

Stream Water Nitrogen Eutrophication During Non-Irrigated Periods in a Paddy-Dominated Agricultural Basin in a Snowfall Area in Japan

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Abstract We measured the concentrations of dissolved inorganic nitrogen (DIN; nitrate, ammonium, and nitrite) in stream water in a paddy-dominated agricultural basin in a snowfall area from August 2009 to October 2010 to facilitate evaluation of stream water eutrophication from nitrogen during the non-irrigated period. We compared the nitrogen budget in a paddy field between irrigated and nonirrigated periods, from information about nitrogen fertilizer, denitrification, harvested rice, and atmospheric nitrogen deposition. We also estimated stream nitrogen exports from DIN concentrations and stream flow rates. DIN concentrations in stream water were higher during the non-irrigated period (October–March) than during the irrigated period (April–September). Stream flow was also higher during the non-irrigated period (5.9 mm day⁻¹) than during the irrigated period (2.5 mm day⁻¹), which possibly reflects snow melting. Although nitrogen fertilizer was applied during the irrigated period,

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the amount of nitrogen removed by the rice harvest and denitrification was sufficiently large to reduce nitrogen exports from paddy fields. Atmospheric nitrogen deposition was higher during the nonirrigated period (755 kg N km⁻²) than during the irrigated period (410 kg N km−²). DIN exports were also higher in the non-irrigated period (860 kg N km^{-2}) than in the irrigated period (120 kg N km⁻²). The higher exports in the non-irrigated period may reflect the lack of nitrogen removal by a rice harvest and denitrification and increased runoff and higher atmospheric nitrogen deposition. Our study highlights the important contribution of the nonirrigated period to nitrogen eutrophication in stream water in this particular environment.

Keywords Stream water quality · Paddy field · Nonirrigation . Snowmelt . Atmospheric N deposition

1 Introduction

Because of excessive applications of nitrogen (N) fertilizer, agricultural land can be a major source of non-point pollutants that result in eutrophication of stream water and enclosed coastal areas (Carpenter et al. [1995](#page-8-0); Swaney et al. [2012](#page-9-0)). The surplus N fertilizer that is applied to agricultural land translates into nitrate $(NO₃⁻)$ leaching from agricultural soils, which results in enhanced $NO₃⁻$ concentrations in ground water and stream water (Díaz et al. [2012\)](#page-8-0).

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It is thought that paddy fields, in contrast to other types of agricultural land, can reduce N exports during the irrigation period. As with other types of agricultural land, fertilizers are applied to paddy fields. However, denitrification in paddy fields and N assimilation of rice plants during the irrigation period are both considered to reduce the amount of N exported to downstream reaches (Ishikawa Prefecture [2007](#page-9-0)). Many studies have shown that paddy fields located within an N-polluted watershed can remove N, thereby reducing N loads to downstream reaches (Toda et al. [1997](#page-9-0); Nira et al. [2005;](#page-9-0) Hama et al. [2007](#page-8-0); Maruyama et al. [2010](#page-9-0)). Studies of N budgets in paddy fields have shown that the amount of N removed by the rice plant harvest is larger than the amount of N fertilizer applied, which suggests that N input from other sources, including atmospheric N deposition on rice plants, is assimilated (Hashimoto et al. [2007](#page-8-0); Maruyama et al. [2008,](#page-9-0) [2009](#page-9-0)).

During the non-irrigated period, however, paddy fields may not reduce N loads to downstream reaches. The absence of both a rice plant harvest and denitrification during the non-irrigation period may halt the natural N removal processes in the paddy field. Further, enriched concentration pulses of contaminants have been observed in stream water during the snowmelt period (Williams and Melack [1991](#page-9-0); Tachibana et al.1996; Brooks and Williams [1999](#page-8-0); Unoki et al. [2001](#page-9-0); Piatek et al. [2005](#page-9-0); Chiwa et al. [2015b\)](#page-8-0), which coincides with the nonirrigation period. Snowmelt stream water is enriched with contaminants and causes stream water quality deterioration because it comprises surface water that has passed through polluted soil (Hazlett et al. [2001](#page-9-0); Hayakawa et al. [2003](#page-8-0); Piatek et al. [2005](#page-9-0)). Despite the fact that paddy areas account for half of the agricultural land in the snowfall area in Japan (Ministry of Agriculture, Forestry and Fisheries in 2010 data, [http://www.maff.go.jp/j/tokei/kouhyou/](http://www.maff.go.jp/j/tokei/kouhyou/sakumotu/sakkyou_kome/index.html) [sakumotu/sakkyou_kome/index.html](http://www.maff.go.jp/j/tokei/kouhyou/sakumotu/sakkyou_kome/index.html)), to date, few studies have examined N-related eutrophication in stream water in paddy-dominated agricultural basins during the non-irrigated period. Such a study would provide an insight into how the water quality in paddy-dominated agricultural lands in snowfall areas can be managed more effectively.

