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Title	Assessment of river water quality during snowmelt and base flow periods in two catchment areas with different land use
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ASSESSMENT OF RIVER WATER QUALITY DURING SNOWMELT AND BASE FLOW PERIODS IN TWO CATCHMENT AREAS WITH DIFFERENT LAND USE

Abstract. River water quality was evaluated with respect to eutrophication and land use during spring snowmelt and summer base flow periods in Abashiri (mixed cropland–livestock farming) and Okoppe (grassland-based dairy cattle farming), eastern Hokkaido, Japan. Water from rivers and tributaries was sampled during snowmelt and summer base flow periods in 2005, and river flow was measured. Total N (TN), NO₃-N, and Si concentrations were determined using standard methods. Total catchment and upland areas for each sampling site were determined with ArcGIS hydrology modeling software and 1:25 000-scale digital topographic maps. Specific discharge was significantly higher during snowmelt than during base flow. In both areas, TN concentrations increased, whereas Si concentrations decreased, with increased specific discharge, and were significantly higher during snowmelt. The Si:TN mole ratio decreased to below or close to the threshold value for eutrophication (2.7) in one-third of sites during snowmelt. River NO₃-N concentrations during base flow were significantly and positively correlated with the proportion of upland fields in the catchment in both the Abashiri ($r = 0.88$, $P < 0.001$) and Okoppe ($r = 0.43$, $P < 0.01$) areas. However, the regression slope, defined as the impact factor (IF) of water quality, was much higher in Abashiri (0.025) than in Okoppe (0.0094). The correlations were also significantly positive during snowmelt in both areas, but IF was four to eight times higher during snowmelt than during base flow. Higher discharge of N from upland fields and grasslands during snowmelt and the resulting eutrophication in estuaries suggest that nutrient discharge during snowmelt should be taken into account when assessing and monitoring the annual loss of nutrients from agricultural fields.

Keywords: eutrophication; impact factor; land use; mole ratio; nitrogen; phosphorus; silica; spring snowmelt; summer base flow

Introduction

Runoff from agricultural land is a major cause of non-point source pollution (Daniel *et al.*, 1998), and eutrophication has been identified as a resulting critical problem in surface waters (Artola *et al.*, 1995; Stapleton *et al.*, 2000; Camargo *et al.*, 2005). This anthropogenic disturbance results from activities that enhance N cycling in the environment: production and application of fertilizers, discharge of human waste, animal production, and combustion of fossil fuels (Nixon, 1995). These activities mobilize N and P and accelerate the fluxes of these elements to coastal waters. Fertilization of coastal ecosystems is now a serious environmental problem, because it stimulates plant growth and disrupts the balance between the production and metabolism of organic matter in the coastal zone (Cloern, 2001). There is increasing concern that the ratio of Si to N (or P) is decreasing, potentially limiting diatom productivity, because human activities have selectively enhanced the loading of N and P, but not that of Si, to coastal waters (Cloern, 2001). Particularly during snowmelt periods, phytoplankton increase in coastal seas; siliceous species increase first, and then nonsiliceous species take their place when the mole ratio of Si to N in water bodies falls below 2.7, considered the threshold value for eutrophication (Kudo and Matsunaga, 1999). The mole ratio of Si to TN concentrations in river water is a useful predictor of eutrophication in coastal seas during the snowmelt season. The Si:TN mole ratio in river water has been reported to be less than the threshold value in 10%–40% of rivers in those regions of southern and central Hokkaido that are favorable to animal husbandry or dairy farming (Nagumo and Hatano, 2001). Hatano *et al.* (2005) also reported that the Si:TN mole ratio in river water in Hokkaido falls considerably below the threshold value during the snowmelt season, and that 90% of the N loading occurs during rainfall and spring snowmelt events.

Magnitude of nutrient leaching from agricultural soils is dependant on land use in the drainage basins (Sileika *et al.*, 2005). A positive relationship has been reported between the proportion of farmland in drainage basins and the NO₃-N concentration in river water (Smart *et al.*, 1985; Neill, 1989; Tabuchi *et al.*, 1995; Jordan *et al.*, 1997; Cronan *et al.*, 1999; McFarland and Hauck 1999; Woli *et al.*, 2002; Buck *et al.*, 2004; Woli *et al.*, 2004; Hayakawa *et al.*, 2006). Woli *et al.* (2002) found that the upland field proportion is significantly positively correlated with the NO₃-N concentration during summer base flow, and that the regression slope of the relationship varies with land use. As the regression slope appeared to be an index of the impact of land use on river water quality, Woli *et al.* (2002) defined it as the impact factor (IF). However, very few water quality studies have been carried out during the snowmelt season, so the impact intensity of farmland on river water quality during snowmelt events is still unclear. Moreover, river N concentrations are generally lower in grassland-based livestock farming areas than in intensive agricultural areas (Tabuchi *et al.*, 1995). Therefore, this study was carried out to evaluate and compare river water quality in relation to eutrophication and land use during spring snowmelt and summer base flow periods between a grassland-based dairy cattle farming area and a mixed cropland–livestock farming area.

Materials and Methods

STUDY AREA

Two catchment areas with different land use in eastern Hokkaido, Japan, were selected for this study (Fig. 1). The Abashiri area (43°46'N, 144°11'E), which comprises Abashiri and Memanbetsu cities and Bihoro and Tsubetsu towns, is characterized by mixed cropland–livestock husbandry. The Okoppe area (44°21'N, 143°2'E), which comprises

Okoppe and Nishi Okoppe towns, is dominated by dairy cattle farming. Both catchment areas drain into the Okhotsk Sea. Characteristics of each area are listed in Table 1. About 81% of the total area in Abashiri is occupied by common upland fields cultivated with sugar beet (*Beta vulgaris* L.), wheat (*Triticum aestivum* L.), or potato (*Solanum tuberosum* L.). In contrast, 98% of the total agricultural area in Okoppe is occupied by grasslands. Livestock in Abashiri consists of pigs, and beef and dairy cattle, and the livestock density is 1.0 animal unit per hectare (au ha⁻¹), whereas in Okoppe the density of livestock (mainly dairy cattle) is 1.9 au ha⁻¹ (Table 1). The major soil types are volcanic ash-derived Andosols and Brown Forest Soils in Abashiri, and in Okoppe, Brown Forest Soils and Brown Forest Lowland Soils. The climate in both areas is temperate: annual mean temperature is 6.2 °C and annual mean precipitation 802 mm in Abashiri (<http://www.city.abashiri.hokkaido.jp/>), and they are 6.5 °C, and 1073 mm in Okoppe (<http://www.vill.nishiokoppe.hokkaido.jp/>).

