulated N-cycle processes in riparian zones and that water table levels between 10 and 30 cm depth favored denitrification. Van Beek et al. (2004) also reported that the level of the ground water table determined the distribution of denitrification rates at all depths in peat soil under grassland and that the highest denitrification rates were observed above the level of the ground water table at depths of between 0 and 40 cm in the soil profile. In the Akkeshi catchment, stream water flowing into the wetland was affected by tidal sea level, and the level of the ground water table fluctuated daily between 0 and 40 cm depths from the soil surface (Fig. 8). Under these conditions, aerobic and anaerobic hot spots coexist in the soil profile, allowing both nitrification and denitrification to occur (McClain et al., 2003). Therefore, stream NO_3–N could have been removed in the wetlands of the Akkeshi catchment.

The linear regression analysis showed a significantly high correlation between stream NO_3–N concentration and the proportion of upland area in the drainage basins, and the regression slope (impact factor) was lower for the Akkeshi catchment than that for the Shibetsu catchment (Fig. 4). Woli et al. (2004a) reported that the regression slopes varied among various farming systems and that the slopes had a significant positive correlation with the field surplus N as estimated by using the N

Table 5. Relationship among soil moisture, soil organic carbon (SOC) and nitrogen (SON), C to N ratio, water-extractable soil organic carbon (WESOC) and nitrogen (WESON), WESOC to SOC ratio, and ln (denitrification potential) in the soils of three land use types in the Akkeshi catchment (upper triangle of the table, $n = 11$) and the Shibetsu catchment (lower triangle of the table, $n = 12$) expressed as Pearson's correlation coefficients.

	Soil moisture	SON	SOC	C to N ratio	WESON	WESOC	WESOC to SOC ratio	$\log_{10}$ (denitrification potential)
Soil moisture		0.846**	0.864**	0.652*	0.941**	0.951**	0.245	0.441
SON	0.988**		0.987**	0.580	0.822**	0.817**	−0.177	−0.057
SOC	0.989**	0.998**		0.695*	0.823**	0.838**	−0.149	−0.015
C to N ratio	0.859**	0.864**	0.887**		0.503	0.586	−0.010	0.114
WESON	0.970**	0.983**	0.979**	0.834**		0.961**	0.302	0.443
WESOC	0.955**	0.817**	0.973**	0.832**	0.982**		0.390	0.475
WESOC to SOC ratio	0.415	0.450	0.459	0.309	0.523	0.566		0.848**
$\log_{10}$ (denitrification potential)	0.627*	0.637*	0.592*	0.309	0.666*	0.557	0.346	

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.