The objective of this study is to evaluate stream water N eutrophication during the non-irrigated period in a paddy-dominated agricultural basin in a snowfall area. To achieve this objective, we measured dissolved inorganic nitrogen (DIN) concentrations in stream water in such a basin over a period of a year, including the irrigated and nonirrigated periods. In addition, we calculated the N budget using information about N fertilizer, denitrification, harvested rice, and atmospheric N deposition to evaluate the factors influencing stream water quality.

2 Materials and Methods

2.1 Site Description

This study was carried out in the Wakayama River Basin in the Noto Peninsula, Hokuriku, Japan (37.436° N, 137.260° E; Fig. [1a](#page-2-0)). Noto Peninsula has been registered as an important agricultural heritage system (GIAHS). The study sites were located in Suzu City, where the annual mean precipitation, temperature, and maximum snow depth from 2000 to 2010 were 2039 mm, 13.3 °C, and 39.1 cm, respectively.

The Wakayama River has a catchment area of 52.0 km^2 and a channel length of 17.4 km (Fig. [1b\)](#page-2-0). The maximum elevation of the catchment is 471 m. The catchment area and the proportion of each land use (forest, paddy fields, other agricultural areas, and urban) were calculated from data and land use statistics obtained from the Geospatial Information Authority of Japan and the National Land Information Division, respectively, using ArcGIS V10.1 (ESRI). Forests, paddy fields, other agricultural land, and urban areas account for 83, 13, 2, and 2 % of the total area of the downstream reaches (site 10) of the Wakayama River, respectively (Table [1](#page-2-0)). Agricultural land in the Wakayama River, therefore, mainly comprises paddy fields. To obtain baseline information from a basin where the main agricultural activity was something other than paddy fields, the same investigations were carried out in the Kana River Basin, which was adjacent to the Wakayama Basin (Fig. [1b](#page-2-0)). The Kana River has a catchment area of 14.0 km^2 and a channel length of 4.5 km. Forested land, paddy fields, other agricultural land, and urban areas account for 68 , 8 , 22 , and 2% , respectively, of the downstream reach (site 12) of the Kana River Basin (Table [1](#page-2-0)).

Fig. 1 Location of the study basin in Noto Peninsula, Hokuriku District, Japan. Sites 1–10 are in the Wakayama River. Sites 11 and 12 are in the Kana River. Site K indicates the inflow dam

Small areas in the upstream reaches of the Wakayama (190 heads of cattle/ 0.585 km^2) and Kana (113 heads of cattle/0.2 km^2) Rivers are used for livestock farming and dairy farming, respectively. The sewer diffusion rate in Suzu City is 60.8 % (sewer 39.2 %, village drainage 5.3 %, purified water tank 16.3 %). The population (16,300 people) and the population density (68.8 people km^{-2} in 2010) in Suzu City are small and have decreased in recent years.

The irrigated and non-irrigated periods were defined as the periods from April to September and from October to March, respectively, according to the cultivation calendar [\(http://www.is-ja.jp/suzu/tok-eno/suzumai/](http://www.is-ja.jp/suzu/tok-eno/suzumai/kosihikari_l.html) [kosihikari_l.html\)](http://www.is-ja.jp/suzu/tok-eno/suzumai/kosihikari_l.html). There is an agricultural dam in the upstream reaches of each river, from which water is supplied to the agricultural areas during the irrigated period, and little water is stored in the dams through winter. In both basins, puddling, rice planting, and the rice plant harvest take place in April, at the beginning of May, and at the end of September, respectively.

2.2 Discharge and Meteorological Data

Discharge data were not available for the Wakayama River, so we assumed that the specific discharge at

	Wakayama River basin (km ²)	Kana River basin (km^2)
Forest	8.0(90)	2.5(66)
Paddy	0.8(9)	0.1(3)
Agriculture	0(0)	1.2(32)
City	0.1(1)	0(0)
Forest	21.8 (86)	$\qquad \qquad -$
Paddy	3.0(12)	
Agriculture	0.2(1)	
City	0.4(2)	
Forest	31.5(83)	4.0(68)
Paddy	5.0(13)	0.5(8)
Agriculture	0.9(2)	1.3(22)
City	0.7(2)	0.1(2)

Table 1 Land use type in the Wakayama and Kana River basins

Site 1 was defined as upper part, sites 2–7 middle part, and sites 8–10 down part in Wakayama River. Site 11 was defined as upper part and site 12 down part in Kana River. Number in parenthesis indicates land use percentage (%)

site 7 (Fig. [1b](#page-2-0)) was the same as that at site K in the Ukai River (located adjacent to the study basin, Fig. [1b\)](#page-2-0) and calculated the flow rates from water level data measured at site 7 and the specific discharge measured in site K. The discharge at site 7 was calculated from the discharge at site K using Eq. 1,

$$
Q_{\text{d site } 7} = Q_{\text{d site K}} \times \frac{A_{\text{site } 7}}{A_{\text{site K}}} \tag{1}
$$

where Q_d (m³ day⁻¹) is the daily quantity and A (km²) is the size of the catchment area. The height (H) –quantity (Q) curve is expressed by Eq. 2,

$$
Q_{\rm d\,\,site\,\,7} = a\,\left(H_{\rm d\,\,site\,\,7} + b\right)^2\tag{2}
$$