WATER SAMPLING AND CHEMICAL ANALYSIS

In both catchment areas, water samples were collected from the main river channels and from tributaries to these rivers. In Abashiri, a total of 63 sites were sampled during both spring snowmelt and summer base flow periods, and in Okoppe, 46 and 49 sites were sampled during snowmelt and base flow, respectively (Fig. 2). Water samples were collected manually once in the snowmelt season (9–15 April) and once during base flow (12–16 August) in 2005, and at the same time river velocity was also measured with a flow velocity meter (TK-105; Toho Dentan, Tokyo) at each sampling point. River discharge was calculated by multiplying the river cross-sectional area by flow velocity at 60% depth at various points along a transect across the main river and its tributaries. The river discharge per unit drainage area, that is, specific discharge, was later

calculated by dividing discharge by the catchment area above the sampling site. After sampling, water samples were stored on ice and transported to the laboratory. At the laboratory, a part of the samples were filtered through prerinsed 0.2- μ m filter paper, and the NO₃-N concentration was determined with ion chromatography (QIC Analyzer; Dionex, Sunnyvale, CA), and the Si concentration was determined colorimetrically by the molybdenum blue method. The TN concentration was determined in unfiltered samples by alkaline persulfate digestion using the HCl-acidified UV detection method (Japanese Standard Association, 1993).

LAND USE ANALYSIS

The size of the catchment above each sampling site in both areas was determined using ArcGIS 9.0–hydrology modeling software (ESRI Press, New York). The upland fields were delineated on digital topographic maps of 1:25 000 scale, and the total area and the area of upland fields in all catchments were calculated using a digital elevation model. The drainage basin of lower reach streams was calculated by including the drainage basins of all upper streams and tributaries that flow into it. Common upland fields, including grasslands but excluding lowland paddy fields, are referred to as "upland fields" in this study. The proportion of upland fields was estimated as the percentage of upland fields relative to the total area of the subcatchment above each sampling point.

STATISTICAL ANALYSIS

Simple linear regression (Esumi Co. Ltd., Tokyo, Japan) was applied to evaluate the relationship between the proportion of upland fields in each catchment and the NO₃-N concentration in the river water. The seasonal and spatial variations in element concentrations, Si:TN mole ratios, and specific discharge were compared by using

analysis of variance. For this study, effects with probabilities of $p < 0.05$ were assumed to be significant. Regression slopes of the relationship between upland proportion and river nitrate concentration were compared by using Excel Tahenroukaiseki version 4.0 for windows (in Japanese).

Results

SPATIAL AND TEMPORAL VARIATION IN SPECIFIC DISCHARGE AND MINERAL CONCENTRATIONS

River discharge per unit drainage area, that is, specific discharge, and the concentrations of Si and TN in river water samples during the spring snowmelt and summer base flow periods in the Abashiri and Okoppe areas are shown in Fig. 3, and the results are compared between the areas and the periods by using ANOVA (Table 2). The mean specific discharge was significantly ($P < 0.001$) lower in Abashiri than in Okoppe during snowmelt. However, there was no significant difference in specific discharge during base flow. The mean concentrations of Si, TN, and $\text{NO}_3\text{-N}$ were significantly higher in Abashiri than in Okoppe. The mean specific discharge was significantly higher during snowmelt than during base flow in both Abashiri and Okoppe ($P < 0.001$). The mean concentrations of TN during snowmelt were also significantly higher ($P < 0.001$) than during base flow in both Abashiri and Okoppe. On the other hand, the mean concentration of Si was significantly lower during snowmelt than during base flow in both catchment areas ($P < 0.001$). In Abashiri, some sites had remarkably high TN concentrations, reaching a maximum of 26 mg L^{-1} , during snowmelt, while in Okoppe concentrations were less than 3 mg L^{-1} , even when discharge per unit drainage area was significantly higher (Fig. 3).

MOLE RATIO OF Si TO TN CONCENTRATIONS

The distribution of Si:TN mole ratios between snowmelt and base flow periods in Abashiri and Okoppe are illustrated in Figs. 4 and 5, respectively. During base flow, at more than 96% of the sampling sites in both catchment areas, the mole ratio was above the threshold value for eutrophication. However, the ratio decreased during snowmelt, when the number of sites with the ratio below the threshold value increased to more than one-third of the total sites in the two catchment areas. The mean Si:TN mole ratios were significantly lower ($P < 0.001$; t test) during snowmelt than during base flow in both catchment areas (Table 2). Most sites with Si:TN below the threshold value were located in the lower reaches of rivers and at river mouths (Figs. 4 and 5) and where TN concentrations were comparatively higher.

THE PROPORTIONS OF UPLAND FIELDS AND $\text{NO}_3\text{-N}$ CONCENTRATIONS

In the mixed agricultural Abashiri area, the proportion of upland fields in the catchment above each sampling site ranged from 0% to 91%, and for about one-third of the total sites, the upland field proportion was more than 20% (Fig. 6). However, the proportion of upland fields in the grassland-based dairy cattle farming Okoppe area was 0%–20%. In both catchment areas, the proportion of upland fields increased from upstream to downstream sampling sites. In Abashiri, the $\text{NO}_3\text{-N}$ concentration range was 0.02–3.2 mg L^{-1} during base flow, while it was 0.04–22.2 mg L^{-1} during snowmelt, and it exceeded the drinking water standard of 10 mg L^{-1} set by the U.S. Environmental Protection Agency (Spalding and Exner, 1993) at four sites. In contrast, in the Okoppe area, the concentration range was 0.01–0.47 and 0.05–0.91 mg L^{-1} during base flow and snowmelt, respectively (Fig. 7).

