SESSION 3

SOIL AND WATER CONSERVATION ZONES FOR POLLUTION CONTROL

Water Conservation Zones in Agricultural Catchments for Biomass Production, Food Security and Environmental Protection

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ABSTRACT

This paper reports the preliminary results obtained from an FAO/IAEA coordinated research project (CRP) involving eight countries. Results obtained are discussed with respect to sources and sinks of water and nutrients in water conservation zones that help farmers to use water when it is required. Three types of water conservation zones, namely farm ponds, wetlands and riparian buffer zones were studied using stable isotopes of oxygen-18 ($\delta^{18}O$) and hydrogen-2 ($\delta^{2}H$) to trace the movement of water, and nitrogen-15 (^{15}N) to trace nitrogen (N) and determine N use efficiency. Preliminary results showed that $\delta^{18}O$ and $\delta^{2}H$ effectively identified sources of water in water conservation zones and the interactions between water conservation zones and water from the catchment. Approximately 90 percent of water in water conservation zones was provided by runoff from the catchment while the remainder came from sub-surface flows and/or direct rainfall inputs. Water balance estimations showed that these water conservation zones with a surface area of less than three percent of the catchment area were able to capture more than 90 percent of water generated as runoff. Besides water retention, one water conservation zone in Estonia trapped N in the runoff water (up to 60 percent) effectively and converted nitrate into N_2 gas (170 to 350 kg·ha/yr) through denitrification, thus potentially reducing nitrate inputs into downstream receiving waters. The nitrate and ammonium trapped in water conservation zones could also be used to provide N for crops through irrigation.

Key words: *water conservation zones, stable isotopes, wetlands, ponds, riparian buffer zones.*

INTRODUCTION

Global land and water resources are under threat as land use transforms from natural to urban and agricultural uses, and through population growth, increased demands for food security and socio-economic well-being and the contamination of the environment (UNESCO, 2006). Poor crop yields as a result of water stress are one of the main reasons for prevailing hunger and rural poverty. The Green Revolution of the sixties and seventies in many parts of the world, particularly in Latin America and Asia depended partly on water management (Das, 2002). However, in the foreseeable future the majority of food supply will still need to come from rain-fed agriculture. Water conservation zones in agricultural catchments play an important role in the capture and storage of water and nutrients from farmlands and providing these for crop and biomass production in times of need in rain-fed areas.

In many regions, water conservation zones are considered as an important part of water resource management strategies that have been developed to prevent reservoir siltation, reduce water quality degradation, mitigate flooding, enhance groundwater recharge and provide water for farming (Gonfiantini, 1986). In addition to making crop production possible in dry areas, water conservation zones minimize soil erosion, improve soil moisture status through capillary rise and enhance soil fertility and quality (SIWI, 2001). These water conservation zones include (i) natural and constructed wetlands (including riparian wetlands), (ii) farm ponds, and (iii) riparian buffer zones. They provide a wide range of socio-economic and environmental services including food, fibre, water supply and purification, carbon storage and biodiversity protection (Fasina, 2005).

The management of water conservation zones has been a challenge due to the poor understanding of the relationship between upstream land use and the functions of these zones and their internal dynamics. Activities and hydrological processes occurring in the upper catchment often affect water and nutrient capture and storage in these zones (Bramley and Roth, 2002). Knowledge of the sources and sinks of water such as the magnitude, frequency, duration, timing, rate of the water flow regimes and nutrient cycling into and out of the system as influenced by upland activities is therefore needed to identify management practices to optimize their performance for conservation and re-use of water and nutrients (Akhter *et al.,* 2005). Redefining water and nutrient budgets for water conservation zones is important for optimizing the capture, storage and use of water and nutrients in agricultural landscapes.

This paper presents and discusses preliminary results obtained from a coordinated research project (CRP) on "Strategic Placement and Area-Wide Evaluation of Water Conservation Zones in Agricultural Catchments for Biomass Production, Water Quality and Food Security" initiated in 2008 by the Joint FAO/IAEA Programme of Nuclear Techniques in Food and Agriculture. The overall objective of this CRP is to assess and enhance ecosystem services provided by wetlands, ponds and riparian buffer zones for improving water storage and nutrient use within agricultural catchments. The specific objectives are to (i) determine the capacity of water conservation zones for water storage, (ii) assess nutrient attenuation capacities, (iii) assess the link between water and nutrient dynamics, and (iv) optimize water conservation zones for improving water storage and quality.

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MATERIALS AND METHODS

The research network operated within the framework of the CRP included eight research contract holders (China, Estonia, Iran, Lesotho, Nigeria, Romania, Tunisia and Uganda), supported by two technical contract holders (France and United States) and two research agreement holders (France and United States). Three types of water conservation zones were used in all participating countries based upon their use in agricultural catchments, namely: (i) water and nutrient storage for downstream irrigation use (farm ponds), (ii) *in situ* crop and biomass production (wetlands including riparian wetlands), and (iii) downstream water quality (riparian buffer zones). Piezometers were installed in and around most of the zones at various depths to more than four m to record groundwater depth fluctuations and to collect water samples. Oxygen-18, hydrogen-2, and nitrogen-15 stable isotopic signatures were used to identify sources and factors influencing water and nutrient capture, dynamics and storage in these water conservation zones. For each country, one catchment was selected for field studies based on the importance of agricultural production and water management practices. Preliminary land-use surveys were carried out for experimental catchments in all eight countries and the results are provided in Table 1.

Based on the CRP objectives, the water conservation zones in Tunisia (farm pond) and Iran (Ab-bandans, i.e. man-made water storage ponds) were grouped under water conservation zones that gather catchment runoff for improving food production through irrigation of crops downstream. China, Lesotho, Nigeria and Uganda (wetlands) were grouped under water conservation zones that are used for improving food production through *in situ* crop production. Finally, Estonia and Romania (riparian zones) were grouped under water conservation zones that regulate nutrient cycling, protect downstream water quality and generate biomass within the system.

A brief description of the studies carried out in each of the zones is provided below:

- The sources of water to the farm pond in the Kamech catchment in Tunisia were investigated using $\delta^{18}O$, $\delta^{2}H$ and hydrological processes.
- Isotopic and water mass balance studies were carried out in 30 Ab-bandans in northern Iran that capture water from the surrounding catchments to irrigate downstream rice fields.
- Field investigations using isotopic and conventional techniques were carried out in northern China to assess water conservation zones for sustainable agricultural production.
- The *in situ* rice production and N use were investigated for rice wetlands in eastern Uganda using ^{15}N isotopic techniques.
- In Nigeria, the environmental issues related to integrated management and characterisation of water conservation zone were studied.
- The hydrological and management constraints in two water conservation zones were examined in Lesotho.
- The N pathways in a riparian buffer zone were investigated in the Arges river catchment in Romania.
- Two riparian buffer zones in Estonia were studied for optimizing N removal through dinitrification.

Data on rainfall and other weather related information were collected for all catchments to establish water balance for the catchment and sources of water inflow to water conservation zones.

Oxygen-18, hydrogen-2 and water chemistry measurements were carried out for water samples collected from water conservation zones, runoff water from the catchment, rainfall, stream water and from the piezometers (four m below the ground). In addition, biomass yield and N uptake in the water conservation zones were measured in all countries.

RESULTS AND DISCUSSION

As the overall objective of the CRP was to optimize the capture and storage of water and nutrients, the preliminary results focussed only on water conservation zones in China, Estonia, Iran, Tunisia and Uganda with emphasis being given to the capture and storage of water and nutrients.

TABLE 1. Land use of experimental catchments.

Country	Catchment	Major land-use	Area (ha)
China	Sanjiang Plains	Rice	92 000
Estonia	Porijogi	Livestock	12 600
Iran	Ab-Bandons	Rice	11 700
Lesotho	Ha-Matela	Maize, sorghum and livestock	300
Nigeria	Ekiti Valley	Rice, maize, yam	2 500
Romania	Galvacioc	Wheat and maize	3 200
Tunisia	Kamech	Wheat, barley, oat, etc.	260
Uganda	Manafwa	Rice	300

TABLE 2. Monthly water budget for the Kamech Lake (m^3)

Month	Sept-09	Oct-09	Nov-09	Dec-09	Jan-10	Feb-10
Net Exchanges	–7871	5511	–3776	–9256	–13 129	–11 352
Month	**Mar-10**	**Apr-10**	**May-10**	**Jun-10**	**Jul-10**	**Aug-10**
Net Exchanges	–16 603	–11 944	–3 047	1119	–2413	–5985

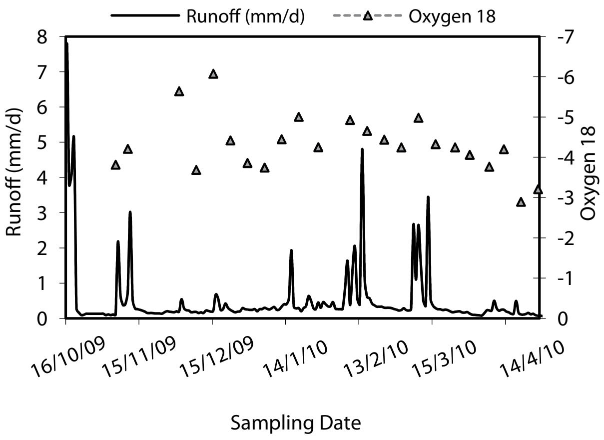

FIGURE 1. Isotopic signature ($\delta^{18}O$) and runoff volume for Kamech streamflow.

TABLE 3. Isotopic signatures of various source waters in the Kamech catchment

Isotope	Rainfall	Stream flow	Farm Pond	Run–off
$\delta^{18}O$	–14 to 0.1	–7 to +3	–4 to +5	–6 to –3
$\delta^{2}H$	–89 to +5	–37 to +3	–199 to +219	

Water conservation zones for downstream irrigation

The water budgets established monthly during 2009–2010 for the farm pond in Kamech catchment in Tunisia revealed that for most of the time the farm pond was recharging the unsaturated zone (Table 2). Runoff in the catchment is mainly produced in autumn and winter (between October and March each year) during which annual rainfall occurs. The water balance data showed that October and June were the only months during which water exchange was dominated by unsaturated zone contribution to the farm pond (positive sign, Table 2).

Stream flow and the corresponding $\delta^{18}O$ values for various time periods are provided in Figure 1. Seasonal variations in isotopic signatures clearly showed that it was influenced by runoff. A more detailed study of this data coupled with flood events will permit understanding of flood processes of the catchment.

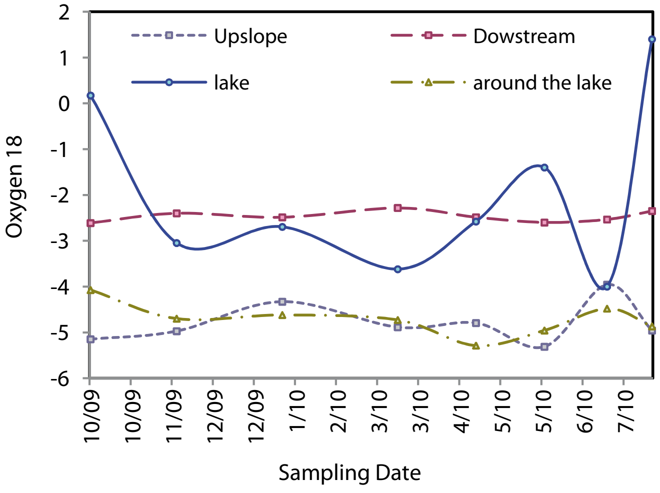

FIGURE 2. Stable isotopes variation of Kamech groundwater.

Delta oxygen-18 ($\delta^{18}O$) and $\delta^{2}H$ values of various water sources in the Kamech catchment are provided in Table 3. The signatures of steam flow have the same range as those of rainfall indicating that direct runoff from rainfall is the major contributor to stream flow. However, these are seasonally variable depending on rainfall and temperature. Isotopic signatures along with water balance calculations indicate that runoff from the catchment is the major source of water to the farm pond.

Different isotopic signatures were found between water in the upslope, around the farm pond and downstream of the farm pond (Figure 2). The water downstream of the farm pond was less enriched, indicating that the downstream recharge was a mixture of overflow, releases and infiltration. Isotopic signatures of water samples collected from the farm pond showed clear seasonal trends closely related to the variations in volume. During the rainy season, isotopic signatures were similar, being influenced by precipitation, stream flow and the volume of water discharged from the water conservation zone. However, during the non-rainfall season, the water was continuously enriched due to evaporation that became the most important component of the water balance during this period (Figure 2).

The water balance calculations (from Table 1) and the closeness of the isotopic signatures of various source waters (Table 3) showed that more than 90 percent of water to the farm pond in the Kamech catchment is contributed by runoff water generated from rainfall.

TABLE 4. Seasonal changes in water quality parameters

Parameters	Spring			Summer			Winter		
	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.
EC (dS/m)	2.8	0.1	0.9	3.3	0.2	1.1	1.0	0.1	0.4
pH	8.4	6.7	7.8	7.8	5.9	7.2	8.9	6.9	8.0
SO_4-S (mg/L)	5.9	0.7	2.5	108	1.3	21.8	5.3	0.9	2.1
P (mg/L)	9.4	0.0	1.3	5.3	1.5	3.2	18.1	0.0	1.4
NO_3-N (mg/L)	13.7	0.2	2.2	33.8	1.1	8.9	30.0	1.0	15.4
NH_4-N(mg/L)	7.4	0.0	2.2	25.6	0.0	2.1	1.4	0.0	0.1
$\delta^{18}O$ (‰)	3	–7	–4	5	–7	–1			
$\delta^{2}H$ (‰)	0.2	–43	–28	19	–38	–12			

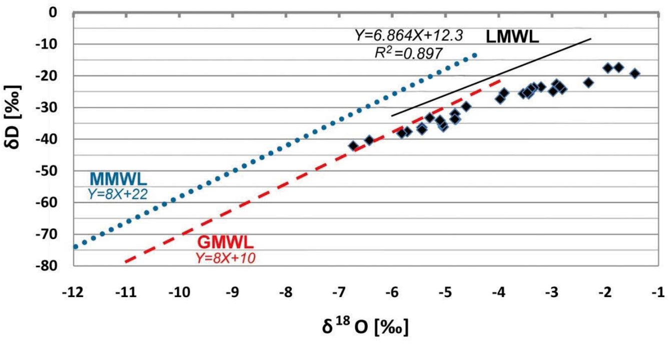

FIGURE 3. Plot of δ^{18}O versus δ^{2}H values from 30 Ab-bandans in the north of Iran shown in relation to the global meteoric water line (GMWL), Mediterranean meteoric water line (MMWL) and local meteoric water line (LMWL) (Vreča *et al.*, 2006; Ogrinc *et al.*, 2008; Wassenaar, Athanasopoulos and Hendry, 2011).

Water quality and isotopic signatures for water samples collected from 30 Ab-bandans during winter, spring and summer are shown in Table 4. The analysis of variance between water quality and isotopic signatures showed that a number of factors including land use, fertilizer application and the location of these Ab-bandans influenced the amount of water captured and the chemical characteristics and isotopic signatures of the water (Table 4).

Figure 3 shows the plot of δ^{18}O versus δ^{2}H of selected Ab-bandans in relation to the global meteoric water line (GMWL) and the Mediterranean meteoric water line (MMWL). The local meteoric water line (LMWL) was determined from the linear regression of precipitation data collected during the water sampling period. Data showed that the isotopic signatures for almost all Ab-bandans lay below the LMWL and GMWL, indicating that water in these Ab-bandans was affected by evaporation. The results showed that most Ab-bandans in the north of Iran do not receive sufficient inputs of water to minimize the effects of summer evaporation on isotopic signatures (with average δ^{18}O and δ^{2}H values of –4‰ and –29‰, respectively). Runoff from precipitation (rainfall and snow melt) during autumn and winter (September to March) was the main contributor to the Ab-bandan water.