where H (m) is the daily water level and a and b are empirical parameters. This equation can be rearranged as follows:

$$
\sqrt{Q_{\text{d site}}} = \sqrt{a} H_{\text{d site}} + \sqrt{a} b \tag{3}
$$

 Q_d site K has been measured at site K and daily water levels have been measured at sites 7 and 12 by the River Division of the Ishikawa Prefectural Government. We determined the a and b parameters using the least squares method, based on the linear relationship between the square root of the daily discharge at site 7 $(Q_{\rm d \, site \, 7})$ and the daily water level at site 7 ($H_{\rm d \, site \, 7}$) for 2009–2010 (Fig. 2). The geological features in site K (non-alkaline mafic volcanic rocks, non-alkaline felsic volcanic rocks and marine and non-marine sediments) is similar to Wakayama basin and calculated the flow rates from water level data measured at site 7.

Meteorological data for Suzu City were analyzed for temporal variations in air temperature, snow depth, and

Fig. 2 Relationship between daily quantity (Q_d site 7) and daily water level ($H_{\text{d site}}$ 7) during from 2009 to 2010. Linear line is regression line calculated by least squares method

precipitation depth ([http://www.data.jma.go.jp/obd/](http://www.data.jma.go.jp/obd/stats/etrn/) [stats/etrn/\)](http://www.data.jma.go.jp/obd/stats/etrn/).

2.3 Sample Collection and Chemical Analysis

Stream water samples were collected from upstream to downstream at 10 sites in the Wakayama River and two sites in the Kana River. Samples were collected every month from August 2009 until October 2010. Water samples comprised near-surface water collected from the center of the channel.

Stream water samples were transported to the laboratory after collection. The water samples were filtered through a 0.45-μm cellulose acetate filter paper (DISMIC-25CS, Advantec, Tokyo, Japan) and stored in the dark at −20 °C until chemical analysis. Nitrate $(NO₃⁻),$ nitrite $(NO₂⁻),$ and ammonium $(NH₄⁺)$ concentrations in the filtered samples were determined using an autoanalyzer (AACS III (2CH), BRAN+LUEBBE GmbH, Norderstedt, Germany). NO₃⁻ was determined by the Cd reduction naphthyl ethylene diamine absorbance method; NO_2 ⁻ was determined by the naphthyl ethylene diamine absorbance method, and NH_4^+ was determined by the indophenol blue method. The detection limit of each chemical species was <0.05 mg L^{-1} . DIN concentrations were the sum of the NO_3^- , NO_2^- , and NH_4^+ concentrations. The amount of N exported at site 7 was calculated by multiplying DIN concentrations and flow rates.

2.4 Nitrogen Budget in a Paddy Field of Wakayama Basin

To evaluate the difference of N flow in paddy field between irrigated and non-irrigated periods, N budget in the paddy fields was separately estimated during irrigated and non-irrigated periods. The N inputs to the paddy field, including the amount of N fertilizer and atmospheric N deposition, were estimated. N outputs, comprising the amount of N removed by the rice plant harvest and denitrification, were calculated each irrigated and non-irrigated periods. In irrigated period, the amount of N fertilizer was taken from the reported N use rate in Suzu (6700 kg N km−² , The Ministry of Agriculture, Forestry and Fisheries of Japan). Denitrification rates reported by Maruyama et al. ([2008](#page-9-0)) for reclaimed land paddy fields at Kahokugata, also in Ishikawa Prefecture, were used for this study. The amount of N removed by the rice plant harvest was estimated by multiplying the rice plant yield in Suzu City (480,000 kg km⁻² year⁻¹; The Ministry of Agriculture, Forestry and Fisheries of Japan) by the N concentration in brown rice (11.4 g N kg⁻¹; Maruyama et al. [2009](#page-9-0)). Denitrification from rice field amount is 2590 kg N km⁻² year⁻¹, and N permeation amount is 20–60 kg N km^{-2} year⁻¹ (Hashimoto et al. [2007](#page-8-0)), which was calculated by the difference between N amount between input and output. These budgets can be considered as crude estimates because the parameters including the amount of N fertilizer, N removal by the rice plant harvest, and denitrification have a large uncertainty. Nevertheless, these estimates can compare the general difference of N flow between irrigated and non-irrigated periods. NH₃ volatilization loss is low (90–280 kg N km⁻² $year⁻¹$), and this amount accounts for 0.8–3.1 % of applied N fertilizer in Japanese paddy field (Hayashi et al. [2006\)](#page-9-0).

Atmospheric N wet deposition was estimated using inorganic N $(NO_3^-$ and $NH_4^+)$ concentrations and the precipitation depth measured in three sites in Hokuriku region (Kanazawa City and Imizu City in Toyama prefecture and Fukui City in Fukui prefecture, there Toyama and Fukui prefectures are neighbor prefectures) (National Institute for Environmental Studies, [http://db.](http://db.cger.nies.go.jp/dataset/acidrain/ja/05/data.html) [cger.nies.go.jp/dataset/acidrain/ja/05/data.html](http://db.cger.nies.go.jp/dataset/acidrain/ja/05/data.html)).