3.4. RELATIONSHIP BETWEEN THE UPLAND FIELD PROPORTION AND THE NO₃-N CONCENTRATION

Regression analysis showed that NO₃-N concentrations in river water during base flow were significantly correlated with the proportion of upland fields in the catchments in both Abashiri ($r = 0.88$, $P < 0.001$) and Okoppe ($r = 0.43$, $P < 0.01$) (Fig. 7). However, the regression slope for Abashiri (0.0249) was 2.6 times that for Okoppe (0.0094). The NO₃-N concentration was also significantly positively correlated with the upland field proportion during snowmelt in both Abashiri ($r = 0.84$, $P < 0.001$) and Okoppe ($r = 0.79$, $P < 0.001$), and the regression slope for Abashiri was significantly higher (0.1920) than that for Okoppe (0.0354). The regression slopes for base flow and snowmelt differed seasonally ($P < 0.01$) in both Abashiri and Okoppe areas.

4. Discussions

The discharge per unit drainage area during snowmelt was significantly higher than that during base flow, and the increase in specific discharge was associated with decreased Si concentrations and increased TN concentrations. This result is consistent with study results for the Kepau River, which flows through a livestock farming area in southern Hokkaido, Japan (Hayakawa *et al.*, 2003; Hatano *et al.*, 2005), where the Si:TN mole ratio frequently dropped below the threshold value, enhancing eutrophication, during the snowmelt season. Winter and spring concentrations of nutrients are generally found to be high in areas of similar climate (Macdonald *et al.*, 1995; Buck *et al.*, 2004). However, Si concentrations relate to soil type, being higher in areas with weathered volcanic-ash soils (Nagumo and Hatano, 2001). Our results showed that Si

concentrations were significantly higher (Table 2) in rivers flowing through the Abashiri area with its volcanic-ash soils (Andosols) than in the Okoppe area with its Brown Forest Soils. In both areas, Si concentrations were significantly lower, possibly owing to a dilution effect, and TN concentrations increased significantly during the snowmelt season, thus lowering the Si:TN mole ratio, leading to eutrophication in the estuaries at the river mouths.

Nitrate concentrations in river water during both snowmelt and base flow were significantly correlated with the proportion of upland fields in the catchment in both Abashiri and Okoppe areas. Several other studies also found significant positive correlations of river $\text{NO}_3\text{-N}$ concentrations with upland field proportions (Tabuchi *et al.*, 1995; Woli *et al.*, 2002, 2004; Hayakawa *et al.*, 2006), with pasture land proportions (Smart *et al.*, 1985; Buck *et al.*, 2004), with the percentage of agricultural cropland (Jordan *et al.*, 1997; Cronan *et al.*, 1999; McFarland and Hauck, 1999), or with the percentage of land area ploughed (Neill, 1989). Woli *et al.* (2002) reported that the regression slope of the relationship of IF on water quality, varied in accordance with the land use. Woli *et al.* (2004) compared IF values obtained from seven large catchment areas in Hokkaido, Japan, with data from the Chesapeake Bay watershed (Jordan *et al.*, 1997), Aroostook River basin (Cronan *et al.*, 1999), and Missouri Ozark Plateau Province (Smart *et al.*, 1985) in the United States, and concluded that the largest (0.04) IF values were associated with intensive agriculture or livestock farming, intermediate (0.02–0.04) values with mixed agriculture and livestock farming, and the lowest (0.006–0.02) values with grassland-based dairy cattle or horse farming areas. The results of the present study during base flow are consistent with these previous results, as the IF value was 0.0249 for Abashiri, a mixed cropland–livestock farming area, and 0.0094 for Okoppe, a grassland-based dairy cattle farming area. However, the IF values

were significantly higher during snowmelt than during base flow in both the Abashiri and Okoppe areas. The higher concentrations of TN and NO₃-N, and the resulting larger IF values, during the snowmelt season can possibly be attributed to N accumulated or remaining in soils or remaining from the application of chemical fertilizer and manure during autumn being mobilized by surface runoff or leaching during the snowmelt season. Other studies have also reported that spring floods are significant sources of nutrients in river water (Macdonald *et al.*, 1995; Buck *et al.*, 2004). Cambardella *et al.* (1999) and Hayashi and Hatano (1999) also reported that most of the nitrate in subsurface drainage water is removed from fields when crops are not present during the winter. Randall and Mulla (2001) recommended that N management in agricultural fields could be improved by applying N at the correct rate at the optimum time, thus reducing nutrient losses to surface water. Ulén *et al.* (2004) reported that no manure has been spread during autumn in recent years and that there is a decreasing concentration of TN in Swedish catchments. Therefore, appropriate fertilizer management for summer and autumn crops in Hokkaido, where the winter snow-covered period is long, is apparently crucial for preventing excess nutrient losses to surface runoff during the snowmelt season.

Woli *et al.* (2004) evaluated how different agricultural activities affect IF values and reported that surplus N in croplands had a better correlation with IF. They scaled up their evaluation using the regression model, associating IF values with all cities, towns, and villages of Hokkaido, and found that the distribution pattern of predicted IF values was very close to that of the measured NO₃-N concentrations during the snowmelt season for all major rivers in Hokkaido. They also estimated the NO₃-N concentration for all sampling sites in Hokkaido by multiplying the predicted IF values by the upland field proportion and found that the prediction underestimated the measured values to

some extent; the measured values at approximately 7% of the total sites in Hokkaido were higher than the predicted values. Although they used base flow $\text{NO}_3\text{-N}$ concentrations to predict IF values, values measured during snowmelt were used in the comparison (Woli *et al.*, 2004). Thus, their results are consistent with those from this study, which also showed that measured $\text{NO}_3\text{-N}$ concentrations, as well as calculated IF values, during the snowmelt season were much higher than those during base flow.

5. Conclusions

The results of this study confirmed that the land use pattern in catchments affects river water quality and that a greater proportion of upland fields is associated with higher concentrations of $\text{NO}_3\text{-N}$ in river water. The impact intensity of the upland field proportion on river $\text{NO}_3\text{-N}$ concentrations varied according to the intensity of agriculture; the river $\text{NO}_3\text{-N}$ concentrations were higher in mixed cropland–livestock farming areas than in grassland-based dairy cattle farming area. The higher discharge of N from uplands and grasslands and the decrease in the Si:TN mole ratio below the threshold value for eutrophication during the snowmelt season suggest that the nutrient discharge during snowmelt events should be taken into account when estimating the annual loss of nutrients from agricultural fields to surface runoff. Maintaining an appropriate proportion of upland fields in a catchment and proper fertilizer management of agricultural fields, especially regarding applications in autumn before the winter snow-covered period, can reduce N discharge to surface runoff and the resulting eutrophication of estuaries.