Water balance calculations showed that on average 7.6 million m^3 of water with 86 and 17 t of N and P, respectively were captured annually by 30 Ab-bandans mainly through runoff and were available for irrigation. Flood irrigation using this water at a rate of 10 000 m^3/ha over the growing season (April to September) was able to produce rice in an area of 730 ha with a yield of 3.5 t/ha. However, changing the irrigation method from flood to an eight-d irrigation interval was able to cultivate 1500 ha with a similar yield and a significantly increased water use efficiency and reduced energy use (Figure 4).

Water conservation zones for *in situ* biomass production

Isotopic signatures for surface water and unsaturated zone water (water depth at four m below ground) in three typical rice wetlands in Honghe (HH), Qianfeng (QF) and Qianshao (QS) farms in China, showed that different processes were occurring in these three rice wetlands during the period 2005–2009. At inter-annual scale (between years), water levels tended to decrease, with that in the HH wetland decreasing the most, followed by QF and QS farms. At intra-annual scale (within a year especially from April to the middle of May), water levels decreased by up to four m, being controlled by unsaturated zone water extraction, i.e. for rice-farming. This demand decreases when rain appears in May each year. As a result, water levels rise back to levels before irrigation.

In July, average values of δ^{2}H and δ^{18}O in rain water were -81.5‰ and -11.2‰, respectively. The δ^{2}H and δ^{18}O for unsaturated zone water (four m below ground) in Honghe farm ranged from –98.6‰ to -68.3‰, and from –13.5‰ to –8.8‰ respectively, with mean values of –92.6‰, and –12.1‰. Similarly, the δ^{2}H and δ^{18}O of unsaturated zone water in Qianfeng farm ranged from –86.1‰ to –102.4‰, and from –13.8‰ to –10.8‰, respectively with mean values of –97.0‰ and –12.8‰. Isotopic signatures of irrigation water from paddy fields entering drainage channel ranged from –9.0‰ to –12.6‰ for δ^{18}O with a mean value of –10.4‰. These values are comparable with those in rain water. This closeness between the isotopic signatures of rain water and unsaturated zone water suggest that the unsaturated zone water in this area is recharged during the rainy period. As the unsaturated zone water level decreased before the rainy season (April and May each year), it is evident that the contribution of unsaturated zone water to the wetland is minimum.

The performance of wetlands for *in situ* rice production and nutrient use in the Manafwa catchment, Uganda (Doho rice scheme) showed that these rice wetlands remove 64 t of N in a single growing season from the incoming river water through biomass production. The three water management practices in these wetlands, namely (i) irregular and low (poor), (ii) regular and low (moderate) and (iii)

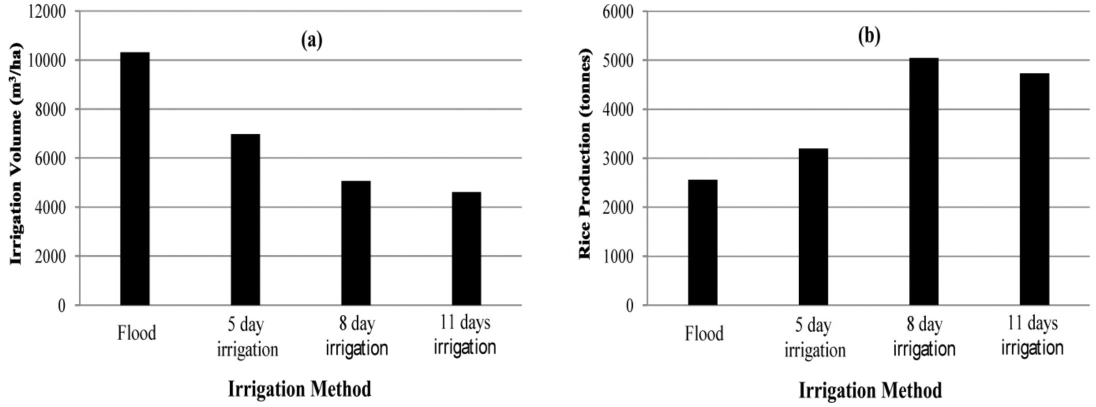

FIGURE 4. Influence of irrigation methods on (a) amount of water used and (b) total rice production of Ab-Bandans.

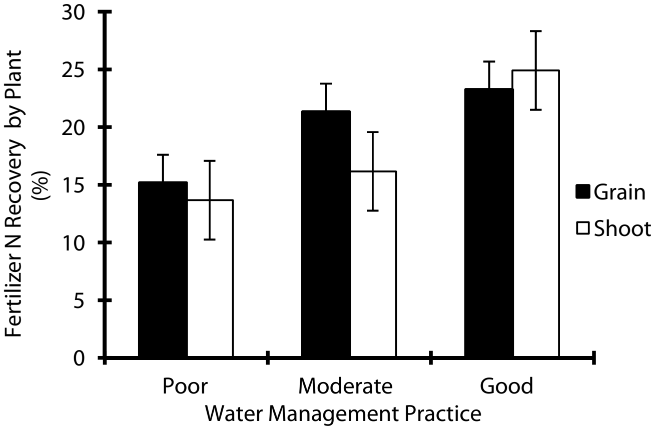

FIGURE 5. Fertilizer N recovery by rice crop as influenced by water management practice in Doho rice wetlands.

TABLE 5. Grain yield, biomass production and N uptake by rice in Doho wetlands

Treatments	Yield (t/ha)		N uptake (kg/ha)	
	Grain	Biomass	Grain	Biomass
Fertilized	7.7	24.7	96	184
Unfertilized	6.2	19.3	70	144

regular, high and continuous (good) demonstrate that good water management practice played an important role in biomass production and nutrient use efficiency of rice (Figure 5). However, fertilizer application made a significant difference to biomass productivity in wetlands, increasing grain yield by 25 percent and biomass production by 27 percent, while N uptake increased by 36 percent and 28 percent, respectively in grain and biomass (Table 5).

^{15}N isotopic signatures of rice grain and shoot showed that water management practices affected the amount of fertilizer N taken up by the rice crop, ranging from 34.6 kg N/ha under poor water availability to 57.7 kg N/ha under permanent water availability (Figure 5).

At the end of rice growing season, less than two percent of fertilizer N was present in the top 30 cm soil depth suggesting possible N losses through leaching, denitrification and volatilization. The rice wetland removed more than 70 percent of the applied fertilizer. The wetland rice production provided a minimum net economic return of US$1300 per ha per cropping season.

Regulating water and nutrient cycling in water conservation zones

Studies on nitrous oxide (N_2O) emissions from two differently loaded riparian grey alder (*Alnus incana)* dominated forests in agricultural landscapes of southern Estonia showed a negative correlation between the concentration of N_2O-N and the rate of conversion of nitrate to N_2O in groundwater in both Porijõgi and Viiratsi catchments (Figure 6A). The negative correlation suggests that the majority of nitrate denitrified is converted to N_2 gas. The isotopic signatures of $\delta^{18}O$ exhibited a relatively large variability and site preference (SP), typically ranging between 10‰ and 50‰ and with a close correlation between $\delta^{18}O$ and ^{15}N (Figure 6B) (Well, Weymann and Flessa, 2005). Results obtained are in agreement with those reported by Mander *et al* (2003) and Well, Weymann and Flessa (2005), showing that N_2O emissions at both sites were significantly lower (0.5 and 0.6 $kg \cdot ha^{-1} \cdot yr^{-1}$ in Porijõgi and Viiratsi, respectively) than emissions of N_2 (51.2 and 47.4 $kg \cdot ha^{-1} \cdot yr^{-1}$, respectively).

These results show that in riparian alder forests, denitrification leads mainly to the release of N_2 rather than N_2O, which is a significant boost to reducing N_2O emission to the atmosphere (Well, Weymann and Flessa, 2005). These riparian buffer zones can remove between 170 and 350 kg·N/ha from the incoming water, mainly as N_2 gas.

CONCLUSIONS

Water conservation zones are major sources of water for groundwater recharge as shown by similar δ^2H (–102‰ to –68‰) and $\delta^{18}O$ (–14‰ to –9‰) signatures. Isotopic signatures of water in runoff, rainwater, stream water and water conservation zones along with water balance calculations showed that more than 90 percent of the water captured by water conservation zones is by surface runoff during rainy periods. Nitrogen captured in water conservation zones is a major source of N for biomass production (215 $kg \cdot N \cdot ha \cdot yr^{-1}$)

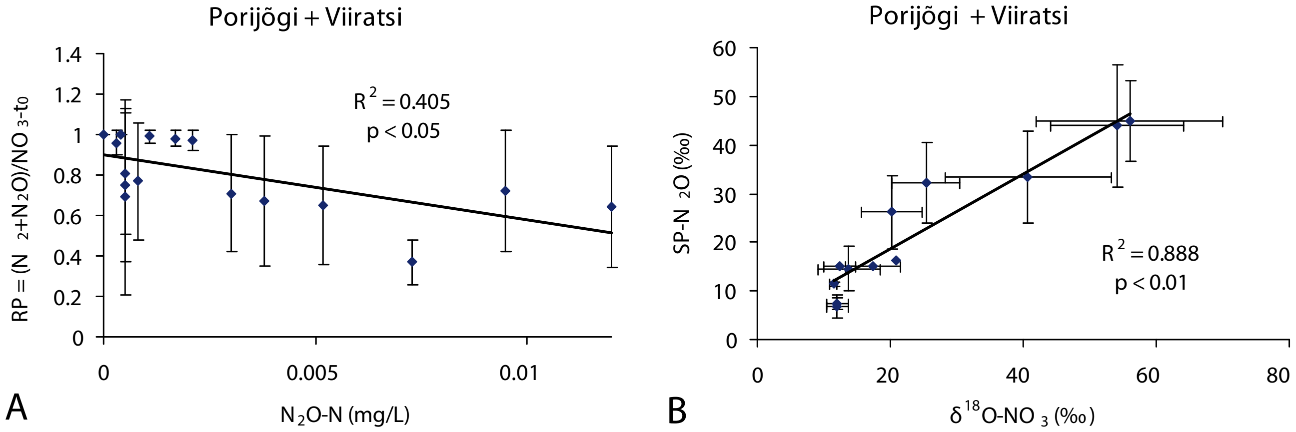

FIGURE 6. Groundwater N_2O vs reaction progress (RP) (A) and $\delta^{18}O$ vs SP (B) in riparian grey alder forests of Porijõgi and Viiratsi, Estonia.

within these zones and for irrigating adjacent farmlands and potentially reducing N input to downstream water. More than 60 percent of N removed by water conservation zones in agricultural catchments occurred through denitrification in Estonia as shown by N-15 techniques. Nitrogen-15 labelled nitrate and urea were useful for quantifying denitrification and biomass N use efficiency in wetlands, farm ponds and riparian buffer zones. These preliminary results showed that in wetlands and riparian buffer zones, denitrification is a major process leading to N removal from water (>60 percent of N removal), and that most of this denitrification leads to the formation of N_2 gas rather than N_2O thus reducing greenhouse gas emissions to the atmosphere. Information collected from this research is useful for preparing guidelines and management practices that help farmers to optimize the capture and storage of water and nutrients in water conservation zones and their subsequent use for agricultural production, as well as to improve downstream water quality and quantity.

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Nutrient (Nitrogen and Phosphorus) Management in Agricultural Catchments for Improving Crop Productivity and Water Quality

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ABSTRACT

Managing land and water resources is increasingly challenging as a result of increasing competition for natural resources because of population and economic growth, climate change and other drivers. Nutrient management in agriculture plays an important role in crop production intensification and improving the quality of land and water resources in agricultural catchments. In this paper, a brief overview is presented on critical issues related to nutrient management in agricultural catchments for improving crop productivity, nutrient use efficiency and water quality. Nitrogen (N) and phosphorus (P) are critical nutrients for global agricultural productivity and food security. Increased demand for food production has resulted in extensive use of these nutrients resulting in impacts on surface and groundwater quality. Optimal nutrient management can be established with knowledge of nutrient budgets for site-specific conditions, nutrient use efficiency by crops and availability of legacy nutrients. Long-term goals of nutrient management in agricultural watersheds should include conservation and enhancement of soil quality. Future soil and nutrient management practices should consider nutrient imbalances resulting from surplus and deficits in fertilizer use in the catchment.

Key words: *soil quality; nutrient use efficiency; nutrient budgets; nitrogen isotopes; watersheds.*

INTRODUCTION

Globally, land and water resources are threatened by land-use shifts from natural to urban or agricultural environments and increased population. This change in land use has altered the demography as a large number of people moved from rural to urban environments, resulting in increased demand for food, water security and socio-economic well-being, and in environmental impacts from industrial, municipal and agricultural pollution (UNESCO, 2006). Agricultural, forested, rangeland and urban land management play an integral part in influencing sustainable land and water resource use for crop production and natural resource protection and conservation. The objective this paper is to provide a brief overview of nutrient management in agricultural catechements for sustainable agricultural productivity by improving nitrogen (N) and phosphorus (P) use efficiency by crops/grasslands and reducing non-point source pollution.

Agricultural ecosystems include: crops, livestock and horticultural production systems, rangelands, aquaculture and animal agriculture. Non-point source pollution of water resources such as streams, rivers, groundwater, lakes, wetlands and estuaries is linked to the agricultural water and nutrient management practices used in the watershed. The questions of immediate concerns are:

- Are current agricultural practices compatible with sustaining economic crop productivity and preserving the quality of our natural resources?
- Are current agricultural practices adequate to meet current demands and future needs to sustain economic crop productivity and protect the quality of natural resources?

Many current agricultural management practices may be compatible, but not adequate to sustain natural resource quality. Society demands that the quality of natural resources be protected, placing a greater demand on producers to deliver environmentally sound goods. The major challenges for sustainable global agriculture are: (i) meeting the food and fibre needs of a world population projected to exceed nine billion by the year 2050, (ii) decreasing the rate of soil degradation and ameliorating degraded soils, and (iii) protecting the quality of natural resources. During the past decade, implementation of best management practices (BMPs), mostly in developed countries, has helped to improve soil and water quality. However, many watershed management practices currently used around the world are clearly insufficient to deal effectively with stresses placed on land and water resources from burgeoning populations. For sustainable land use and management, integration of the information from diverse domains (e.g. physical, biogeochemical, economic, social, cultural and demographic) at spatial and temporal scales is required to develop predictive tools across environmental, hydrologic, economic and social gradients. The US National Research Council Committee (NRC, 1993) on long-range soil and water conservation defined four broad issues that show promise for maintaining sustainable agriculture, while protecting water quality. These include: (i) conserve and enhance soil quality as a fundamental step to environmental improvement, (ii) increase nutrient, pesticide, and irrigation use efficiencies in farming systems, (iii) increase the resistance of farming systems to erosion and run-off, and (iv) make greater use of field and landscape buffer zones. Although these issues were identified almost two decades ago, many are not adequately addressed in both developed and developing regions of the world.

Understanding the nature of soil quality, which is defined as "The ability of the soil resource to produce and maintain ecosystem production of plant, animal, and microbial biomass and to buffer or improve water quality", is fundamental to meeting the challenges identified above (Figure 1).