2.5 Dissolved Inorganic Nitrogen Load Estimation

DIN exports were estimated by load-discharge (LQ) regression (Smith and Stewart [1977](#page-9-0)), based on monthly sampling intervals during the irrigated and non-irrigated periods, respectively. The equation is expressed as follows:

$$
L = aQ^b \tag{4}
$$

where L is the load (g N km⁻² day⁻¹), Q is the discharge (mm day⁻¹), and *a* and *b* are empirical parameters. Monthly DIN exports were calculated by summing the daily values of L.

3 Results

3.1 Seasonal Changes in River Water Level, Precipitation Depth, and Snow Depth

The total precipitation from August 2009 to October 2010 was 2771 mm. Precipitation during the nonirrigated period (October to March) accounted for 60 % of the total precipitation depth (Fig. 3), about 60 % of which fell in the snowy season from December to February. In the irrigated period (April to September), the depth of precipitation was especially high in September 2010 because of a typhoon.

The water levels tended to be higher during the nonirrigated period than during the irrigated period (Fig. [4a](#page-5-0)). Snow accumulated from December to February (Fig. [4b](#page-5-0)) when the air temperature was low (Fig. 3). During snowmelt, the water levels increased sharply and peak flow was observed (Fig. [4a\)](#page-5-0).

3.2 Seasonal Changes in NO_3^- , NH_4^+ , and NO_2^- Concentrations in River Water

 $NO₃⁻$ concentrations were higher during the nonirrigated period, especially the snowmelt period, than during the irrigated period in both rivers (Fig. [5a\)](#page-5-0). The $NO₃⁻$ concentrations were significantly and positively correlated with discharge (Fig. [6a\)](#page-6-0).

 NH_4^+ concentrations were higher during the nonirrigated (non-snowmelt and snowmelt) period than dur-ing the irrigated period in both rivers (Fig. [5b](#page-5-0)). NH_4^+ concentrations in stream water in January were relatively low. The spatial variation in the NH_4^+ concentrations from upstream to downstream was less than the seasonal variation. Discharge and NH_4^+ concentrations were significantly and positively correlated (Fig. [6b\)](#page-6-0).

 $NO₂⁻$ concentrations were also higher during the non-irrigated (non-snowmelt and snowmelt) period than during the irrigated period in both rivers. NO_2^- concentrations were higher in the Wakayama River than in the Kana River. The spatial variation in the NO_2^-

Fig. 3 Monthly variations in precipitation and temperature in Suzu City from August 2009 to October 2010. The non-irrigated period is indicated in gray

Fig. 4 Seasonal variation in a water levels in the Wakayama and Kana Rivers and b snow depth in Suzu City between August 2009 and October 2010. The non-irrigated period is indicated in gray

concentrations from upstream to downstream was less than the seasonal variation.

3.3 N Budgets in a Paddy Field

Table [2](#page-6-0) shows the difference of N budget in a paddy field of the Wakayama Basin between the irrigated and non-irrigated periods. N fertilizer was applied during the irrigation period (6700 kg N km⁻²) and N fixation (3000–4000 kg N km⁻²), but a large amount of N was also removed by the rice harvest (5480 kg N km^{-2}),

denitrification (2590 kg N km⁻²), and NH₃ volatilization (90–280 kg N km−²). Atmospheric N deposition was higher during the non-irrigated period (755 kg N km⁻²) than during the irrigated period (410 kg N km⁻²).

3.4 N Exports

Monthly DIN exports from the Wakayama are shown in Fig. [7.](#page-7-0) In the Wakayama River, DIN exports were higher during the non-irrigated period than during the irrigated period. N exports from the Wakayama River were estimated to be 120 and 860 kg N km−² during the irrigated and non-irrigated periods, respectively. DIN export during the non-irrigated period accounted for 79 % of the annual DIN export.

4 Discussion

4.1 Seasonal Changes in Meteorological Parameters, River Flow, and Stream Water Quality

The higher river water levels during the non-irrigated period (Fig. 4a) may reflect the fact that precipitation depths were greater (Fig. [3](#page-4-0)), and evapotranspiration was lower, during the non-irrigated period than in the irrigated period. Other studies have reported lower evapotranspiration during the non-irrigated period (from October to March) than during the irrigated period (from

Fig. 5 Seasonal variations in a NO₃⁻, b NH₄⁺, and c NO₂⁻ concentrations in the upstream, midstream, and downstream sites of the a Wakayama and **b** Kana Rivers. *Error bars* show the standard deviation. Months shaded in gray indicate the non-irrigated period

Fig. 6 Relationship between discharge and concentrations of a NO_3^- ($p = 0.017$), **b** NH_4^+ ($p = 0.049$), and **c** NO_2^- ($p = 0.74$). NO₂⁻ was not detected during irrigated period

April to September) in this district (Maruyama et al. [2012](#page-9-0), [2014\)](#page-9-0). The increased peak discharge during the non-irrigated period (Fig. [4a](#page-5-0)) may reflect snowmelt (Fig. [4b](#page-5-0)); similar increases in peak flow have been observed in other agricultural areas during the snowmelt season because of increased surface runoff (Hayashi and Hatano [1999](#page-9-0); Iwanami et al. [2013](#page-9-0)).