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Figure legends

Figure 1. Locations of the study areas in eastern Hokkaido, Japan.

Figure 2. River systems and sampling site distributions in the (a) Abashiri and (b) Okoppe areas.

Figure 3. Specific discharge and concentrations of TN and Si in river water during spring snowmelt and summer base flow periods in the (a) Abashiri and (b) Okoppe areas.

Figure 4. Mole ratio of Si:TN at each sampling site in the Abashiri area during (a) spring snowmelt and (b) summer base flow.

Figure 5. Mole ratio of Si:TN at each sampling site in the Okoppe area during (a) spring snowmelt and (b) summer base flow.

Figure 6. Proportions of upland field in subcatchments in the (a) Abashiri and (b) Okoppe areas.

Figure 7. Relationships between proportion of upland fields in catchments and the NO₃-N concentration in river water for the (a) Abashiri and (b) Okoppe areas.

TABLE I
Area, population, land use, and livestock in the Abashiri and Okoppe areas

	Abashiri area	Okoppe area
Population	85596	10891
Total area (km ²)	1969	671
Agricultural land (ha)	39988	7928
Common upland	32554	168
Paddy field	389	0
Grassland	7041	7760
Livestock (head)		
Beef cattle	16400	1620
Dairy cattle	13990	13330
Pig	76230	0
Livestock density (au ha ⁻¹)*	1.0	1.9

*1 au is equivalent to one head of dairy or beef cattle or eight pigs, based on The amount of excrement produced (Nyukantori Editor, 1976).

TABLE II
Specific discharge ($\text{m}^3 \text{ s}^{-1} \text{ km}^{-2}$), concentrations (mg L^{-1}) of Si, TN, and $\text{NO}_3\text{-N}$, and Si:TN mole ratio in river water samples. Values are means $\pm$ SD, and significant ($P < 0.05$) differences are indicated

Variable		Abashiri area (Mixed cropland-livestock husbandry)	Okoppe area (Dairy cattle farming)	P-value
Specific discharge	Snowmelt	0.023 ($\pm$ 0.017)	0.056 ($\pm$ 0.023)	***
	Base flow	0.010 ($\pm$ 0.005)	0.011 ($\pm$ 0.006)	
	P-value	***	***	
Silica	Snowmelt	17.88 ($\pm$ 3.85)	5.86 ($\pm$ 0.98)	***
	Base flow	22.10 ($\pm$ 6.56)	7.70 ($\pm$ 2.16)	***
	P-value	***	***	
TN	Snowmelt	3.53 ($\pm$ 4.58)	0.84 ($\pm$ 0.34)	***
	Base flow	1.07 ($\pm$ 1.13)	0.37 ($\pm$ 0.24)	***
	P-value	***	***	
$\text{NO}_3\text{-N}$	Snowmelt	2.93 ($\pm$ 4.37)	0.39 ($\pm$ 0.20)	***
	Base flow	0.37 ($\pm$ 0.51)	0.12 ($\pm$ 0.10)	**
	P-value	***	***	
Si:TN mole ratio	Snowmelt	6.99 ($\pm$ 7.38)	4.25 ($\pm$ 2.70)	*
	Base flow	15.89 ($\pm$ 8.20)	13.19 ($\pm$ 8.0)	
	P-value	***	***	

*, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$

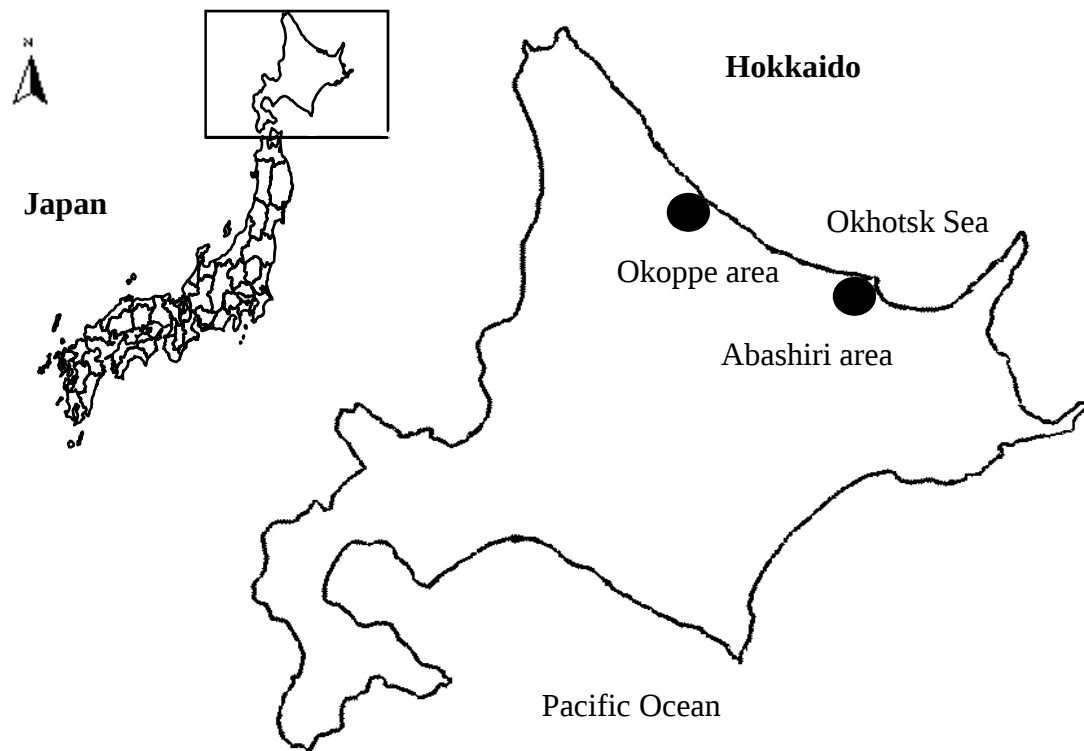


Figure 1. Locations of the study areas in eastern Hokkaido, Japan.