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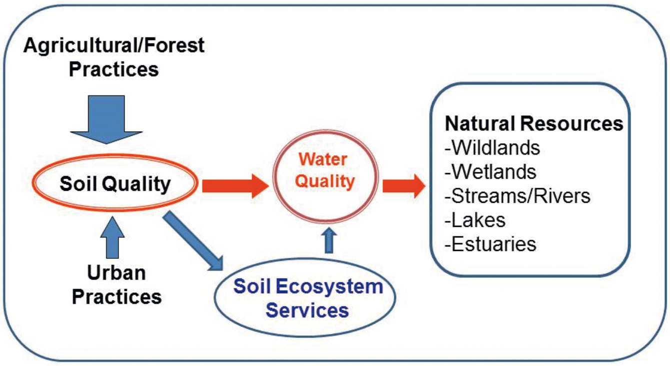

FIGURE 1. The linkage between soil and water quality.

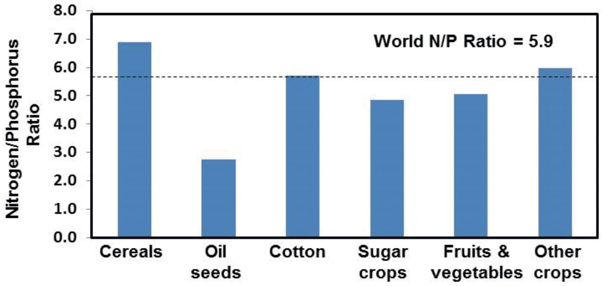

FIGURE 2. Nitrogen and phosphorus ratio of fertilizers used by major crops in the world during the year 2008 (Heffer, 2009).

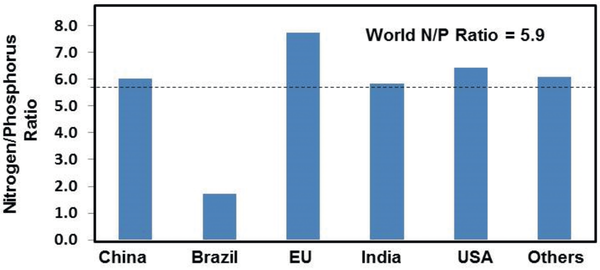

FIGURE 3. Nitrogen and phosphorus ratio of fertilizers used by selected counties in the world during the year 2008 (IFA, 2009).

Land-use changes and alterations in management practices are having significant impacts on the quality of groundwater, adjacent streams, wetlands, lakes and estuaries. For example, approximately 218 million Americans in USA live within 10.6 km of an impaired water body. In the United States, agricultural and forest management alone contribute 70 percent of the pollution in rivers and 60 percent of the pollution in lakes (Carey, 1991). Excess nutrients in aquatic systems have detrimental effects on designated or existing uses, including drinking water supply, recreational use, aquatic life and fisheries (USEPA, 2000). In the southeastern United States, approximately four million ha of lakes, and 560 000 km of rivers are impacted by pollutants, with sediment and nutrients as major types. New regulations place a burden and demand on farmers to change current practices or develop new practices in order to protect water quality while maintaining a profitable production system. To meet this demand, it is critical to review and analyse the available databases and develop new data at both site-specific and watershed levels, with a focus on developing tools that will help farmers and managers to assess soil quality and its linkage to water quality and sustainable productivity.

A holistic, integrated approach to research and education is required to develop alternate practices that will maintain environmentally sound management of these land and water resources. Since the soil is the primary driver regulating ecosystem processes and functions, its quality has a direct influence on water quality and ecosystem productivity. Soils are integral players in biogeochemical cycles that regulate ecosystem functions. Thus, it is appropriate to define soil quality in terms of functions that soil plays in these ecosystems. Policies that protect soil resources should sustain the soil's capacity to serve several functions simultaneously, including the production of food, fibre and fuel, nutrient storage, carbon sequestration, waste storage and the maintenance of ecosystem stability and resilience.

GLOBAL NITROGEN AND PHOSPHORUS FERTILIZERS USE

Nitrogen and P are critical nutrients for global food security. However, the use of these nutrients is not only linked to food production but also the potential environmental impacts on surface and groundwater quality (Heathwaite, Sharpley and Gburek, 2000; McDowell, Sharpley, and Kleinman, 2002; Reddy and Jawitz, 2010). Global N fertlizer consumption stayed on a par with increasing population and demand for food and fibre. It is estimated that approximately 100 million tonnes (t) of N fertilizer was consumed during 2008, representing 55.3 percent of world fertilizer N applied to cereal crops (corn, rice, wheat and other cereals), with oil seed crops accounting for 6.3 percent, cotton and sugarcane for 7.1 percent, fruits and vegetables for 15.3 percent and other crops 15.9 percent, respectively (IFA, 2009). It is estimated that approximately 17 million t of P fertilizer was consumed during 2008, representing 46.6 percent of world fertilizer P applied to cereal crops (corn, rice, wheat and other cereals), with oil seed crops accounting for 12.3 percent, cotton and sugar crops for 8.0 percent, fruits and vegetables for 17.8 percent and other crops 15.3 percent, respectively (IFA, 2009).

Global distribution of N fertilizer consumption in 2008 (100.5 million t), with China (32 percent) and India (14.5 percent) accounted for more than 35 percent, countries in the European Union (EU; 11.5 percent), United States (11.5 percent), Brazil (2.7 percent), and all other countries (27.9 percent), respectively (IFA, 2009). Global distribution of P fertilizer consumption in 2008 (17.1 million t), was led by China (31 percent), followed by India (14.7 percent), United States (10.5 percent), Brazil (9.4 percent), EU (8.8 percent), and all other countries (26.9 percent), respectively (Heffer, 2009).

The global N and P fertilizer consumption ratio is estimated to be 5.9 (IFA, 2009), while the ratio is 6.1 for North America (Mullins, Joern and Moore,, 2005), and 6.8 for the State of Florida (Reddy, Lowe and Fontaine, 1999 and Reddy et al, 2011), respectively. Fertilizer N and P consumption ratios for crops ranged from 2.7–6.9 (Figure 2), with low ratios observed for oil seed crops and high ratios for cereal crops. Geographically, N and P consumption ratios ranged from 1.7–7.7 with low ratios observed for crops grown in Brazil and high ratios for crops grown in the EU countries. The low fertilizer N and P consumption ratios in Brazil are probably due to the high P fixation capacity of soils and low plant available P. This results in high rates of P application in relation to N. High ratios for crops in EU countries are probably the result of reductions in P application rates. Similarly, higher ratios were noted for North America and the State of Florida, reflecting reductions in P fertilization (Figure 3).

The demand for N fertlizers will contiue to increase as the world population is projected to exceed nine billion by 2050. A significant correlation was noted between global population increase and N fertilizer use for agriculture (Raun and Schepers, 2008). It is estimated that world-wide demand for N fertilizers may increase to 186 million t by 2050, placing a major demand on energy to produce this fertilizer (Raun and Schepers, 2008). Similarly,, the 2008 estimate for world P fertilizer consumption was 17.1 million t. Rock phosphate is a non-renewable resource and currently is the major source of inorganic P, with current annual production estimated to be about 20 million t (Cordell *et al.*, 2011). It is estimated that peak P production will occur in 2035, and after that period demand would outweigh supply, suggesting P fertilizer scarcity (Cordell, Drangert and White, 2009; Carpenter and Bennett, 2011; Childers *et al.*, 2011; Neset and Cordell, 2012). Global distribution of soil P content is uneven. In some areas of the world the soils are saturated with P as a result of long-term application of fertilizers and other sources including manures and other organic wastes. Soils in other areas may be P deficient as a result of low P applications and highly reactive soils (dominant in iron and aluminum). Recommended P application rates to crops grown in these highly reactive soils are relatively high to maintain adequate plant available P. In some areas, inorganic N and P fertilizers are supplemented with organic wastes and manures. However, application of manures and organic wastes based on needed N results in excessive P load, and when based on P needs results in N limitation. In many cases, applications of organic solids based on crop N needs may result in application of P in excess of ecosystem requirements, resulting in adverse impacts on surface and groundwater quality. For example, the average N content of biosolids is about three percent of the dry weight and the average P content is about 1.8 percent (Reddy, Lowe and Fontaine, 1999). The N:P ratio of the biosolids is 1.7, which means that when land application rates are calculated based on the N content, there is a potential to apply high levels of P which can potentially create water quality problems. However, if land application rates are determined based on P content, rates would be much lower and supplemental inorganic N fertilizer would be required to meet the N requirement of the crop. Organic waste loading rates should be based on site soil characteristics, the bioavailability of N and P and the hydrologic characteristics of the site. In order to protect the aquatic ecosystems of watersheds, organic waste loading rates should also be based on the P content and the soil's capacity to retain P. Considering potential future deficits in inorganic P supply, manures and other organic wastes offer potential sources of P to crops.

NUTRIENT BUDGETS

Accounting of various inputs and outputs of N and P at multiple scales (field plot to watershed scales) in agricultural ecosystems will aid in improving nutrient use efficiency by crops and in developing strategies to reduce the environmental impact of non-harvestable nutrients on adjacent water bodies. Nutrient budgets typically identify major flow paths of a nutrient in question and associated stores in various pools in the soil–plant system and biogeochemical transformations within and between pools. For example, N budgets in various agricultural ecosystems have been used for more than 100 years to determine sources and sinks for N (Meisinger *et al.*, 2008). The basic principle in developing nutrient budgets is simple: nutrient inputs minus nutrient outputs equals change in stores in the system. These stores can be positive or negative depending on inputs and outputs and the nutrient use efficiency of the cropping system used. Nutrient budgets are useful for guiding land managers in determining where to apply the most effort for increasing crop nutrient use efficiency, reducing environmental pollution, or for reducing the waste of a nutrient that would decrease agricultural profitability. Budgets depend on an understanding of the sources, flows and fates of a nutrient. Budgets help determine the balance of nutrients in the agricultural system, a negative balance resulting from more outputs relative to inputs and a positive balance from more inputs relative to outputs. Negative balances could mean there are losses of nutrients to the environment. Positive balances do not always demonstrate good nutrient management because the buildup of nutrients in the system could lead to large nutrient release should a production practice change or a sudden wet period occur leading to erosion. Knowing the particular nutrient balance and understanding the pools and fates of the nutrients are key to adjusting the balance.

Major nutrient pools

In an agricultural setting there are four major nutrient pools. These are inputs, those nutrients being stored and cycled, exports and outputs (losses) to the environment. Note that in a farm budget, nutrient outputs can be separated into loss to the environment and exportation via the produce or animal meat transported to market. Nutrient inputs and outputs for an agricultural setting are shown schematically in Figures 4 and 5. Nutrient budgets are created from numerous sources of information. Some pools are easy to quantify from farm records, such as fertilizer brought onto the farm and used for crop production. Some farms are equipped to collect and weigh livestock manure, especially farms that operate under a USDA Natural Resource Conservation Service comprehensive nutrient management plan. The amounts of crops harvested, packaged, and sold off the farm can be obtained from farm records. Some researchers quantify certain nutrient pools from published information in the scientific literature pertaining to similar farm operations. Some nutrient pools must be measured for the best accuracy. For example, crop uptake can be measured by analysing above-ground and below-ground plant parts for nutrient content. Nutrients in the irrigation water can be determined by laboratory analyses. Nitrogen and P have distinct transformations and flow paths that regulate fate and transport of these nutrients (Figures 4 and 5). A major portion of soil N is in organic form (95 percent of total soil N) and it is tightly coupled to soil organic carbon. Thus, breakdown of organic matter through decomposition processes can result in mineralization of organic N and release of inorganic N.

Some examples of different types of nutrient budgets can be found in the literature and this has become a popular area of research, probably due to the strong interest in nutrient losses from farms. Davis *et al.* (2003) took advantage of the Magruder Plots at Oklahoma State University in Stillwater, Oklahoma that have been under continuous tillage since 1892. These researchers calculated an average N use efficiency of 33 percent for wheat. Gentry *et al.* (2009), used direct measurements of several N pools in a watershed in Illinois, finding that fertilizer N and soybean N2 fixation dominated the N inputs and grain export dominated the outputs. In a dry year, inputs were greater than outputs and in a wet year, outputs were greater than inputs.

Scale of nutrient budgets

It is important to determine the specific goal for developing the nutrient budget to understand the effects of changes in fertilization rates on nutrient pools. A nutrient budget can be determined for different scales depending on the needs of the farm operator. Budgets can describe the nutrient pools at the field, farm or watershed level. A budget can be developed for a specific farm process, for example cattle feeding operations, urban areas (N in a residential watershed)

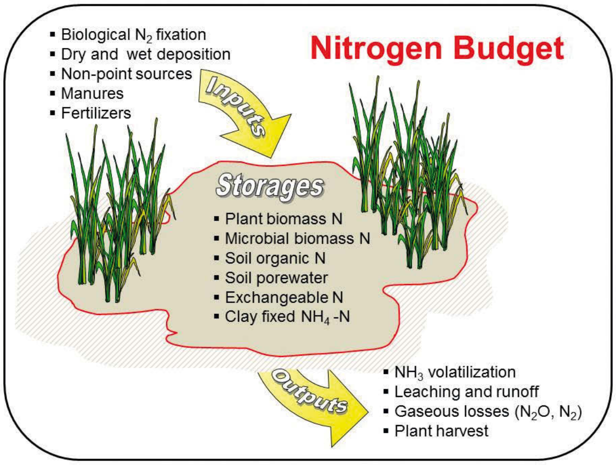

FIGURE 4. Schematic showing nitrogen budget for a typical cropping system.

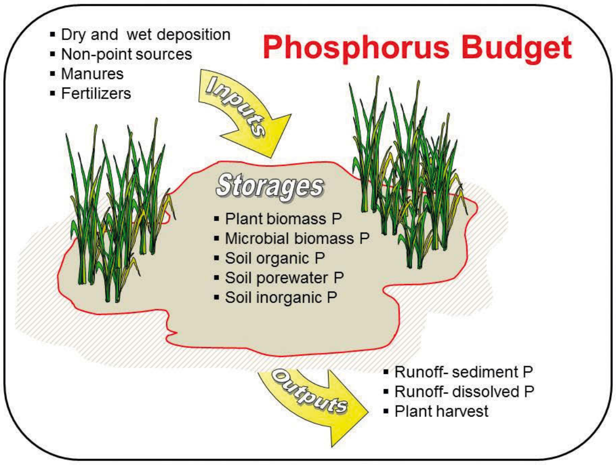

FIGURE 5. Schematic showing phosphorus budget for a typical cropping system.

and natural areas such as forests. Many times the nutrient budget for agriculture is a component of a larger watershed nutrient budget. Therefore, one objective of a nutrient budget should be to determine the specific scale of the budget to be developed. Several reviews of N budget research in agriculture have been made (Allison, 1955 and 1966; Legg and Meisinger, 1982; Meisinger *et al.*, 2008).

Nutrient budgets and balances have been determined for watersheds that include agricultural and urban areas. For example, McMahon and Woodside (1997) studied eight sub-basins in the Albemarle-Pamlico drainage basin in the United States. They used published information about agriculture in the basins and directly measured values to construct a N budget for the watershed. Greatest stream N concentrations were found in areas dominated by agriculture, intermediate loads were from mixed agricultural/urban areas, and lowest outputs were from agricultural/forested areas. Atmospheric N comprised a significant source of N and pointed to challenges in managing this source in the budget. One-half of the nutrient inputs could not be accounted for by stream loads or crop removal. Using a similar approach, Harned, Brian Atkins and Harvill (2004) found that high N concentrations in streams were associated with high urban development, and high P concentrations were associated with agriculture. Improvements in waste water treatment probably were associated with decreasing trends in stream N levels after 1987. Annual variations in animal populations and fertilizer consumption were associated with changes in stream N and P concentrations.