The higher $NO₃⁻$ concentrations during the nonirrigated period in both rivers (Fig. [5a](#page-5-0)) may be the result of the increased volume of snowmelt water. The snowmelt water comprises surface water that has passed through polluted surface soil (Kunimatsu et al. [1994\)](#page-9-0). Consistent with this study, other researchers have reported increased $NO₃⁻$ concentrations in high flows caused by snow melting in agricultural areas and meadows (Tabuchi et al. [1995](#page-9-0); Buck et al. [2004;](#page-8-0) Woli et al. [2008;](#page-9-0) Chiwa et al. [2015b](#page-8-0)).

The distinctly higher NH_4^+ concentrations during non-snowmelt (from October to November and March) and snowmelt (from December to February) seasons in the non-irrigated period in both rivers (Fig. [5b](#page-5-0)) indicate that NH_4 ⁺ was also an important fraction of stream N eutrophication during the non-irrigated period. Unoki et al. ([2001](#page-9-0)) also reported higher NH_4^+ concentrations in stream water in agricultural watersheds during the snowmelt period, which reflected the transport of surface water through soil close to the surface. There were significant relationships between discharge and NH_4^+ concentrations (Fig. 6b), which suggests that the higher discharge observed during the non-snowmelt (from October to November and March) and snowmelt (from December to February) seasons of the non-irrigated period (Fig. [4a\)](#page-5-0) caused higher NH₄⁺ exports from agricultural surface soil in the study watershed.

In this study, higher NO_2^- concentrations were also detected during the non-snowmelt (from October to

Period			Rate (kg N km^{-2})
Irrigated (April–September)	Input	Fertilizer to rice filed	6700
		Nitrogen fixation	$3000 - 4000$ ^b
		Atmospheric N wet deposition	410
	Output	Rice harvest	5480
		Nitrogen permeation	$20 - 60^{\circ}$
		Denitrification from rice field	$2590^{\rm a}$
		NH ₃ volatilization	$90 - 280$ °
Non-irrigated (October-March)		Atmospheric N wet deposition	755

^a Hashimoto et al. [\(2007\)](#page-8-0)

 b Kyuma ([2005](#page-9-0))

^c Hayashi et al. ([2006](#page-9-0))

Fig. 7 Seasonal variation in DIN exports from the Wakayama River (site 7). The non-irrigated period is indicated in gray

November and March) and snowmelt (from December to February) seasons of the non-irrigated period (Fig. [5c\)](#page-5-0). Usually, NO_2^- concentrations in stream water are low (Chiwa et al. [2015a](#page-8-0)). However, elevated NO_2 ⁻ concentrations, at levels comparable to those detected in this study, were also reported in stream water in agricultural areas in Canada (0.156 mg N L⁻¹; Corriveau et al. [2010a\)](#page-8-0) and in urban and agricultural areas in Japan (0.482 mg N L^{-1} ; Takeda et al. [2005\)](#page-9-0). Seepage water (Corriveau et al. [2010b](#page-8-0); Takeda et al. [2005](#page-9-0)) and surface water from agricultural areas (Corriveau et al. [2010a\)](#page-8-0) are thought to be major sources of stream water NO_2^- . Therefore, higher NO_2^- concentrations during the nonirrigated period at our study site may have been the result of surface water runoff from the agricultural areas. In addition, surface water from paddy fields during the non-irrigated period may be a more important source of $NO₂⁻$ than surface water from other agricultural fields because the NO_2^- concentrations in the Wakayama River were higher than those in the Kana River (Fig. [5c](#page-5-0)).

The process of N export may vary during the snowmelt period. For example, NO_3 ^{$-$} export was reported to be higher in the initial snowmelt period than in the later snowmelt period in Hokkaido, northern Japan (Tachibana et al. [1996;](#page-9-0) Unoki et al. [2001](#page-9-0)). However, the length of the snowmelt period at our study site in Hokuriku differed from that at the site in Hokkaido. The snowmelt period from the initial snowmelt to the late snowmelt in Hokkaido lasted about 3 months (Tachibana et al. [1996;](#page-9-0) Unoki et al. [2001\)](#page-9-0), whereas the period in Hokuriku was much shorter and lasted only for about 2 weeks. Also, the snow-accumulating and melting cycle were repeated in Hokuriku during the snowfall period (Fig. [4b\)](#page-5-0), which suggests that the period between the early and the late snowmelt in Hokuriku may be too short to be divided. The significant relationship between discharge and inorganic N concentrations (Fig. [6a, b](#page-6-0)) suggests that discharge is an important driver that enhances inorganic N concentrations during the nonirrigated period at this study site.