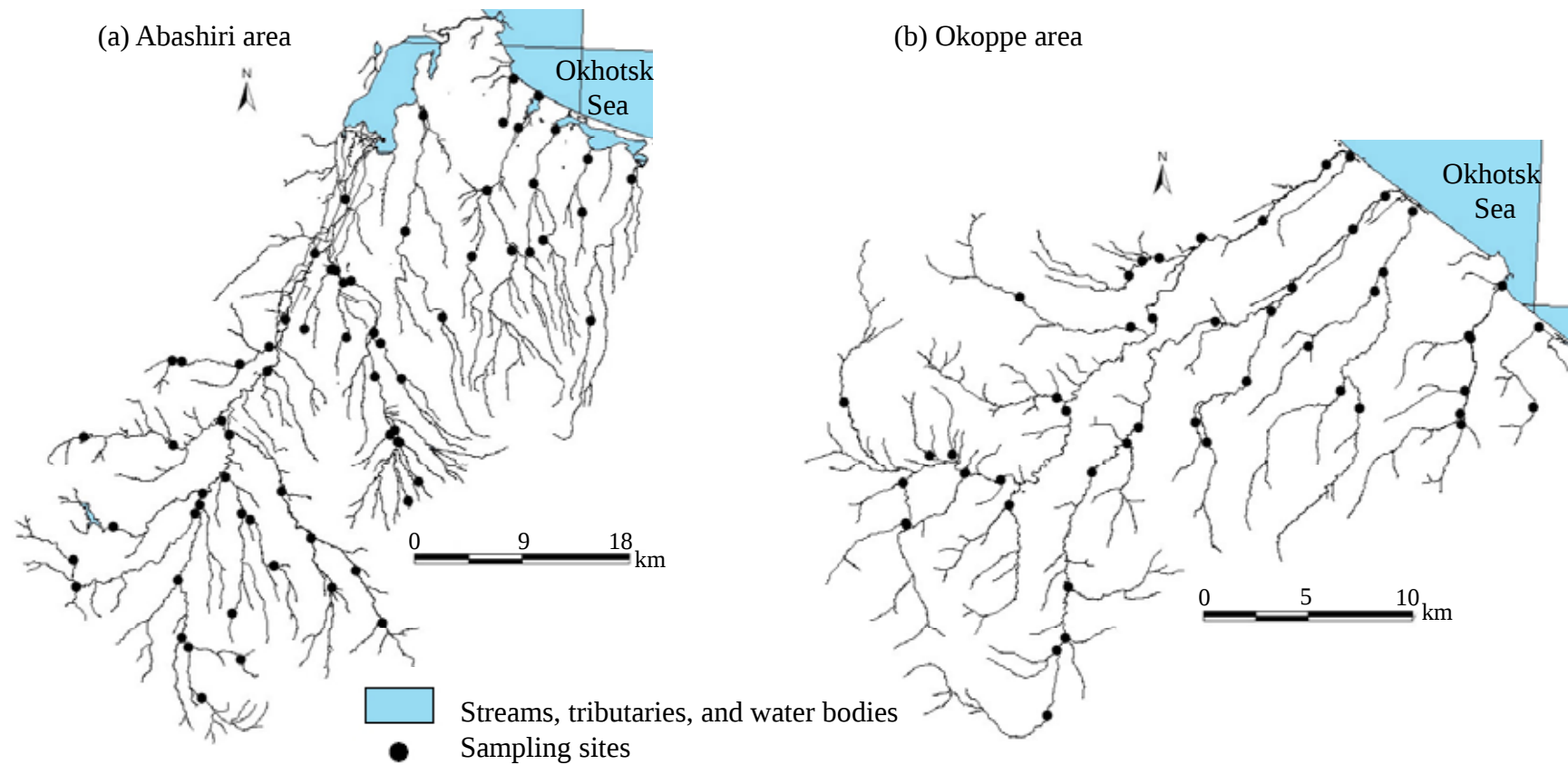


Figure 2. River systems and sampling site distributions in the (a) Abashiri and (b) Okoppe areas.