Challenges for nutrient budgets

Nutrient budgets are still difficult to calculate, even by today's scientists. Nitrogen, for example, exists in various oxidation states in the environment, so different analytical methods are required to quantify all the N forms and processes in the soil. Nitrogen undergoes numerous transformations in the environment and can move between pools in the budget. Nitrogen uptake by crops can be determined by the "difference" method where N accumulation by plants growing without N fertilization are compared with N accumulation by fertilized crops. Phosphorus can precipitate with calcium and can be adsorbed onto soil particles so that it becomes difficult to measure the P pool that is currently important for plant uptake in a nutrient budget. Quantifying the pools of stored N and P (Figures 4 and 5) and tracking mineralization and immobilization in these pools are particularly challenging aspects of nutrient budget research. Some scientists have used controlled-environment greenhouse-scale and micro-plot studies to calculate nutrient budgets, often as a prelude to larger-scale field studies.

Pools of nutrients lost from the farm are a challenge to quantify because of the need for special equipment and the associated operational costs. If there are streams entering or leaving the farm, stream flow and nutrient content can be measured. Leaching loads can be measured by drainage lysimeters. Run-off and leaching loads are sometimes measured directly in a nutrient budget calculation, but more often are included in the "unaccounted-for" nutrient pool. In addition to leaching and runoff, gaseous losses (volatilization and denitrification) are often not measured directly and included in the unaccounted-for pool.

Animal production in agriculture has been at the forefront in understanding nutrient budgets and balances on the farm, especially dairy farms around the world (Castillo *et al.*, 2000; Spears, Young and Kohn, 2003; Cabrera *et al.*, 2006; Wang *et al.*, 2010). Cornell University (2013) developed a nutrient balance calculator in Excel format for any type of farm (livestock, crops, etc.) to help farmers understand more about the quantities of inputs and outputs on their own farms.

Information on nutrient budgets for horticultural crops is limited. In a study on N budgets for butternut squash in Canada, Van Eerd (2010), found that apparent N losses increased significantly when fertilizer N rates increased above the recommended rate and that squash did not respond to fertilization on some soils. The author pointed out that farmers should identify those soils that would likely be non-responsive to N fertilizer before they apply fertilizer. Jackson (2000) followed nitrogen-15 (^{15}N) in a lettuce and cover crop system in California, found that of the 40 percent of N mineralized from a cover crop, 50 percent was taken up by the lettuce, 25 percent was lost in gaseous forms, and the remainder ascribed to potential leaching loss and inorganic and microbial N in the soil. Hochmuth and Bennett (2011) used published information from numerous sources to calculate a P budget for Florida watermelons. Over the last 20 yr, the Florida watermelon crop has transitioned from using seeded to seedless cultivars. The seeds contain most of the P in the fruits and therefore a significant amount of P left the State when seeded cultivars were shipped. When farmers switched to seedless cultivars (very little P in the fruits) the P fertilizer inputs were not reduced resulting in considerable P accumulation in the Statewide budget today compared with 20 yr ago. Nearly 55 times as much P was exported in the 1985 watermelon crop compared with 2008.

Importance of nutrient budgets

Nutrient budgets can provide information on surplus or deficit of nutrients with respect to crop needs. In many areas of the world, both N and P fertilizers are applied in excess of crop needs. Application rates are usually determined based on nutrient use efficiency of crops and yields. Long histories of fertilizer and other P-rich material applications have built up soil P levels in many watersheds, and the residual P may be sufficient to meet some or all the requirements of the crops grown on these soils. Agricultural scientists and some farmers use plant and soil analyses to determine the P status and requirements of crops. The most common approach is to use soil test procedures, which involve extraction of soils with selected chemicals. The amount of P extracted is related to crop yields to determine the P fertility of soils. These relationships have been developed for various crops and soil types. Calculating agricultural nutrient budgets and balances like those illustrated above will be increasingly important for determining and refining nutrient best management practices on farms. This process will take considerable and continued investment in research and education. Unless the inputs and outputs in agricultural watersheds are understood and can be demonstrated to farmers it will be difficult to make progress in reducing nutrient losses from farms (Vitousek *et al.*, 2009).

ROLE OF ISOTOPIC AND NUCLEAR TECHNIQUES IN NUTRIENT MANAGEMENT

The ^{15}N stable isotope can be used to determine N uptake from labelled N fertilizers by plants and to trace the flows of applied N as well as developing more accurate nutrient budgets. With labelled N, the researcher must know the goal of the research and select the proper labelled N form, for example N-15 nitrate ($^{15}NO_3$-N) or N-15 ammonium ($^{15}NH_4$-N) (Jankowski, Schindler and Holtgrieve, 2012). More information on the benefits and challenges with using labelled N in crop- and watershed-scale N budgets is provided by Meisinger, Calderon and Jenkinson (2008). Methodology based on the use of a novel isotope tracer, oxygen stable isotope in phosphate (delta oxygen-18 [δ^{18}O-P]), to investigate P transport in soil–plant systems is currently being evaluated to bring new insights into the understanding of the processes driving P cycling in the soil and environment (Tamburini *et al.*, 2010).

CONCLUSIONS

Long-term goals of nutrient management in agricultural watersheds should include conservation and enhancement of soil fertility and soil quality. Environmental regulations and related policies to reduce nutrient loads from ecosystems should seek to improve soil quality as a first step for improving nutrient use efficiency by crops. Future soil and nutrient management practices must be compatible with extreme climatic change events. Economic values of soil ecosystem services and tradeoffs associated with changes in soil and nutrient management practices should be considered in crop production. Nutrient budgets should be determined for site-specific conditions and used in developing recommendations for sustainable production of crops while reducing nutrient loads to adjacent water bodies.

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Assessment of the Impact of Reclaimed Lands for Rice Fields on Water Budget and Quality for Sustainable Agriculture in Northeast China: Using Isotopic Tracers

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ABSTRACT

The Sanjiang Plain in Northeast China is one of the main grain production areas in the country and is supporting a rich biological diversity. However, the wetlands and forest lands have shrunk to one fifth of their original size in the last five decades because of increasing population and land reclamation for agriculture. A major part of the reclaimed land has been used for rice production (rice wetlands). Sustainable management of these rice wetlands is important to protect water resources. Isotopic signatures of oxygen-18 (delta O-18, $\delta^{18}O$) and hydrogen-2 ($\delta^{2}H$), water chemistry and depth of groundwater were monitored on three farms, namely, Honghe (HH), Qianfeng (QF) and Qianshao (QS). Results showed that the $\delta^{18}O$ for groundwaters in all three farms varied from –8.8 per 1000 (expressed as mil, ‰) to –13.8‰ with an average of –12.4‰. However, $\delta^{18}O$ for groundwater from a single farm showed large variations, suggesting a complex source and mixing in the groundwater. Groundwater nitrate (NO_3^-) levels underneath these rice wetlands were less than baseline values (6 mg NO_3^-/L) suggesting that NO_3^- contamination of groundwater under the Sanjiang Plain wetlands is not a major environmental issue. The groundwater $\delta^{18}O$ in HH (–12.9‰) and QF (–13.0‰) farms showed that lateral groundwater flow probably dominates the groundwater recharge. However, the groundwater on the QS farm is uniformly enriched with an average $\delta^{18}O$ of –12.2‰. This suggests that the aquifer on the QS farm is probably influenced by the vertical infiltration, and there exists a strong groundwater–surface water interaction. The results have important implications for wetland reclamation and agricultural production on the Sanjiang Plain.

Key words: *isotopic signatures, groundwater, nitrate, wetlands, Sanjiang, water management.*

INTRODUCTION

Sustainable agricultural development requires optimized water management at the watershed or river basin scale in order to achieve efficient water use and sustainable agricultural productivity. Therefore, it is necessary to understand the storage and nutrient attenuation capacities of water systems and the interactions of wetlands rice. Northeast China, especially in the so-called Songhuajiang and Sanjiang catchments where there are many wetlands, is probably one of the most suitable regions for agriculture on the North China Plain (Liu *et al*., 2005). The region is a major source of food supply for the population. The 'black soil' prevalent in the area is very rich in nutrients, and the annual precipitation is high in most part of the region. Other conditions are also favourable for agriculture. In order to ensure food security for the country, the local governments have launched plans to increase crop production in the region by an estimated five million tonnes (t) per year through improved water conservation measures. To achieve this ambitious goal means that more water will be diverted from surface and groundwater sources to meet irrigation needs in the crop areas and reclamation of more wasted land will have to be carried out in the west of Jilin Province and the low land of Heilongjiang Province. The excess water from these irrigated rice wetlands will recharge groundwater leading to a groundwater table rise and salinization risks. It will also impose an additional risk on the quality of surface water. Therefore, it is of paramount importance to assess these impacts in order to sustain the agricultural production in this area.

The Sanjiang Plain in the northeast of China, with an area of about 1.2 million ha, is the largest food supply base in China. It is famous for large-scale land reclamation and 35 percent of the wetlands have been reclaimed for rice paddies since the 1950s. In order to meet the crop water requirement for paddy cultivation, groundwater exploitation is at about 2.2 million mega litres (L/yr). This will lead to a steady decline of groundwater level and deterioration of water quality.

In short, issues of water and nutrient budgets of agricultural wetlands, as well as hydrological and biogeochemical processes within and around a wetland system require thorough investigation and understanding in order to increase the efficiency and reduce the risks of agricultural activities on surface and groundwater resources. There is a major water conservation and quality issue in the reclaimed rice lands in the Northeast China region. The question is whether or not irrigation using groundwater can be sustainable in view of the water table decline and surface water quality deterioration. The overall objective of this project is therefore to study the hydrological and biogeochemical processes in rice wetlands systems and to develop and optimize water conservation measures for sustainable agriculture in Northeast China.

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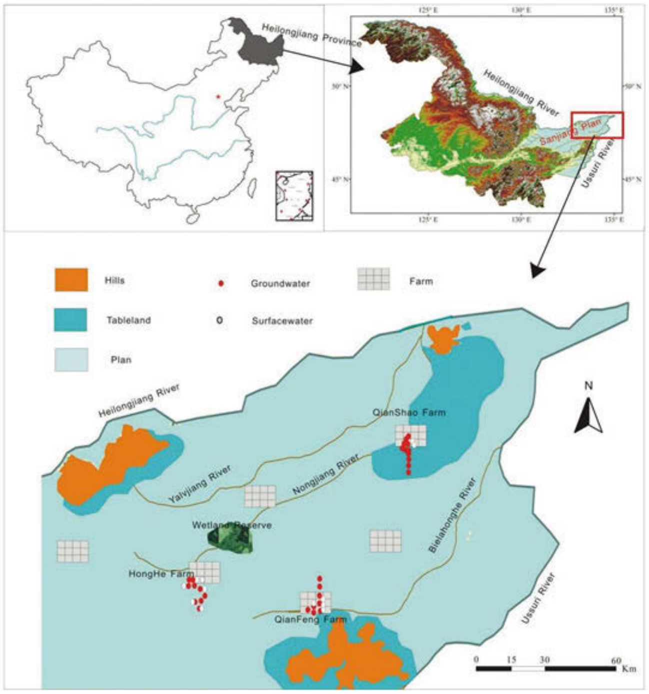

FIGURE 1. The Sanjiang Plain with the Nongjiang and Bielahonghe rivers and the three farms, namely Honghe (HH), Qianfeng (QF) and Qianshao (QS).

MATERIALS AND METHODS

Study area

The Sanjiang Plain (43°49′–48°27′N, 129°11′–135°05′E) is located in the northeastern part of Heilongjiang Province, Northeast China (Figure 1). It encompasses a total area of 6.2 million ha. The Sanjiang Plain is bounded by mountains to the west and south, and the Heilongjiang river and Wusuli river to the north and east, respectively (Figure 1). Two sites namely Heilongjiang and Jilin Provinces were selected for this study.

The elevation of the low plain ranges from 50 to 60 m, while the elevation of the highest mountain is 1 429 m. The mean annual temperature increases from 1°C in the southern mountain region to 3°C in the northern plain (Liu, 2007). The mean annual precipitation in the plain is around 600 mm, most of which falls between June and September, accounting for about 70 percent of annual rainfall. Except for the Songhua River which is a perennial river, there are many ephemeral rivers, e.g. the Nongjiang and Bielahonghe rivers running through the Sanjiang Plain (Figure 1).

The Sanjiang Plain contains a historically famous marsh, named Bei Da Huang (Huang *et al.*, 2009). In the 1940s, more than 5 million ha of marshes and wet meadows existed (Liu and Ma, 2002). However, in order to meet the food demand for the increasing population, part of the plain was reclaimed for agriculture. Thereafter, the cultivated land area increased from about 0.79 million ha in 1949 to 5.24 million ha in 2000. As a result, the wetland area has decreased from 5.35 million ha in 1949 to 0.84 million ha in 2000 (Li, Zhang and Zhang, 2002). Paddy cultivation dominates the agricultural sector, leading to considerable groundwater exploitation (6.65 mega L·ha^{-1}·yr^{-1}, corresponding to 665 mm) and fertilizer application dominates rice production with rice crop receiving 170 kg N·ha^{-1}·yr^{-1} (mainly urea, diammonium and ammonium bicarbonate).

Sampling and analyses

Groundwater samples, as well as surface water in paddy fields, drainage channels, and the rivers, were taken for isotopic (^{2}H and ^{18}O) and chemical analyses from three farms (HH, QF and QS, respectively) at the northeastern part of the Sanjiang Plain in July 2009. Following preliminary interpretation of the data, a further sampling campaign was conducted in August of 2011 along a transect throughout the plain extending 250 km in an east–west direction for measuring ^{2}H and ^{18}O isotopic signatures. Two typical hydrogeological conditions, namely unconfined aquifer to the west and confined aquifer to the east are present on the Plain. Precipitation samples from the Sanjiang station (China precipitation isotope network, CPIN) were collected every month from August 2010 to July 2011. Groundwater monitoring wells were established on each farm (10, 9 and 11 wells in HH, QF and QS, respectively), and groundwater depth information was collected every year for all monitoring wells. Isotopic signatures for oxygen-18 (δ^{18}O) and hydrogen-2 (δ^2H) along with water chemistry were measured. Locations of all samples and monitoring wells are shown in Figure 1a.

Water chemistry was measured using ion chromatography (Dionex-500™) at the Beijing Research Institute of Uranium Geology. The cation measurements were based on National Analysis Standard DZ/T0064.28-93 while anion determinations were based on DZ/T0064.51-93. Alkalinity was measured on an automatic titrator (785 DMP™). Analytical precision was 3 percent based on the reproducibility of samples and standards, and the detection limit was 0.1 mg/L. The charge balance error for all samples was within ± 4 percent. Stable isotope signatures were analysed using a Picarro L1102-i laser absorption water isotope spectrometer in the Water Isotope Lab of Institute of Geology and Geophysics, Chinese Academy of

TABLE 1. Initial isotopic signatures (δ^{18}O and δ^2H) and total dissolved solids for groundwater on three farms

Farm	Groundwater depth (m)	δ^{18}O (‰)	δ^2H (‰)	TDS (mg/L)
HH	15	−12.5	−93	229
QF	18	−12.8	−97	231
QS	20	−12.2	−93	136
HH-Paddy Field		−11.1	−80	103
QF Paddy Field		−10.6	−79	89
HH Channel		−9	−73	92
QS Channel		−9	−77	93

The concentrations of major cations and anions, such as Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, HCO_3^-, CO_3^{2-}, and SO_4^{2-} in groundwater are similar to the baseline of natural groundwater as shown in Figure 2 (Zhang, 2009)

Sciences. Tritium was determined on electrolytically enriched water samples by low-level proportional counting and the results reported as tritium unit (TU) with a typical error of 1 TU. The measurement was performed at the Open Laboratory of Environmental Geology and the Central Laboratory of Hydrogeology, the Ministry of Land Resources, China.