4.2 N Budgets in a Paddy Field of the Wakayama Basin

N fertilizer is added during the irrigated period, which means that the N input is higher during the irrigated period than during the non-irrigated period (Table [2\)](#page-6-0). The N fertilizer inputs (6700 kg N km⁻² year⁻¹) during the irrigated period in this study are similar to N inputs to other paddy fields (Hashimoto et al. [2007](#page-8-0); Maruyama et al. [2011](#page-9-0)). Further, N inputs from fertilizer to paddy fields in the Wakayama Basin were more than 15 times higher than the inputs from atmospheric N deposition (410 kg N km⁻²) in the study area (Table [2\)](#page-6-0). Higher N inputs during the irrigated period may have resulted in increased N exports. However, the N removal by the rice harvest and denitrification was sufficiently large to reduce N exports from paddy fields during the irrigation period (Table [2\)](#page-6-0). This N removal reflects N assimilation by rice plants (Hama et al. [2007\)](#page-8-0) and denitrification promoted by anoxia in the paddy fields during the irrigated period (Xing et al. [2002;](#page-10-0) Nishimura et al. [2004](#page-9-0)).

In contrast, N assimilation by rice plants and denitrification do not occur during the non-irrigated period because, during that period, paddy fields are not used for rice planting and are not irrigated. Therefore, denitrification has less influence on DIN export during the non-irrigated season than during the irrigated season. Thus, without the rice harvest and denitrification during the non-irrigated period, there was no reduction in N exports from the paddy field.

4.3 The Importance of Water Quality Management in Snowfall Areas During the Non-Irrigated Period

Our results show that the non-irrigated period is very important from the perspective of water quality management in paddy-dominated agricultural basins in snowfall areas. During the non-irrigated period, DIN exports in river water were higher than during the irrigated period (Fig. 7), when runoff increased because of snowmelt (Fig. [4](#page-5-0)). In this period, concentrations of DIN in stream water were higher, and the flow volume was also higher, than during the irrigated period. Other

studies have also reported significant increases in N exports because of snowmelt (Hatano et al. 2005; Oczkowski et al. [2006](#page-9-0)). Further, in other agricultural areas subject to snow cover, N exports were highest during the snowmelt season (Hayashi and Hatano [1999](#page-9-0); Unoki et al. [2002;](#page-9-0) Iwanami et al. [2013\)](#page-9-0).

Paddy fields in N-polluted areas can reduce N loads to downstream reaches (Toda et al. [1997;](#page-9-0) Nira et al. [2005](#page-9-0); Hama et al. 2007; Maruyama et al. [2010\)](#page-9-0). However, there is no reduction in N exports during nonirrigated period because of the absence of the rice harvest and denitrification. As shown earlier, without the rice harvest and denitrification, there is no mechanism during the non-irrigated period by which N exports from paddy fields can be reduced.

Higher atmospheric N deposition in winter in the study area could be an additional important contributor to increased N exports in stream water. Atmospheric N deposition was higher during the non-irrigated period than during the irrigated period (Table [2](#page-6-0)). The higher N deposition during the winter is caused by long-range transport of air pollutants from the East Asian continent (Fujita et al. 2003; Seto and Hara [2006](#page-9-0); Wu et al. [2008](#page-10-0); Yoshioka et al. [2009\)](#page-10-0).

5 Conclusion

This study evaluated eutrophication of stream water caused by N throughout the year, including irrigated and non-irrigated periods. Our results indicate that N export was higher during non-irrigated periods in paddy-dominated agricultural basins and may have been caused by increased snowmelt water, the absence of a rice harvest and denitrification, and higher atmospheric N deposition in snowfall areas along the Japanese sea coast. This study shows that non-irrigated periods play a more important role than irrigated periods in stream water eutrophication in paddy-dominated agricultural basins in snowfall regions. Therefore, to improve water quality, N exports during the non-irrigated period should be targeted for reductions.