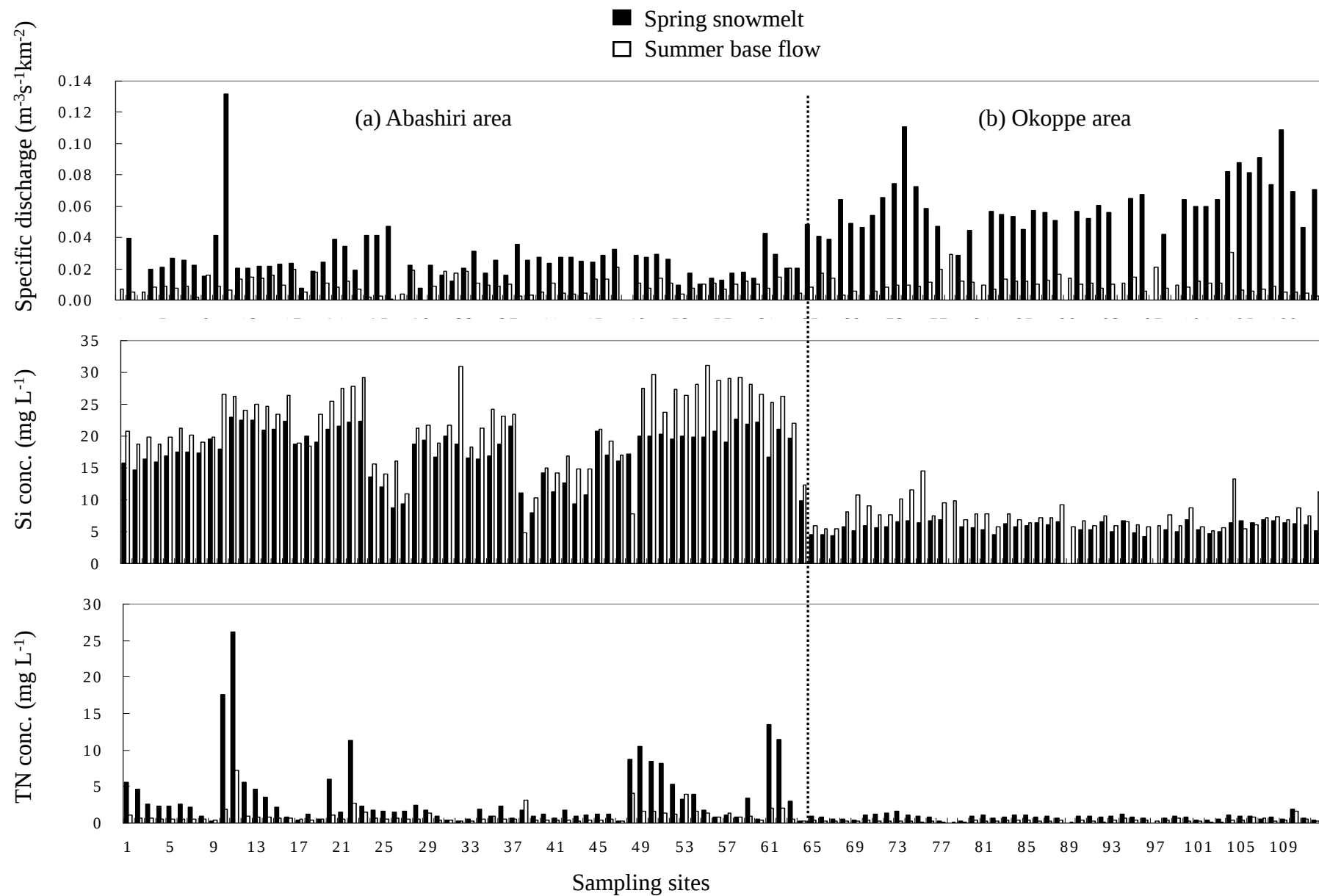


Figure 3. Specific discharge and concentrations of TN and Si in river water during spring snowmelt and summer base flow periods in the (a) Abashiri and (b) Okoppe areas.

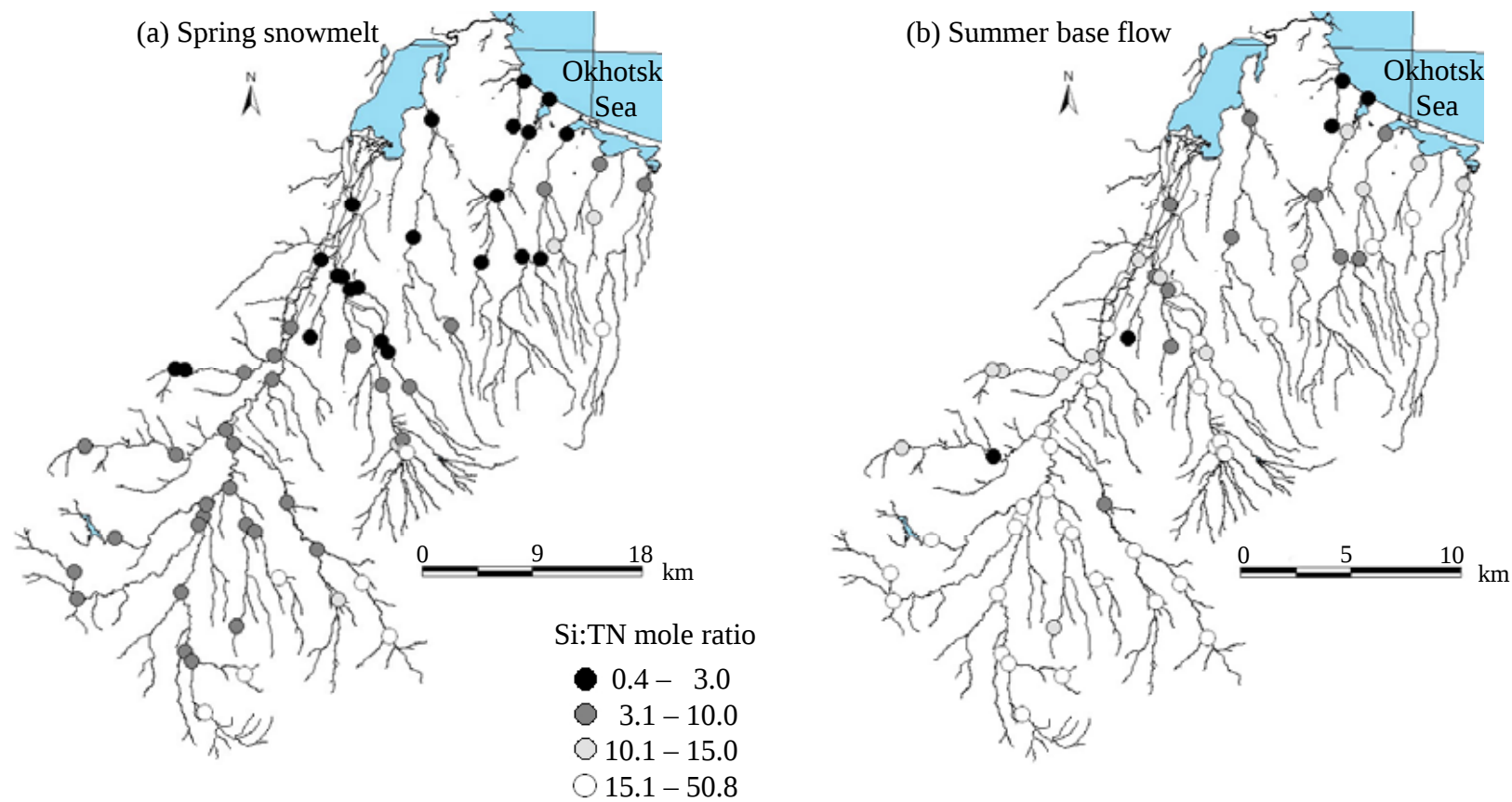


Figure 4. Mole ratio of Si:TN at each sampling site in the Abashiri area during (a) spring snowmelt and (b) summer base flow.