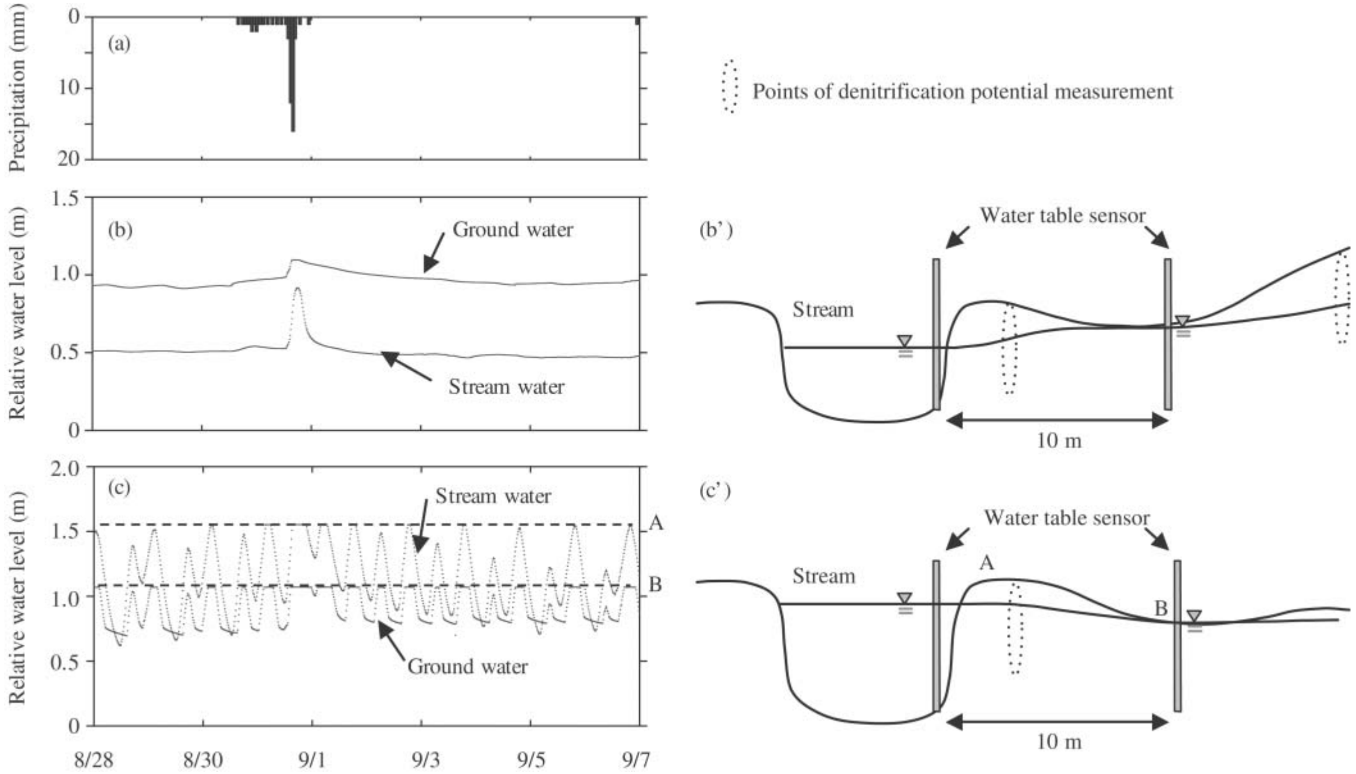

Fig. 8. Precipitation and fluctuation of stream water level and ground water table. Precipitation (a), water table fluctuation in the riparian forest and grassland (b), and water table fluctuation in the wetland (c) near the points where denitrification potentials were measured in the Akkeshi catchment. The diagrams to the right [(b′) and (c′)] show how the water table sensors were set up and the points at which denitrification potentials were measured. "A" shows the ground level at the river bank and "B" shows the ground level in the wetland 10 m from the edge of the river.

budget approach. In our study area, grassland was the major land use type, and the livestock density was similar in both areas (Table 1). Nevertheless, field surplus N was 10 kg N ha^{-1} higher in the Shibetsu catchment than in the Akkeshi catchment (Mishima et al., 2004; Woli et al., 2004a). This could probably result in the difference in stream NO_3–N concentrations between the Akkeshi and Shibetsu catchments.

The regression slopes or impact factors of the relationship between stream NO_3–N concentration and the proportion of upland area in the drainage basins in the Akkeshi and Shibetsu catchments were 0.012 ± 0.001 and 0.016 ± 0.001, respectively, which means that the impact factor in the Akkeshi catchment was 23.6% lower than that in the Shibetsu catchment. Even including the site affected by a possible point source in the Akkeshi area, the impact factor in the Akkeshi catchment (0.0146 ± 0.0012) was 9.3% lower than that in the Shibetsu catchment.

The difference in impact factor between the Akkeshi and Shibetsu catchments could be possibly explained either by the effects of dilution or the removal of NO_3–N or both. Because the mean rate of water discharge per unit area of drainage basin and the variability in the rate are of similar magnitude in the Akkeshi and Shibetsu catchments (Table 2), there was a similar dilution effect in both catchments. Therefore, the difference in impact factors between the Akkeshi and Shibetsu catchments can be explained by a high NO_3–N removal effect in the Akkeshi catchment, which still contains wetlands and riparian forests with high denitrification potentials.

CONCLUSIONS

In a drainage basin of various land uses along with agricultural land area receiving anthropogenic N inputs, the proportion of agricultural land (upland) within the catchment was found to be one of the most important predictors of NO_3–N concentration in stream water. On the other hand, riparian forest and wetland could play an important role in mitigating degradation of water quality. From the results of this study, we concluded that the impact of land uses in catchments on stream N and C concentrations is also strongly influenced by the presence of wetlands and riparian forests, which have a high denitrification potential, arising from the high solubility of SOC and high soil moisture content. It is important to quantify a function of the biogeochemical "hot spot" such as riparian forest and wetland within a catchment for understanding biogeochemical N and C flux of stream water by developing a conceptual framework of varied temporal and spatial monitoring plans.

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