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References

- Brooks, P. D., & Williams, M. W. (1999). Snowpack controls on nitrogen cycling and export in seasonally snow-covered catchments. Hydrological Processes, 13, 2177–2190.
- Buck, O., Niyogi, D. K., & Townsend, C. R. (2004). Scaledependence of land use effects on water quality of streams in agricultural catchments. Environmental Pollution, 130, 287–299.
- Carpenter, S. R., Chisholm, S. W., Krebs, C. J., Schindler, D. W., & Wright, R. F. (1995). Ecosystem experiments. Science, 269, 324–327.
- Chiwa, M., Higashi, N., Otsuki, K., Kodama, H., Miyajima, T., Takeda, K., & Sakugawa, H. (2015a). Sources of hydroxyl radical in headwater streams from nitrogen-saturated forest. Chemosphere, 119, 1386–1390.
- Chiwa, M., Inoue, S., Tashiro, N., Ohgi, D., Uehara, Y., Shibata, H., & Kume, A. (2015b). Assessing the role of forests in mitigating eutrophication downstream of pasture during spring snowmelt. Hydrological Processes, 29, 615–623.
- Corriveau, J., Van Bochove, E., & Cluis, D. (2010a). Sources of nitrite in streams of an intensively cropped watershed. Water Environment Research, 82, 622–632.
- Corriveau, J., Van Bochove, E., Savard, M. M., Cluis, D., & Paradis, D. (2010b). Occurrence of high in-stream nitrite levels in a temperate region agricultural watershed. Water, Air, and Soil Pollution, 206, 335–347.
- Díaz, F. J., O'Geen, A. T., & Dahlgren, R. A. (2012). Agricultural pollutant removal by constructed wetlands: implications for water management and design. Agricultural Water Management, 104, 171–183.
- Fujita, S., Takahashi, A., & Sakurai, T. (2003). The wet deposition of acid and some major ions over the Japanese archipelago. Tellus, 55B, 23–34.
- Hama, T., Nakamura, K., & Mitsuno, T. (2007). Mass balances of nitrogen and phosphorus in the paddy field district implementing cyclic irrigation. Transactions of The Japanese Society of Irrigation, Drainage and Rural Engineering, 250, 437–443 (in Japanese with English summary).
- Hashimoto, I., Maruyama, T., Murashima, K., & Takimoto, H. (2007). Downstream environmental impact evaluation from rice yield and fertilizer application aspect: case study of total nitrogen and total phosphorus balance of paddy at Kahokugata lowland area. Transactions of The Japanese Society of Irrigation, Drainage and Rural Engineering, 250, 385–392 (in Japanese with English summary).
- Hatano, R., Nagumo, T., Hata, H., & Kuramochi, K. (2005). Impact of nitrogen cycling on stream water quality in a basin associated with forest, grassland, and animal husbandry, Hokkaido, Japan. Ecological Engineering, 24, 509–515.
- Hayakawa, A., Nagumo, T., Kuramochi, K., & Hatano, R. (2003). Characteristics of nutrient load in a stream flowing through a livestock farm during spring snowmelt. Soil Science and Plant Nutrition, 49, 301–305.
- Hayashi, Y., & Hatano, R. (1999). Annual nitrogen leaching to subsurface drainage water from a clayey aquic soil cultivated with onions in Hokkaido, Japan. Soil Science and Plant Nutrition, 45, 451–459.
- Hayashi, K., Nishimura, S., & Yagi, K. (2006). Ammonia volatilization from the surface of a Japanese paddy field during rice cultivation. Soil Science and Plant Nutrition, 52, 545–555.
- Hazlett, P. W., Semkin, R. G., & Beall, F. D. (2001). Hydrologic pathways during snowmelt in first-order stream basins at the Turkey Lakes Watershed. Ecosystems, 4, 527–535.
- Ishikawa Prefecture (2007). Report on conservation measures for Kahokugata water quality. Ishikawa Prefecture. [http://www.](http://www.pref.ishikawa.lg.jp/mizukankyo/shiryo/kahoku/documents/hukaryou.pdf) [pref.ishikawa.lg.jp/mizukankyo/shiryo/kahoku/documents/](http://www.pref.ishikawa.lg.jp/mizukankyo/shiryo/kahoku/documents/hukaryou.pdf) [hukaryou.pdf.](http://www.pref.ishikawa.lg.jp/mizukankyo/shiryo/kahoku/documents/hukaryou.pdf) Accessed 7 July 2013. (in Japanese)
- Iwanami, H., Wada, T., Sakamoto, K., Kudo, I., & Chikita, K. A. (2013). Mechanism of nutrients supply from the Tokachi River catchment considering characteristics of discharge and land use. Journal of Japanese Association of Hydrological Sciences, 43, 3–24 (in Japanese with English summary).
- Kunimatsu, T., Rong, L., Sudo, M., & Takeda, I. (1994). Runoff loadings of materials causing water pollution from a paddy field during a non-planting period. The Japanese Society of Irrigation, Drainage and Rural Engineering, 170, 45–54 (in Japanese with English summary).
- Kyuma, K. (2005). What is soil? Kyoto: Kyoto University Press (in Japanese).
- Maruyama, T., Hashimoto, I., Murashima, K., & Takimoto, H. (2008). Evaluation of N and P mass balance in paddy rice culture along Kahokugata Lake, Japan, to assess potential lake pollution. Paddy and Water Environment, 6, 355–362.
- Maruyama, T., Hashimoto, I., Takimoto, H., & Nakade, D. (2009). Assessment for nitrogen pollution loads from farmland, Japan, by objective yield and standard fertilizer usage. Paddy and Water Environment, 7, 151–159.
- Maruyama, T., Noto, F., Murashima, K., Hashimoto, I., & Kitada, K. (2010). Analysis of the nitrogen pollution load potential from farmland in the Tedori River alluvial fan areas in Japan. Paddy and Water Environment, 8, 293–300.
- Maruyama, T., Noto, F., Takimoto, H., Nakamura, K., & Onishi, T. (2011). Assessment of the long-term variation in the nitrogen pollution load potential from farmland to groundwater in the Tedori River Basin, Japan. Paddy and Water Environment, 9, 441–449.
- Maruyama, T., Noto, F., Yoshida, T., Nakamura, K., Horino, H., Murashima, K., & Takimoto, H. (2012). Analysis of water balance at the Tedori River alluvial fan areas in Japan. Journal of Japan Society of Hydrology and Water Resources, 25, 20–29 (in Japanese with English summary).
- Maruyama, T., Noto, F., Yoshida, M., Horino, H., & Nakamura, K. (2014). Analysis of water balance in the Tedori river alluvial fan areas of Japan: focused on quantitative analysis of groundwater recharge from river and ground surface, especially paddy fields. Paddy and Water Environment, 12, 163–171.
- Nira, R., Atsumi, K., & Miyaji, N. (2005). Nitrate outflow from tea fields and nitrate removal potential of paddy fields in Makinohara area. Japanese Journal of Soil Science and Plant Nutrition, 76, 901–904 (in Japanese).
- Nishimura, S., Sawamoto, T., Akiyama, H., Sudo, S., & Yagi, K. (2004). Methane and nitrous oxide emissions from a paddy field with Japanese conventional water management and