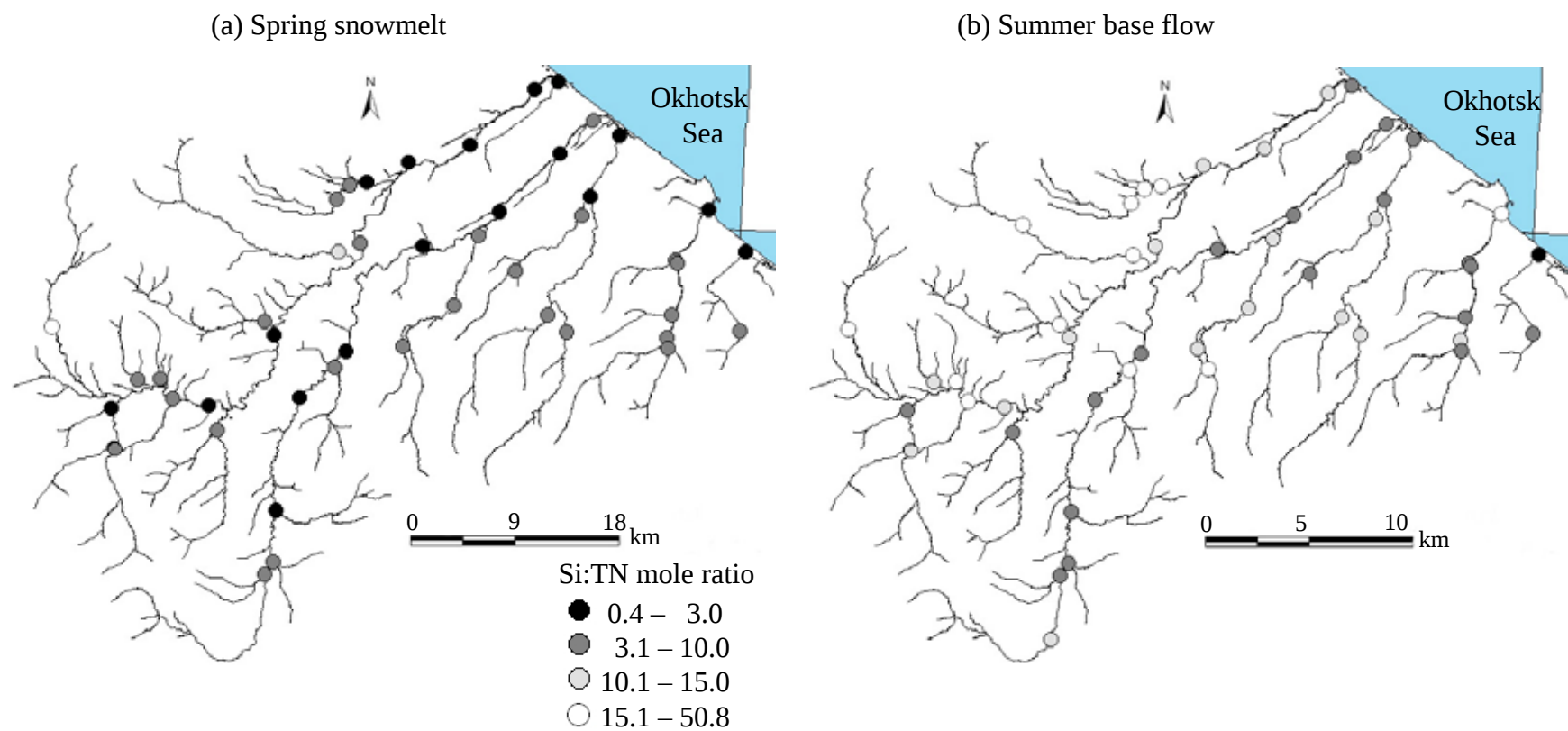


Figure 5. Mole ratio of Si:TN at each sampling site in the Okoppe area during (a) spring snowmelt and (b) summer base flow.