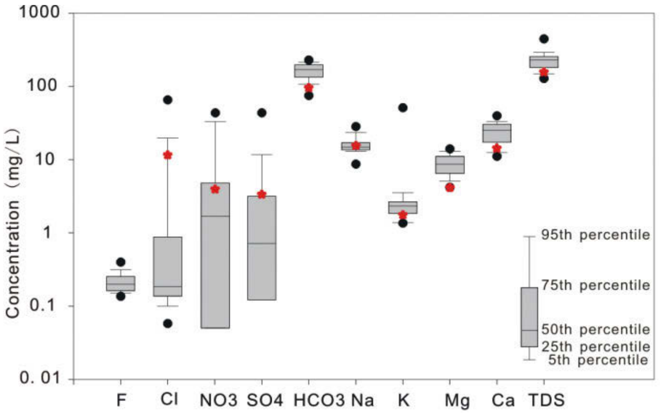

FIGURE 2. Box plots of major anions, cations and total dissolved solids (TDS) of groundwater samples. The red pentagon represents the baseline of the groundwater.

RESULTS AND DISCUSSION

Groundwater quality

The initial groundwater data are presented in Table 1. The total amount of dissolved anions and cations (total dissolved solids, TDS) in groundwater varied widely between the three farms compared with the differences in $\delta^{18}O$ and $\delta^{2}H$ in groundwater between these farms. The channels and the paddy field also had similar $\delta^{18}O$ and $\delta^{2}H$ values as those presented in groundwater.

Concentrations of nitrate (NO_3^-) in groundwater beneath agricultural land concern people most, which is considered to be one

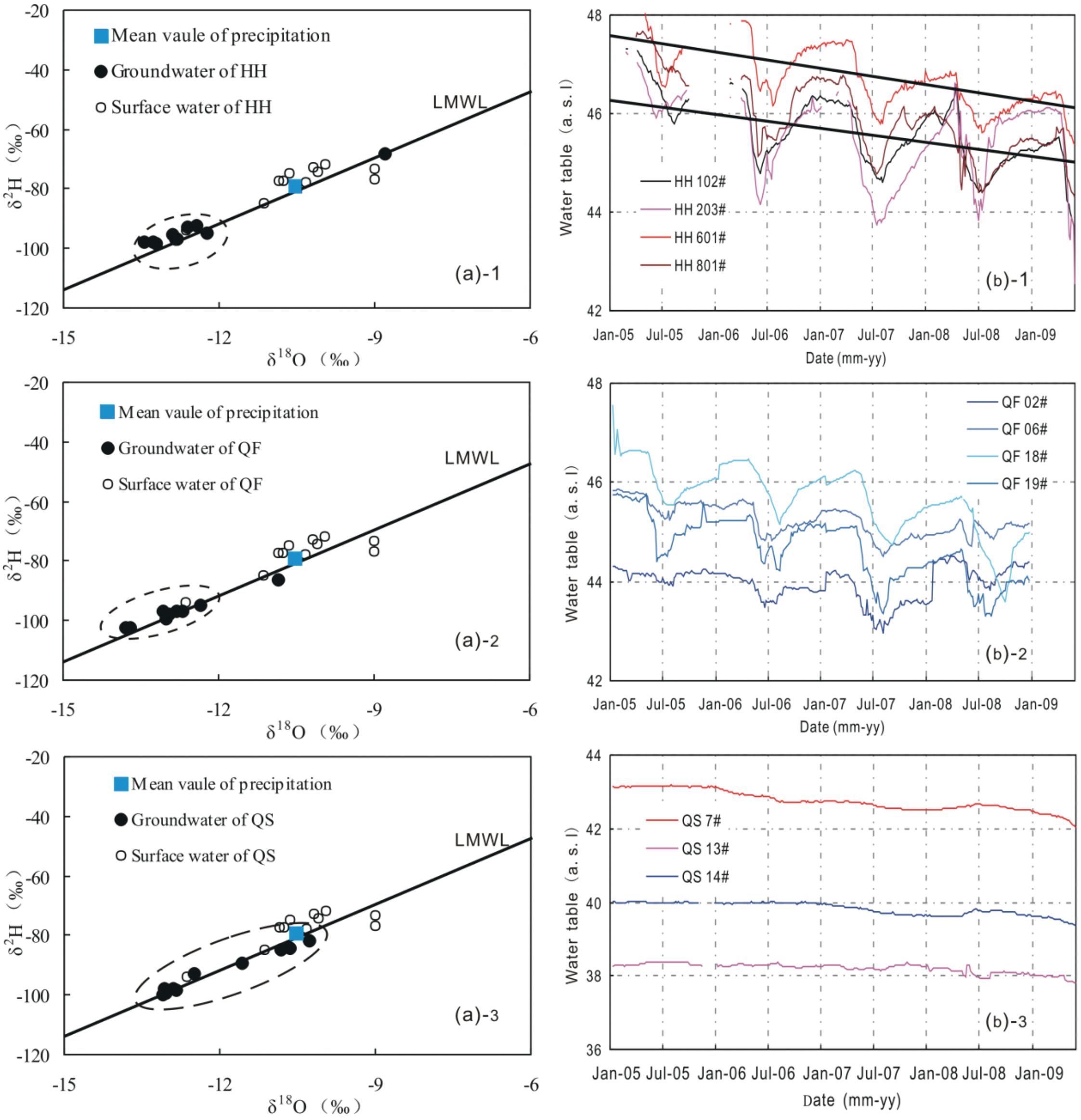

FIGURE 3. Isotopic signatures of precipitation and groundwater on Honghe (HH), Qianfeng (QF) and Qianshao (QS) farms and groundwater depth regimes (LMWL) regression of $\delta^2H = 7.4\ \delta^{18}O–3.1$ with a correlation coefficient of 0.8 (n = 12).

of the parameters for evaluating the sustainability of an agricultural system. About 75 percent of the groundwater samples collected from beneath the rice wetlands had NO_3^- concentrations lower than the baseline (6.6 mg NO_3^- /L). Groundwater NO_3^- ranged from values lower than the detection limit to 17.9 mg/L. The HH9 and QF7 were exceptions, having relatively higher NNO_3^- concentrations (32.9 and 43.2 mg/L, respectively during one sampling event), indicating that elevated NO_3^- input may occur locally. Possible reasons include sampling time relative to the time of fertilizer application, land management practices and probably high spatial variability of NO_3^- in the groundwater. This needs to be further investigated for the respective locations.

Groundwater recharge and residence time

Groundwater recharge

Four categories of recharge to the groundwater are possible on Sanjiang Plain including local rainfall, river recharge, irrigation returns and lateral groundwater flow (flow from the mountain areas with high altitude). According to the rainfall samples collected from Sanjiang station, modern rainfall can be characterized by the $\delta^{18}O$ and δ^2H values. The local meteoric water line (LMWL) is provided by the relationship $\delta^2H = 7.4\ \delta^{18}O - 3$ (Figure 3(a)-3).

The annual weighted rainfall $\delta^{18}O$ and δ^2H values in 2005 at Sanjiang station were –10.7‰ and -79.0‰, respectively. The $\delta^{18}O$ and δ^2H values of water for the Nongjiang River were –10.1‰ and –74.4‰, respectively and the line laid on the LMWL. The $\delta^{18}O$ values of irrigation water from rice wetlands entering the drainage channel ranged from –9.0‰ to –12.6‰, with an average of –10.4‰. The $\delta^{18}O$ for all groundwaters collected from the three farms ranged from –8.8‰ to –13.8‰ with an average of –12.4‰.

The groundwaters were therefore significantly lighter (in ^{18}O) than precipitation, river water and rice wetland and probably reflected high altitude precipitation from the higher mountain range at the west and south (data not shown).

On HH and QF farms, the $\delta^{18}O$ of groundwater ranged respectively from –13.5‰ to –12.2‰ and –13.8‰ to –12.3‰, with averages of –12.9‰ and –13.0‰, respectively. The depleted composition indicates that lateral groundwater probably dominates the groundwater recharge process on these two farms. However, there were exceptions to this observation. Water samples collected from wells HH9 and QF7 had elevated NO_3^- levels and were enriched in $\delta^{18}O$ (–8.8‰ and –10.8‰, respectively). These data suggest that the high levels of NO_3^- are probably accompanied by vertical infiltration (leaching), e.g. rainfall, irrigation, or some combination, which are characterized by enriched $\delta^{18}O$.

Oxygen isotopic composition of groundwater on the QS farm was evenly distributed and ranged from –13.1‰ to –10.3‰ with an average of –12.2‰ (Figure 3(a)–3). The groundwater on the QS farm was enriched with $\delta^{18}O$ compared with that on HH and QF farms. This enrichment suggests that the aquifer on the QS farm is probably influenced by the vertical infiltration of water (irrigation and rainfall water moving through the soil profile) with a relatively strong connection between groundwater and the surface water.

Residence time of groundwater

Tritium is one of the most important transient and ideal tracers used in hydrological research. It is produced naturally in the stratosphere by cosmic radiation on ^{14}N leading to a level of about 15 tritium units (TU) in precipitation (Brown, 1961). The substantial input during late 1950s and early 1960s created a tritium reservoir in the stratosphere, which has contaminated global precipitation systems for over four decades and provides a useful tracer for water originating from this period. A recharge date can be estimated from a decay line, which is constructed using the input function and decay equation with a half-life of 12.32 years (Unterweger *et al.,* 1980). However, there are strong variations in the global distribution of tritium. Circulation in the stratosphere is constrained with respect to latitude, resulting in a latitudinal banding of tritium in rainfall (Eriksson, 1965).

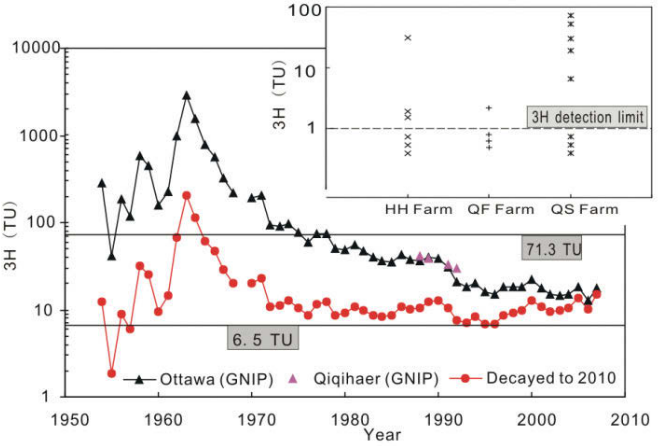

FIGURE 4. Tritium in groundwater, precipitation from 1954 to 2007 and that decayed to 2010.

Figure 4 shows that groundwater recharged before the "bomb test" has tritium levels lower than 6.5 TU. Groundwater with high levels of tritium indicates the influence of the "bomb test" (Figure 4). Tritium levels in the groundwater from HH and QF farms were low, with a narrow range of < 1–1.9 and < 1–2.2 TU respectively, indicating that groundwater on HH and QF farms is older than 50 years.

Groundwater on the QS farm showed a wide range of tritium (< 1–71.3 TU), but levels of tritium are related to the sampling locations. Samples with high levels of tritium (6.5–71.3 TU) were collected near the river, and those collected away from the river showed low levels (< 1 TU). This suggest that groundwater near the river has a relatively short residence time (recharge occurring).

Figure 3 shows the fluctuations in groundwater levels recorded in the period from 2005 to 2009 in the 11 monitoring wells. The measurements highlight the existence of two different groundwater regimes on the three farms. As shown in Figures 3b1 and 2, groundwater levels on HH and QF farms showed similar dynamics. Groundwater levels in these two farms changed significantly and had an intra-annual scale that fluctuated with the groundwater exploitation. On the other hand, groundwater levels in the QS farm declined moderately and the intra-annual fluctuation could not be found. Different regimes suggest that groundwater is more easily recharged at the QS farm, following a short groundwater residence time.

The one exception (HH8) at the HH farm with a tritium level of 31.3 TU further proves the hypothesis that NO_3^- is brought by vertical infiltration. However, groundwater samples with elevated tritium collected at the QS farm were consistently enriched in ^{18}O, but had low levels of NO_3^- (< 17.9 mg/L). A probable explanation is that the source of recharge (precipitation and surface waters) had low levels of NO_3^- (< 6.0 mg/L).

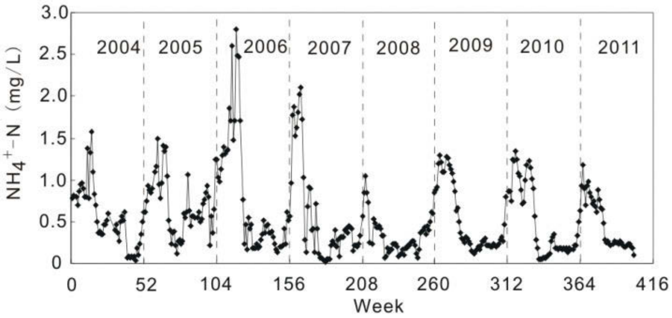

FIGURE 5. Ammonium in the Songhua river (Tongjiang transect) as measured in weekly samples. (Data obtained from the Ministry of Environmental Protection of the People's Republic of China).

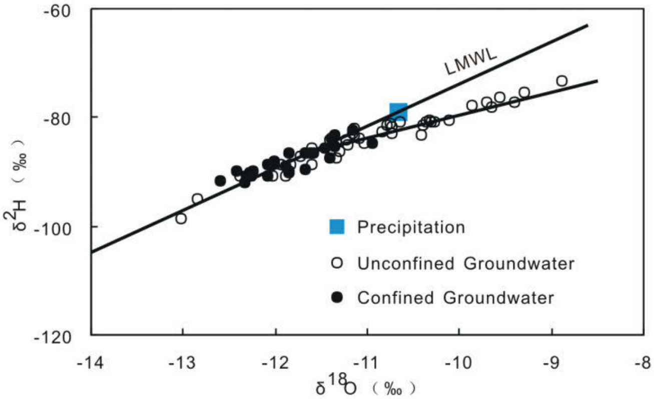

FIGURE 6. Plot of δ^{18}O and δ^{2}H of groundwaters from the Sanjiang Plain.

Implications for agriculture

Nutrient retention capacity of wetland

In April, with N applications amounting to 170 kg/ha (urea or ammonium), the concentrations of ammonium (NH_4^+) and NO_3^- in paddy fields can reach up to 24.2 mg N/L and 3.4 mg·N/L, respectively. However, $NH_4^+$was found in the Songhua River only during the first few weeks of the year (Figure 5). The average concentration of NH_4^+in river water from June to December was 0.3 mg·N/L, and the drinking water standard for NH_4^+ is 0.5 mg N/L. The time of first occurrence of elevated NH_4^+ in water could be due to the leaching of the applied urea fertilizer.