fertilizer application. Global Biogeochemical Cycles, 18, GB2017 1–10.

- Oczkowski, A. J., Pellerin, B. A., Hunt, C. W., Wollheim, W. M., Vörösmarty, C. J., & Loder, T. C. (2006). The role of snowmelt and spring rainfall in inorganic nutrient fluxes from a large temperate watershed, the Androscoggin River basin (Maine and New Hampshire). Biogeochemistry, 80, 191–203.
- Piatek, K. B., Mitchell, M. J., Silva, S. R., & Kendall, C. (2005). Sources of nitrate in snowmelt discharge: evidence from water chemistry and stable isotopes of nitrate. Water, Air, and Soil Pollution, 165, 13–35.
- Seto, S., & Hara, H. (2006). Precipitation chemistry in western Japan: its relationship to meteorological parameters. Atmospheric Environment, 40, 1538–1549.
- Smith, R. V., & Stewart, D. A. (1977). Statistical models of river loadings of nitrogen and phosphorus in the Lough Neagh system. Water Research, 11, 631–636.
- Swaney, D. P., Hong, B., Ti, C., Howarth, R. W., & Humborg, C. (2012). Net anthropogenic nitrogen inputs to watersheds and riverine N export to coastal waters: a brief overview. Current Opinion in Environmental Sustainability, 4, 203–211.
- Tabuchi, T., Yoshino, K., Shimura, M., Kuroda, S., Ishikawa, M., & Yamaji, E. (1995). Relation between land use and nitrate concentration of outflow water from watersheds of agricultural and forest areas. Transactions of The Japanese Society of Irrigation, Drainage and Rural Engineering, 63, 129–135 (in Japanese with English summary).
- Tachibana, H., Shimizu, T., & Nakagawa, Y. (1996). Water quality of Ishikari river during the snow melting period. Journal of Japan Society of Hydrology and Water Resources, 9, 444– 456 (in Japanese with English summary).
- Takeda, K., Shindo, H., Nakatani, N., & Sakugawa, H. (2005). Photochemical formation of hydroxyl radicals from chemical species dissolved in river water. Journal of Japan Society on Water Environment, 28, 509–513 (in Japanese with English summary).
- Toda, H., Mochizuki, Y., Kawanishi, T., & Kawashima, H. (1997). Estimation of reduction in nitrogen load by tea and paddy field land system in Makinohara area of Shizuoka. Japanese Journal of Soil Science and Plant Nutrition, 68, 369–375 (in Japanese with English summary).
- Unoki, K., Nagasawa, T., Inoue, T., & Yamamoto, T. (2001). Characteristics of nitrogen runoff during snowmelt period in agricultural watershed river. Journal of Japan Society of Hydrology and Water Resources, 14, 452–460. in Japanese with English summary.
- Unoki, K., Nagasawa, T., Inoue, T., & Yamamoto, T. (2002). Relationship between water quality environment and landuse in an agricultural watershed during snowmelt period—principal component analysis of river water quality. Journal of Japan Society of Hydrology and Water Resources, 15, 391–398 (in Japanese with English summary).
- Williams, M. W., & Melack, J. M. (1991). Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. Water Resources Research, 27, 1575–1588.
- Woli, K. P., Hayakawa, A., Kuramochi, K., & Hatano, R. (2008). Assessment of river water quality during snowmelt and base flow periods in two catchment areas with different land use. Environmental Monitoring and Assessment, 137, 251–260.
- Wu, J., Nishijima, Y., & Satake, H. (2008). Seasonal variation of δ15N of nitrate ion found in precipitation at Toyama. Chikyukagaku, 42, 1–11 (in Japanse with English summary).
- Xing, G. X., Cao, Y. C., Shi, S. L., Sun, G. Q., Du, L. J., & Zhu, J. G. (2002). Denitrification in underground saturated soil in a rice paddy region. Soil Biology and Biochemistry, 34, 1593–1598.
- Yoshioka, K., Kamiya, H., Kano, Y., Saki, Y., Yamamuro, M., & Ishitobi, Y. (2009). The relationship between seasonal variations of total-nitrogen and total-phosphorus in rainfall and air mass advection paths in Matsue, Japan. Atmospheric Environment, 43, 3496–3501.