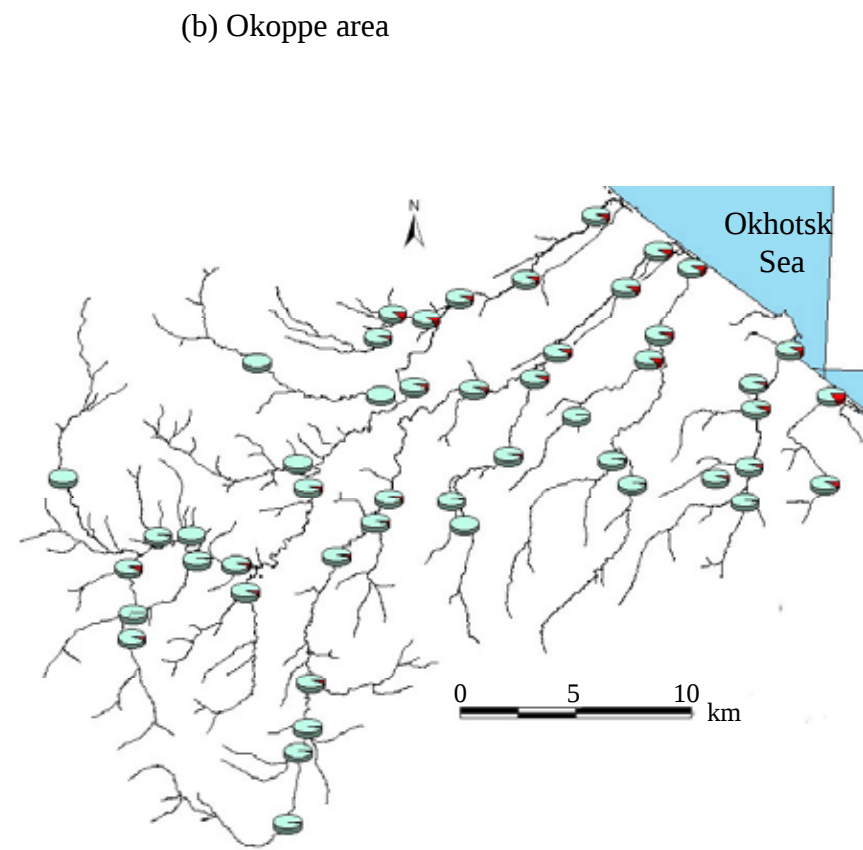
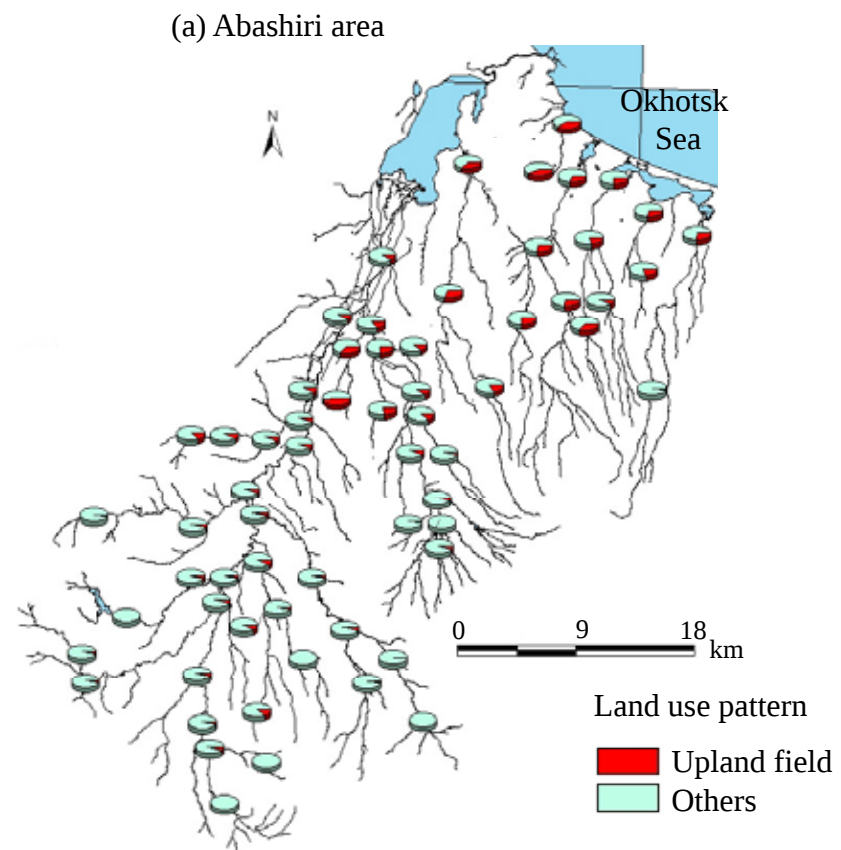


Figure 6. Proportions of upland field in subcatchments in the (a) Abashiri and (b) Okoppe areas.

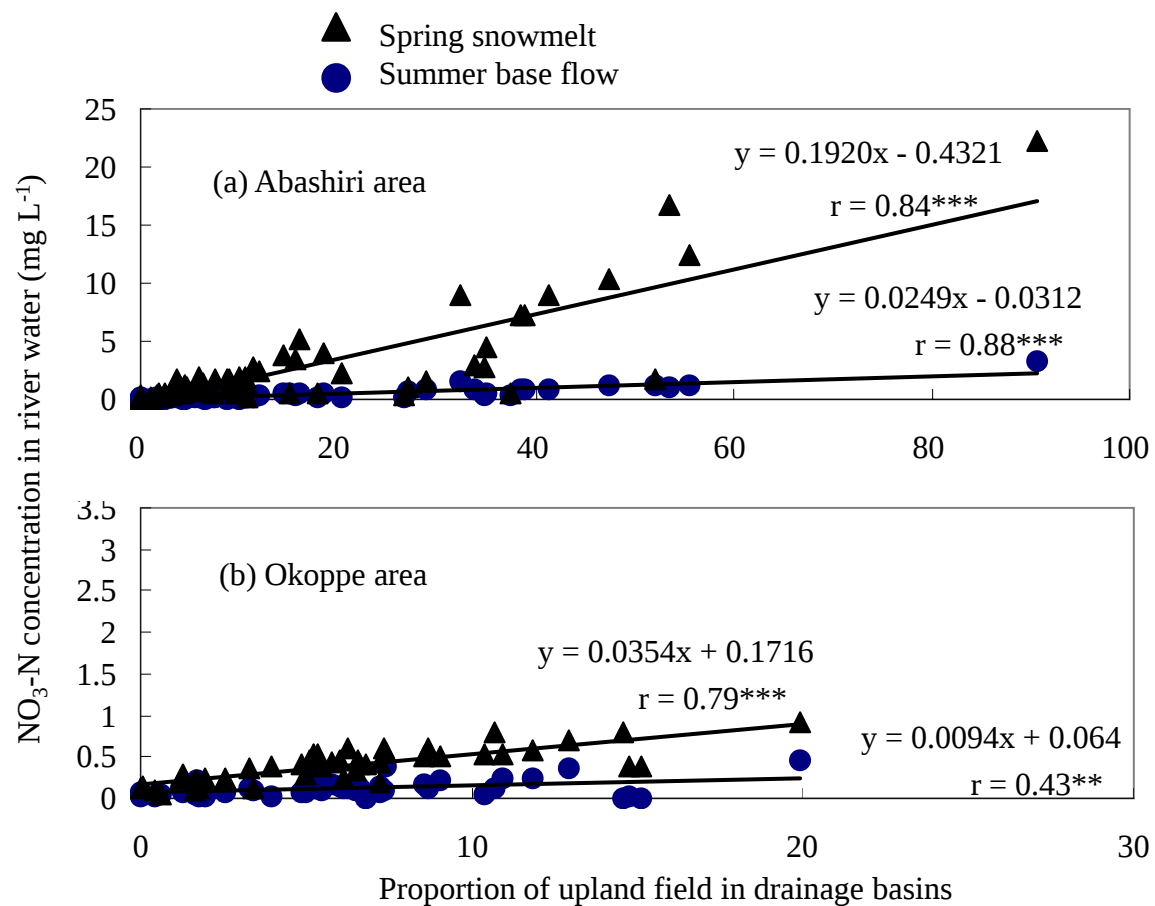


Figure 7. Relationships between proportion of upland fields in catchments and the $\text{NO}_3\text{-N}$ concentration in river water for the (a) Abashiri and (b) Okoppe areas.