During the growing period, groundwater is pumped to the paddy fields, after which it flows into a small drainage channel and to the river. Compared with the elevated NH_4^+ in paddy fields during the growing season (from May to September), the river NH_4^+ levels were low suggesting riverine wetland might have taken most NH_4^+ (Zedler, 2003; Mander, Hayakawa and Kuusemets, 2005). One of the functions of wetland is to remove nutrients (Maltby, Digby and Baker, 2009). Greater nutrient retention of the catchment would be attributable to the high coverage of natural wetland on the Sanjiang Plain. Natural wetland covers about 13 percent of the catchment area. Studies by Mitsch, Day and Gilliam (2001) and Arheimer *et al.* (2005) showed significant increases in water quality at the catchment scale when wetland accounts for about 2–7 percent of the total catchment.

Spatial arrangement of wetland reclamation

Stable isotope signatures of groundwaters collected from unconfined and confined areas displayed significant differences. In the confined area, δ^{18}O values of groundwaters were depleted (average of –11.8‰) compared with the local weighted mean value for the rainfall (–10.7‰). On the other hand, in the unconfined area, the δ^{18}O for groundwaters varied widely (–8.9‰ to –13.0‰), and a plot along a line with a slope of 5.3 had an intercept on the local meteoric water line at –11.8‰ (Figure 6), which is identical to the mean value of groundwaters sampled in the confined area. These data suggest that the Sanjiang Plain aquifer is significantly recharged by the high altitude precipitation from the surrounding mountain which is characterized by depleted isotopic signatures. However, in the unconfined area, extra recharge exists and the groundwater system is recharged from the land surface by rainfall or by infiltration from rivers, irrigation or a combination of each.

CONCLUSIONS

The stable isotopic signatures, tritium and water chemistry data demonstrate that the use of reclaimed land for rice production on the Sanjiang Plain is sustainable as far as water pollution is concerned as it has not affected the quality of groundwaters even though 170 kg N·ha^{-1}·yr^{-1} as composite fertilizer is being applied. Limited vertical infiltration (leaching) of water from rice wetlands reduced the influence of agricultural activities on the NO_3^- contamination of groundwaters. The low levels of NH_4^+ in surface waters (wetlands and channels) and of NO_3^- in groundwaters near the river are probably attributable to NO_3^- and NH_4^+ retention in wetlands. With certain wetland coverage, groundwater quality is safe on the Sanjiang Plain. However, with limited recharge, groundwater levels will continue to decline, imposing a risk on sustainable agriculture. Therefore integrated use of surface water and groundwater is recommended.

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Gaseous Nitrogen Fluxes and Nitrous Oxide Isotopic Signatures in Riparian Grey Alder Forests

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ABSTRACT

Nitrous oxide (N_2O) and nitrogen (N_2) gas emissions and isotopic signatures of N_2O and nitrate (NO_3^-) in groundwater of two differently loaded riparian grey alder stands in southern Estonia were investigated over a period of nine months. One area was a 38-year-old stand in Porijõgi (PJ), where uphill agricultural activities had been abandoned since the middle of 1990s, and the second area was a 55-year-old alder stand in Viiratsi (Vi), which still receives polluted lateral flow from uphill fields applied with pig slurry. Gas fluxes were measured in six sampling sessions, and water samples were analysed for nitrate (NO_3^-), N_2, N_2O, and isotopic signatures of oxygen-18 (delta ^{18}O, $\delta^{18}O$) and nitrogen-15 (delta ^{15}N, $\delta^{15}N$) in N_2O and NO_3^- in four of the six sessions. The N_2O and N_2 fluxes from both riparian zones did not differ significantly, being 9.6 ± 4.7 and 14.5 ± 3.9 μg N_2O–N $m^{-2}\cdot h^{-1}$, and 2 466 ± 275 and 3 083 ± 371 μg N_2–N $m^{-2}\cdot h^{-1}$ in PJ and Vi sites respectively, suggesting that gaseous N_2 is the dominant gas emission from these alder stands. The isotopic signatures of N_2O and NO_3^- were not significantly different between PJ and Vi study sites suggesting possible conversion of NO_3^- to N_2O in both areas. The greater prevalence of N_2 emissions over N_2O in both areas, and the strong relationship between NO_3^- and N_2O concentrations ($r = 0.92$, with $p < 0.01$) further suggested that denitrification is the main source of N_2O and N_2 fluxes in these grey alder stands. The dominant emission of N_2 over N_2O showed that these riparian zones play an important role in reducing the emissions of N_2O while removing NO_3^- from water.

Key words: *denitrification, nitrogen, isotopic signatures, nitrate, nitrification, nitrous oxide, site preference.*

INTRODUCTION

Riparian ecosystems are important landscape elements that control water quality in rivers and other water bodies but they are also potential hot-spots of nitrous oxide (N_2O) emission to the atmosphere (Villain *et al*., 2012). Nitrous oxide plays an important role in altering stratospheric chemistry, including depletion of the ozone layer. The radiative forcing of N_2O is 296 times higher than that of the same amount of carbon dioxide (CO_2), and is therefore a potent greenhouse gas (GHG). Despite its relatively minor contribution to global warming (6 percent), a small increase in emissions can lead to a large accumulation of N_2O in the troposphere, a phenomenon resulting from the long residence time of N_2O, approximately 120 years (Forster *et al*., 2007). Nitrous oxide is produced by (i) reduction of nitrate (NO_3^-) to nitrogen gas (N_2), and (ii) oxidation of ammonium hydroxylamine (NH_2OH) to nitrite (NO_2^-), and the reduction of NO_2^- to N_2O and N_2 under aerobic conditions. Apportioning N_2O to these source oxidation-reduction processes is a challenging task. A better understanding of the N_2O processes is, however, required in order to improve mitigation strategies (Well *et al*., 2012).

Considerable NO_3^- reduction is possible, especially in agricultural areas with high N fertilizer inputs. Dinitrogen (N_2), the main gaseous component of Earth's atmosphere, is the final product of this process, and thus the quantification of groundwater N_2 arising from denitrification (excess N_2) can facilitate the reconstruction of historical N inputs, because NO_3^- loss is derivable from the sum of denitrification products (Weymann *et al.,* 2008). The concentration of excess N_2 produced by denitrification in groundwater is estimated by comparing the measured concentrations of argon (Ar) and N_2 with those expected from atmospheric equilibrium, assuming that the noble gas argon (Ar) is a stable component (Weymann *et al.,* 2008). It is also very important to consider the excess N_2 value when calculating indirect N_2O emission from the aquifer resulting from NO_3^- leaching (Weymann *et al*., 2008).

It has been suggested that the information obtained from measuring the intra-molecular distribution of ^{15}N on the central (α) and the end (β) position of the linear N_2O molecule is crucial for a better understanding of the apportioning of N_2O between nitrification and denitrification, but also source and sink processes (Toyoda *et al*., 2011). The N_2O site-specific ^{15}N signatures from denitrification and the NH_2OH to N_2O pathway of nitrification have been shown to be clearly different, making this signature a potential tool for N_2O

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source identification. Most published studies have been dedicated to the analysis of ^{15}N and ^{18}O isotope and isotopic signature ($\delta^{15}N_\alpha$ and $\delta^{15}N_\beta$) of emitted N_2O (Toyoda *et al.,* 2011), while there are only a limited number of studies dedicated to the analysis of dissolved N_2O in groundwater (Well *et al*., 2012). The main objective of this study was therefore to compare gaseous N_2O and N_2 fluxes with the isotopic signatures of N_2O and NO_3^- in the groundwater of two differently loaded riparian alder stands in southern Estonia.

MATERIALS AND METHODS

Study sites

The study areas are (i) a 38-year-old stand in Porijõgi (58°12′41″N, 26°46′55′E), in which uphill agricultural activities had been abandoned since the middle of the 1990s, and (ii) a 55-year-old stand in Viiratsi (58°20′N, 25°39′20″E), which still receives polluted lateral flow from uphill fields fertilized with pig slurry (Figure 1). The estimated lateral N inflow in Viiratsi is twice as high as in Porijõgi (Soosaar *et al.,* 2011).

In the Poriõgi area, a 20-m-wide grey alder stand grows on a Thapto-Mollic (Endogleyic) Gleysol with groundwater table depths of 0–0.8 m and 0–0.1 m in the upper and lower sites, respectively. In Viiratsi, a 12-m-wide wet patch (*A. incana* — *Filipendula ulmaria*) on Mollic Gleysol (considered as ‘upper’ site with groundwater table depth 0–0.05 m) is followed by a 28-m-wide grey alder forest on Thapto-Mollic Endogleyic Umbrisol (considered to be a ‘lower’ site with groundwater depth of 0–0.5 m; Figure 1). At each study site in both areas, 50 mm water sampling wells and collars for gas sampling chambers were installed.

Gas sampling and analyses

The closed-chamber method was used for the measurement of N_2O fluxes, and the helium–oxygen (He–O) method (Teiter and Mander, 2005) was used for the measurement of N_2 emissions. Gas samplers were installed in five replicates at upper and lower sites in both the Porijõgi and Viiratsi study areas (Figure 1). During each gas sampling session at each microsite, the depth of the groundwater table (cm) in observation wells (using 50 mm internal diameter, 1.5 m deep PVC pipes perforated and sealed in a lower 0.5 m part), and soil temperature were measured at three depths (0–10, 20–30 and 30–40 cm).

Gas sampling was carried out once a month in April, May, July, August, October, November and December 2008 using standard gas collection procedures (Mander *et al.,* 2003). The soil temperature, redox potential and water depth in the sampling wells were measured simultaneously, and the NH_4^+–N and NO_3^- –N concentrations in the soil samples were analysed using standard methods (APHA, 1989). The gas concentration in the collected air was determined using the Shimadzu 2014 gas chromatographic system.

Intact soil cores (0–10 cm) were taken from the sites in which the gas samplers were installed. Soil samples were collected immediately after gas sampling. Soil samples were weighed, kept at low temperature (4°C) and transported to the laboratory for N_2 and N_2O measurements by the He–O method (Soosaar *et al.,* 2011).

Water sampling and analyses

For the analysis of N_2O, N_2, NO_3^- and their isotopic signatures, water samples were taken in 4–9 replicates from water sampling wells using a peristaltic pump. The samples were stabilized with the addition of 0.1 ml saturated mercuric chloride ($HgCl_2$) solution. Nitrous oxide, N_2 and ammonium (NH_4^+) were measured using standard procedures. The N_2 produced from denitrification was calculated using the method of Weymann *et al.* (2008).

Initial water nitrogen concentration as nitrate (NO_3^--N) at a given location ($cNO_3^-{}_{t0}$) on the aquifer surface is defined by the NO_3^--N concentration of the recharging water before alteration by denitrification in the groundwater (Weymann *et al.,* 2008). It is assumed that NO_3^- consumption on the groundwater flow path between the aquifer surface and a given sampling spot originates from denitrification. The process results in the accumulation of gaseous denitrification products (N_2O and N_2) in groundwater. The concentration of N_2 in groundwater is referred to as Excess N_2. From this, $cNO_3^-{}_{t0}$ can be calculated as the sum of the residual substrate and accumulated products (Weymann *et al.,* 2008). Thus $cNO_3^-{}_{t0}$ is given by the following equation:

$$cNO_3^-{}_{t0} = Excess\ N_2 + cNO_3^- + cN2 \tag{1}$$

where cNO_3^- is residual NO_3-N; and cN_2O is N_2O-N concentration (i.e. N concentration as N_2O) in the groundwater.

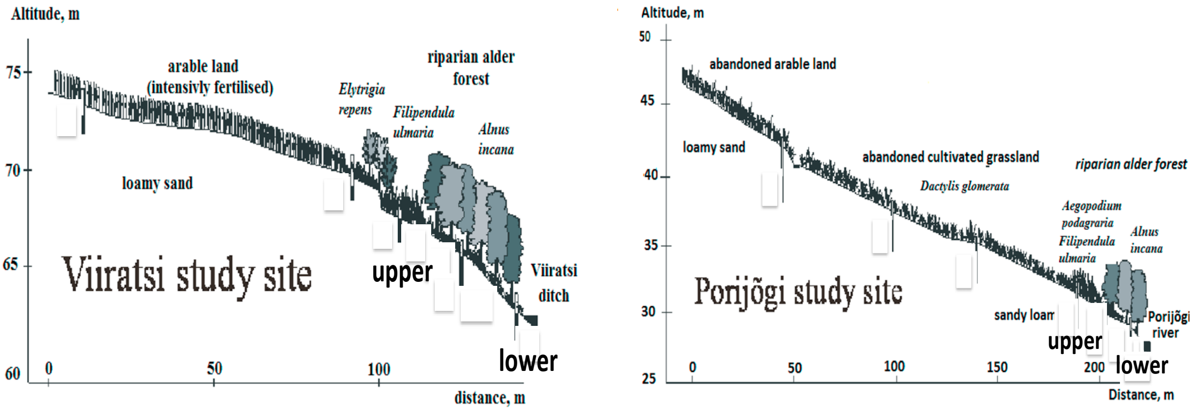

FIGURE 1. Illustrations of riparian study sites in Estonia.

Reaction progress (RP), the ratio between the products and the starting material of a process can be used to characterize the extent of NO_3^- elimination by denitrification. It is calculated as follows:

$$RP = \frac{Excess\ N_2 + cN_2O}{cNO_{3\,t0}^-} \qquad (2)$$

In this study, all of the concentration values are calculated to mg/L.

Isotope analyses

The isotopic signatures ($\delta^{18}O$ and of $\delta^{15}N$) in N_2O, the bulk ^{15}N (the total ^{15}N signature in N_2O, $^{15}N^{bulk}$-N_2O) and ^{15}N from the central N position ($^{15}N^{\alpha}$), were measured using isotope ratio mass spectrometry (Well *et al.,* 2012).

The site preference (SP‰) ^{15}N (i.e. the ^{15}N in the N^{β} position of N_2O) was obtained using the following equation:

$$SP = 2(^{15}N^{\alpha} - {}^{15}N^{bulk}N_2O) \qquad (3)$$

The isotopic ratios of a sample (R_{sample}) were expressed as the deviation from the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of the reference standard materials (R_{std}), atmospheric N_2 and standard mean ocean water (SMOW) respectively as

$$\delta X = \left(\frac{R_{sample}}{R_{std}} - 1\right)1000 \qquad (4)$$

where $X = {}^{15}N^{bulk}$-N_2O, $^{15}N^{\alpha}$, $^{15}N^{\beta}$, or ^{18}O.

Statistical analysis of data

Linear correlation analysis and a *t*-test were used to compare the relationship between the variables. For all cases, the significance value of $p < 0.05$ was accepted.

RESULTS

Gaseous nitrogen fluxes

The average values of N_2O and N_2 fluxes from both riparian zones did not differ significantly throughout the whole study period (9.6 ± 4.7 and 14.5 ± 3.9 μg N_2O–N $m^{-2}\cdot h^{-1}$ and 2 466 ± 275 and 3 083 ± 371 μg N_2–N $m^{-2}\cdot h^{-1}$ in Porijõgi and Viiratsi, respectively). The N_2:N_2O ratio in Viiratsi (278 ± 60) was significantly lower than in Porijõgi (995 ± 360) (Figure 2).

Different nitrogen forms in water samples

The average N concentrations as NH_4^+(NH_4^+–N) in groundwater for the whole study period in Viiratsi were significantly lower than those in Porijõgi (Figure 3a). The measured groundwater NO_3^--N and N_2O-N concentrations were significantly lower in Porijõgi than in Viiratsi (Figure 3a).

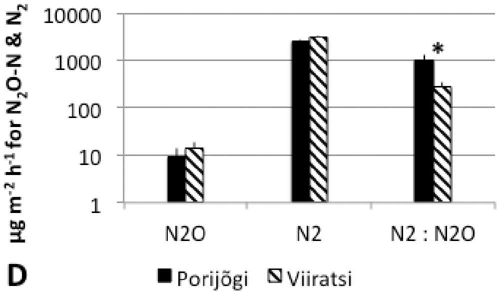

FIGURE 2. N_2O and N_2 emissions and N_2:N_2O ratios averaged over the whole study period (* indicates significant at $p < 0.05$).

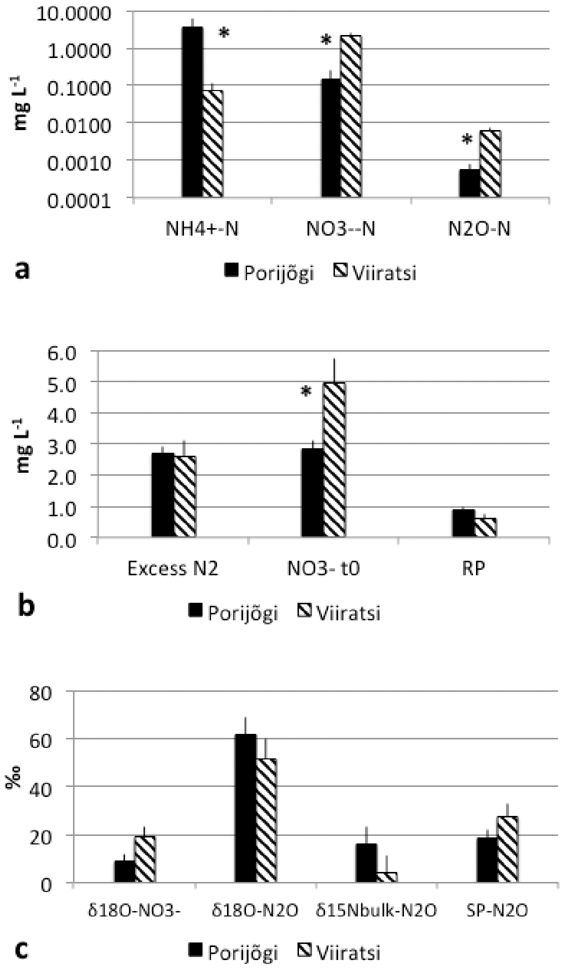

FIGURE 3. NH_4^+-N, NO_3^- -N, N_2O-N (a); excess N_2, initial NO_3^- -N ($NO_3^-t_0$), reaction progress (RP) (b); $\delta^{18}O$-NO_3^-, $\delta^{18}O$-N_2O, $\delta^{15}N^{bulk}$-N_2O, and site preference of the N_2O molecule (SP-N_2O) (c) in Porijõgi and Viiratsi (* indicates significant at $p < 0.05$).

The excess N_2 concentration in both Porijõgi and Viiratsi was quite similar (Figure 3b). The average value of $NO_3^-{}_{t0}$ was significantly higher in Viiratsi than in Porijõgi (Figure 3b). The RP value was also not significantly different between Porijõgi and Viiratsi (Figure 3c)

Isotopic signature ($\delta^{18}O$ in NO_3^-, $\delta^{18}O$ in N_2O, and $^{15}N^{bulk}$ in N_2O) values were not significantly different between Porijõgi and Viiratsi (Figure 3c). Also there was no significant difference in isotopic signature of SP-N_2O between Porijõgi and Viiratsi (Figure 3c).

Relationship between excess N_2, different nitrogen forms in groundwater and N_2O isotopic signatures

Groundwater N_2O-N correlated negatively to reaction progress (RP) (Figure 4A). The excess N_2 related positively to N_2O (Figure 4B), while the site preference (SP) N_2O was correlated negatively to the bulk ^{15}N in N_2O (Figure 4C) and positively to the $\delta^{18}O$ of NO_3^- (Figure 4D). The bulk ^{15}N in N_2O also correlated negatively to $\delta^{18}O$ of NO_3^- values (Figure 4E).

N_2O emissions correlated positively with NO_3^--N, N_2O-N and $NO_3^-{}_{t0}$ concentrations in groundwater (Table 2). Similarly, a signifi-

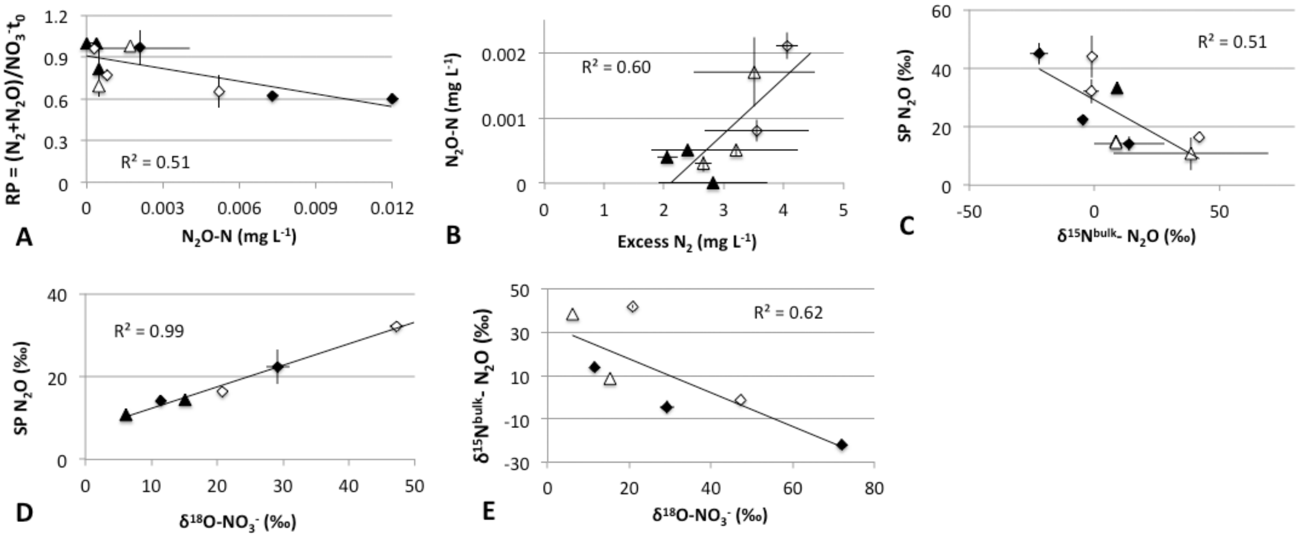

FIGURE 4. Correlation between N_2O, reaction progress (RP), excess N_2, bulk ^{15}N in N_2O, site specific (SP) N_2O, $\delta^{18}O$ in NO_3^- in Porijõgi (triangles) and Viiratsi (diamonds) in Estonia (The open and closed symbols refer to upper and lower sites at each location).

TABLE 2. Correlation coefficients between N_2O and N_2 emission, water characteristics (* = $p < 0.05$; ** = $p < 0.01$)

	NO_3^--N	N_2O-N	NO_3^--t_0
N_2O emissions	0.53*	0.66*	0.92**
N_2 emissions	0.66*	0.86**	0.48

cant positive correlation was also found between N_2 emissions and NO_3^--N and N_2O-N concentrations (Table 2).

DISCUSSION

Gaseous nitrogen fluxes

Due to intensive N cycling in alder stands, gaseous N fluxes in these ecosystems are also intensive. In a long-term study (2001–2009) on gaseous N fluxes from the Porijõgi and Viiratsi areas, the range of N_2O was from -0.6 to 87 µg N_2O-N $m^{-2} \cdot h^{-1}$ in Porijõgi and 0.5–38 µg N_2O-N $m^{-2} \cdot h^{-1}$ in Viiratsi, showing somewhat higher to medium values in Viiratsi (1.7 and 2.1 µg N_2O-N $m^{-2} \cdot h^{-1}$ for Porijõgi and Viiratsi respectively). The N_2:N_2O ratio, however, was significantly higher in Porijõgi, ranging between 10–7600 and 40–1200 in Porijõgi and Viiratsi correspondingly (Soosaar *et al.,* 2011). These results are consistent with earlier studies carried out in Porijõgi and Viiratsi (Teiter and Mander 2005). On the other hand, N_2:N_2O ratio in riparian alder forests was up to two magnitudes higher than that reported for fertilized fields (Bol *et al*., 2003). These high ratios can probably be attributed to relatively long residence time of N_2O due to low diffusivity of N_2O in wet soils and/or further conversion of N_2O to N_2.

Different N forms in water samples

In Viiratsi, NH_4^+-N concentrations were always very low (< 0.5 mg/L), whereas in Porijõgi, high concentrations were recorded in the upper site in May (3.5 ± 2.7 mg/L) and October (22.3 ± 5.7 mg/L). This might be related to the lower groundwater NH_4^+-N level during these sampling sessions. Elevated NO_3^--N (> 1 mg/L) has mostly been found in Viiratsi, but not in Porijõgi. Possible reasons for the relatively low NO_3^- levels in Porijõgi are inhibited nitrification under saturated conditions, NO_3^- leaching and intense denitrification. The excess N_2 ranged from 1.5 to 4.5 mg/L at most sites. The highest values were observed in Viiratsi, which coincided with higher NH_4^+-N and NO_3^--N levels. This can be considered as evidence of intense denitrification with associated N_2O formation (Well, Weymann and Flessa, 2005) and is supported by the higher N_2O-N levels in Viiratsi, with concentrations mostly >10 µg/L and up to 100 µg/L compared with Porijõgi.

Isotopic signatures of NH_4, NO_3^- and N_2O

High values of $\delta^{18}O$ in N_2O (> 40‰) measured in the field are typical for N_2O production by denitrification in aquifers (Well *et al.,* 2012). Such values were also found in Viiratsi at times of elevated NO_3^- levels suggesting that N_2O emission processes are similar and are related to NO_3^- levels. The $\delta^{18}O$ in NO_3^- (varying from 6 to 72‰) reported in this study are comparable with those published in earlier studies on the $\delta^{18}O$ of NO_3^- in groundwater under agriculture (Well *et al*., 2012)

The comparison between $\delta^{15}N$ in NO_3^- and the bulk ^{15}N in N_2O ($\delta^{15}N^{bulk}N_2O$) shows that the difference between these values is approximately 20 to 30‰, which is in line with the isotopic signatures recorded during NO_3^- reduction to N_2O via denitrification, suggesting that denitrification may be the main process responsible for N_2O emissions in alder stands Data from this study showed that $\delta^{18}O$ in N_2O was greater than 35‰ and SP was greater than 10‰. This is indicative of the production of N_2O by denitrification and the partial reduction of N_2O to N_2 (Well *et al.,* 2012).

The relationship between emitted N_2, different N forms in groundwater and N_2O isotopic signature

A significant negative correlation was found between N_2O-N concentrations in gas samples collected from chambers and RP (Figure 4A), which is typical evidence for the domination of denitrification processes in aquifers (Well *et al*., 2012). Another indicative characteristic of denitrification was the strong positive correlation ($R^2 = 0.99$) between $\delta^{18}O$ in NO_3^- and SP values (Figure 4D). However, Porijõgi, with its high $\delta^{18}O$ and low SP values, seems to be different. The low

SP could be explained by nitrification–denitrification with little reduction to N_2. Therefore this might be related to the changing water table in the upper site that temporarily allows sufficient aeration of soil and consequently enhances nitrification.

Perspectives for further studies

The increased N_2 and N_2O emissions in th 1e Viiratsi study area as shown in this study may be a result of the age (> 50 years) of the grey alder stand compared with that at Porijõgi (38 years old), but may also be caused by the long-term nutrient load of this riparian alder stand (Soosaar *et al.*, 2011). However, over time the buffering capacity of continuously loaded riparian buffers will decrease, requiring careful management of these riparian forests (e.g. selective cutting of older trees). Further studies are recommended to clarify the impact of age and environmental stress factors on denitrification of the riparian buffer ecosystems.

In general, for a better understanding of the relationship between nitrification–denitrification processes and in order to distinguish between N_2O sources in riparian zones and wetlands in general, a more detailed and long-term comparison is needed of potential lateral N_2O fluxes (groundwater discharge) using isotopic signatures of both water and gaseous emissions. The latest development in research technology allows the use of novel laser spectroscopic techniques for the continuous analysis of N_2O isotopic signatures *in situ* (Köster *et al.,* 2013). This would open up new horizons in isotope studies in all ecosystems.

CONCLUSIONS

The main gaseous flux from both riparian alder stands was in the form of N_2, which was 278 (Viiratsi) to 995 times (Porijõgi) higher than the amount of N_2O emitted. Nitrous oxide accumulation in the groundwater was moderate, i.e. not higher than typical values in NO_3^-contaminated denitrifying aquifers. Therefore the fluxes of N_2O along with water from both study areas were small in comparison with surface fluxes. The dynamics of N_2O turnover are similar to denitrifying aquifers, with the lowest N_2O accumulation at the start and end of the reaction progress. Site preference signatures are higher than those of N_2O from unsaturated soils, confirming that denitrification in the saturated zone exhibits a broad range of SP with most values > 30‰ (Well *et al.*, 2012). Both N_2:N_2O ratios and isotope data suggest that the main source of N_2O in both areas is denitrification. Due to the more fluctuating groundwater depth in Porijõgi, a significant part of N_2O may be produced by nitrification, at least temporarily. This study also confirms that isotopic signatures of N_2O may be used to distinguish N_2O fluxes from ecosystems with unsaturated and saturated groundwater situations. Further, the study showed that in riparian alder stands saturated with water, N_2 is the predominant denitrification product compared with N_2O which is a significant boost to N_2O emissions to the atmosphere.

ACKNOWLEDGEMENTS

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Importance of Near and In-stream Zones in Small Agricultural Catchments to Buffer Diffuse Nitrogen Pollution

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ABSTRACT

Riparian ecosystems play an important role in removing nitrogen (N) from water and improving water quality downstream. However, factors influencing N retention in these water conservation areas are not fully understood, hindering effective management and their potential use for N removal. The objective of this paper is to evaluate the N buffering capacity of landscape features, including riparian zones, using isotopic signatures of nitrogen-15 (delta ^{15}N, $\delta^{15}N$) of aquatic and riparian vegetation as an indicator for determining sites of biogeochemical N transformation. Studies in fourteen countries across Europe with a range of climatic conditions showed that nitrate (NO_3^-) removal by riparian buffer zones (plant uptake and denitrification) varies from 0 to 30 percent (%), depending on NO_3^- loading to these zones and the local hydraulic gradient rather than climatic conditions. The negative relationship between in-stream NO_3^- concentration and the $\delta^{15}N$ of diatoms in water showed that the ^{15}N natural abundance in diatoms can be used as a proxy for in-stream denitrification and point source pollution of N. In flood plains, the percentage reduction in NO_3^- along the flow path and an increased $\delta^{15}N$ in the remaining NO_3^- suggest NO_3^- is lost through denitrification. However, the increased ^{15}N in the vegetation showed that plants compete with denitrification for NO_3^- . The isotopic signature of ^{15}N is an important tool to assess in-stream, riparian zone and flood plain denitrification thus allowing us to improve management practices for reducing the fluxes from croplands to streams.

Key words: *wetland, riparian zone, denitrification, natural isotopic abundance.*

INTRODUCTION

River ecosystems control the transport of nutrients and organic matter from terrestrial sources (Townsend-Small, McClain and Brandes, 2005), produce organic material within aquatic environments, degrade organic matter while transporting it downstream (Hedges *et al.*, 2000) and carry the fingerprint of human activities (Rosenberg, McCully and Pringle, 2000). Floodplains and in-stream zones are the key components of river ecosystems controlling these functions (Fischer *et al.*, 2005). These riverine landscape features act as biogeochemical hot spots, in particular for nitrogen (N) cycling (Forshay and Stanley, 2005). They also represent functional retention areas (Carling, 1992) which control and maintain river water quality (Pinay and Décamps, 1988). At the landscape scale, three fundamental interrelated principles regulate the cycling and transfer of carbon and nutrients in rivers ecosystems. The first principle, i.e. connectivity, is related to the delivery patterns of carbon and nutrient inputs controlled by the flow regime along river ecosystems. River systems and their retention zones can be viewed as open ecosystems dynamically linked longitudinally, laterally and vertically by hydrologic and geomorphologic processes (Ward, 1989). The second basic principle is that the area of water-substrate interface (i.e. water-sediment or wetland-upland length of contact) is correlated positively with the efficiency of nutrient retention and use in river ecosystems. These positive relationships occur both in the main channel itself and in the riparian and floodplain zones (Jones and Holmes, 1996). The third principle is related to the role of water levels, especially flow and flood pulses affect N cycling in alluvial soils by controlling the duration of oxic and anoxic phases.

THE ROLE OF RIPARIAN ZONES AS NITROGEN BUFFERS

Numerous studies have demonstrated that groundwater NO_3^- concentrations may decrease substantially as water moves through riparian ecosystems before being discharged into streams (Burt, Pinay and Sabater, 2010). As a result, there is considerable interest in exploiting the N 'filtration' capacity of riparian ecosystems in order to improve surface water quality (Figure 1). However, there is still much uncertainty about the mechanisms and controls of N retention in riparian ecosystems, thus hindering their potential use and effective management.

Yet, the evaluation of the N buffering capacity of riparian zones is not a trivial task. For example, in a pan European study, Sabater *et al.* (2003) evaluated N removal efficiency by riparian buffers at 14 sites scattered throughout seven European countries subject to a wide range of climatic conditions. The sites also had a wide range of NO_3^- inputs, soil characteristics and vegetation types. Dissolved forms of N in groundwater and associated hydrological parameters were measured at all sites; these data were used to calculate NO_3^- removal by the riparian buffers (Figure 2).

Nitrate removal rates (expressed as the difference between the input and output NO_3^- concentrations in relation to the width of the riparian zone) were mainly positive, ranging from 5 percent per

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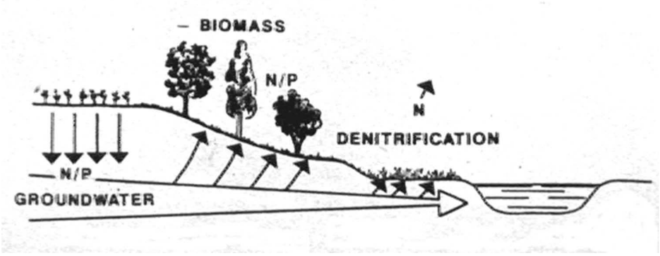

FIGURE 1. Schematic view of the nutrient fluxes under riparian zones.

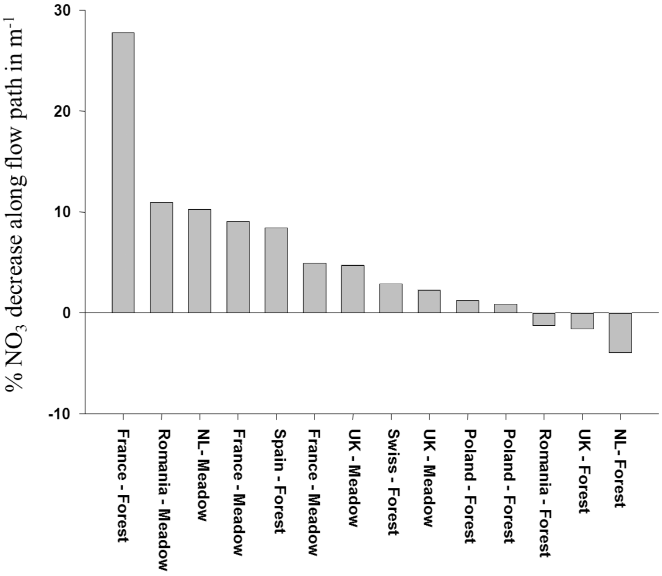

FIGURE 2. Percentage of decrease in NO_3^- in riparian zones (Sabater *et al.,* 2003).

meter (5%/m) to 30%/m, except for a few sites where the values were close to zero (Figure 2). On the basis of this inter-sites comparison, it was concluded that the removal of NO_3^- by biological mechanisms (e.g. denitrification, plant uptake) in the riparian areas is related more closely to NO_3^- load and local hydraulic gradient than to climatic parameters.

Quantifying nitrogen buffering capacity

In order to evaluate the importance of local hydraulic gradient on diffuse N buffering capacity of riparian zones, Ocampo, Oldham and Sivapalan (2006) used the Damköhler ratio to quantify the relative importance of transport *versus* reaction in the attenuation of NO_3^- concentrations within the riparian zones. The Damköhler ratio can be defined as the ratio between a transport timescale ($\tau_{transport}$ = L/v) and a reaction timescale ($\tau_{reaction} = 1/K_1$) where L is the travel length; v is the velocity; and K_1 is the rate of NO_3^- consumption.

This dimensionless number is therefore the ratio between the rate of transport (rate of NO_3^- input to the site) and the rate of reaction (denitrification in the site). Thus, it is a measure of the competition between transport and reaction processes. The higher the ratio is, the more efficient to remove NO_3^- is a given site. The Ocampo, Oldham and Sivapalan (2006) study based on results published in several sites all over the world predicted the N removal capacity of riparian zones with a very good accuracy (Figure 3).

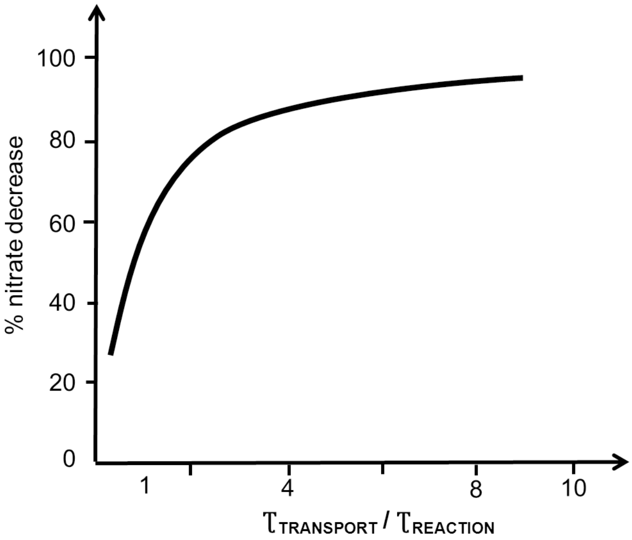

FIGURE 3. Percentage of NO_3^- removal in a riparian zone as a function of the Damkölher ratio (Ocampo, Oldham and Sivapalan, 2006).

Natural isotopic abundance of N as proxy for denitrification

If the Damköhler ratio can provide a good framework to evaluate N buffering capacities at the riparian scale, it does not inform on the processes at stake, i.e. uptake or denitrification. Natural abundance N isotopic signature ($\delta^{15}N$) can provide such insights into the NO_3^- removal processes occurring within riparian zones (Mengis *et al*., 1999). There are two stable isotopes of N, namely ^{14}N and ^{15}N. The most common isotope, ^{14}N, accounts for approximately 99 percent of atmospheric N. Although the N isotopic composition of the standard (atmospheric N_2) is constant, other materials have variable isotopic compositions because some biological processes discriminate (i.e. fractionate) between N isotopes. The lighter isotope (^{14}N) often reacts more rapidly in biogeochemical cycles than the heavy one (^{15}N); therefore processes involved in the N cycle can also affect the ratio between the ^{14}N and ^{15}N isotopes in environmental N pools. Among these processes, microbial denitrification significantly alters the N isotope ratio, resulting in the progressive enrichment of the remaining NO_3^- pool with ^{15}N (Mengis *et al*., 1999). In contrast to denitrification, NO_3^- uptake by terrestrial vegetation appears to fractionate minimally or not at all.

An example of the use of $\delta^{15}N$ to decipher the respective role of denitrification and plant uptake in N buffering capacity of riparian zones has been provided by Clément *et al.* (2003). They used the natural abundance distribution of N isotope in both the groundwater NO_3^- and riparian plant tissues along transects to determine the extent of groundwater NO_3^- decline that resulted from denitrification and/or plant uptake. They found that the decline in groundwater NO_3^- concentration along flow paths under the riparian zone was correlated to an increase of $\delta^{15}N$ in the remaining NO_3^- in groundwater, indicating that denitrification was the main process responsible of NO_3^- decline. However, analysis of $\delta^{15}N$ in plant growing along the transect showed a good correspondence with groundwater NO_3^- $\delta^{15}N$ (1:1 line, Figure 4).

This implies that plant uptake was also contributing to NO_3^- removal along the flow paths. Yet, the seasonal analysis of the $\delta^{15}N$ showed that during the low water period (Figure 4, triangle symbols), groundwater contribution from below the root zone to plant

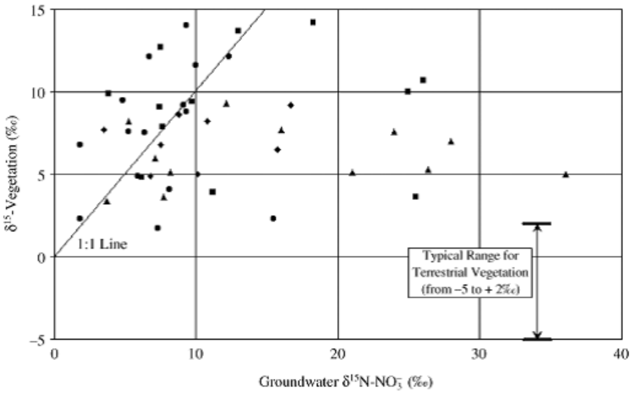

FIGURE 4. Relationship between δ^{15}N-NO_3^- in riparian groundwater and the δ^{15}N isotopic composition of overlying vegetation in April (diamonds), June (squares), August (triangles) and February (circles) (Clément *et al.*, 2003).

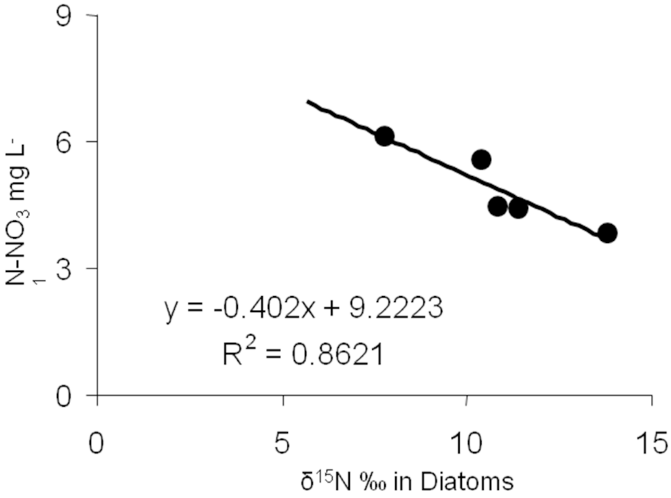

FIGURE 5. Relationship between stream NO_3^- concentration and δ^{15}N in diatoms (Bale, 2010).

NO_3^- uptake was minimal and ^{14}N-NO_3^- resulting from nitrification of ammonium (NH_4^+) in upper soil horizons contributes to plant uptake.

Natural isotopic abundance as a marker of in-stream denitrification

Nitrogen natural isotopic abundance in diatoms was used by Bale (2010) to evaluate potential in-stream denitrification along the Rolleston Brook, a 13 km-long stream situated on the Staffordshire/Derbyshire county boundary, ca. 50 km North West of Birmingham, UK. The results show a negative relationship between stream NO_3^- concentration and δ^{15}N in diatoms present on the stream sediment (Figure 5).

This negative trend was noticeable along the river flow path with high NO_3^- concentration and low δ^{15}N in diatoms in the upstream part of the stream, low NO_3^- concentration and high δ^{15}N in diatoms in the downstream part. This result suggests that in-stream denitrification occurs to reduce NO_3^- concentration, resulting in an increase of δ^{15}N of the remaining NO_3^- available for diatoms. Therefore, diatoms could be used as proxy to in-stream denitrification activity, a self-purification process.

Natural isotopic abundance as a marker of floodplain denitrification

At a larger scale, i.e. the floodplain, Pritchard (2009) used the variation in δ^{15}N measurements of aquatic and riparian vegetation within a small English catchment to identify areas of denitrification. The method used involved sampling river water and plant matter during low flow period (0.6 m^3/sec) along a 23 km stretch of the River Tern (drainage basin 92 km^2), located in the vicinity of Market Drayton in Shropshire, approximately 80 km from the University of Birmingham (UK). The main transect used in the study aimed to capture the N transfer through a small catchment. Eleven study sites were located on the River Tern with three situated on the longest tributaries. A short transect was also chosen to study N transfer at a smaller spatial scale in order to identify local factors which may influence biogeochemical processes. Two different types of plants were selected to determine their ^{15}N signatures. *Salix fragilis* (Crack willow), a medium-large deciduous tree which grows rapidly to between 10 and 20 m, usually found beside rivers on deep, damp soil. *Veronica anagallis-aquatica* (Blue water speedwell), an herbaceous perennial found in or beside streams, marshes and wetlands. *Salix fragilis* and *Veronica anagallis-aquatica* presented a significant relationship in their δ^{15}N content and the percentage of change of NO_3^- load per km of stream flow (Figure 6).

In the Tern catchment context most of the NO_3^- was related to diffuse pollution, with NO_3^- load increasing with distance from the source. A reduction of the slope of change, i.e. a decrease of the percentage of change of NO_3^- load per km, revealed that some NO_3^- was removed from the catchment in these particular areas. The significant increase of δ^{15}N in *Salix fragilis*, a typical tree species of the riparian zones, could be attributed to competition with denitrification for NO_3^- uptake in the riparian sites located in the NO_3^- load reduction (Figure 6A). Similarly, the increase of δ^{15}N in *Veronica anagallis-aquatica* with the decrease in percentage of change of NO_3^- load reveals that similar competition with denitrification of NO_3^- uptake occurred also in-stream (Figure 6B).

Natural isotopic abundance as marker of point source pollution

Natural isotopic abundance of N can also be used to obtain information on the source of N pollution in streams. In this context, Furey (2010) measured NO_3^- concentrations and δ^{15}N in diatoms collected in the riverbed of the Arrow stream, near the city of Reddich, West Midlands, UK. Similar to what was found along the Rolleston Brook (Figure 5), he found a negative relationship between stream NO_3^- concentration and δ^{15}N in diatoms (Figure 7). Yet, two sampling points (open circles) did not fit with this negative trend and presented significantly higher NO_3^- concentration and δ^{15}N in diatoms.

These two data points corresponded to sites downstream from urban sewage treatment plants. Indeed, wastewater N presents a high δ^{15}N because animal and human metabolic wastes lead to enrichment in the ^{15}N. Volatilization of ammonia during waste water treatment also increases the percentage of ^{15}N as well.

CONCLUSIONS

A large range of human activities have increased the fluxes of NO_3^- and $NH_4^+$to such an extent that it has reached the planet's carrying capacity. This increase has affected not only the N cycle but also those of carbon and phosphorus, both on land and in the ocean. Modern agriculture is considered to be the most prominent human activity which increased N fluxes in the last 50 years. As early as the 1980s

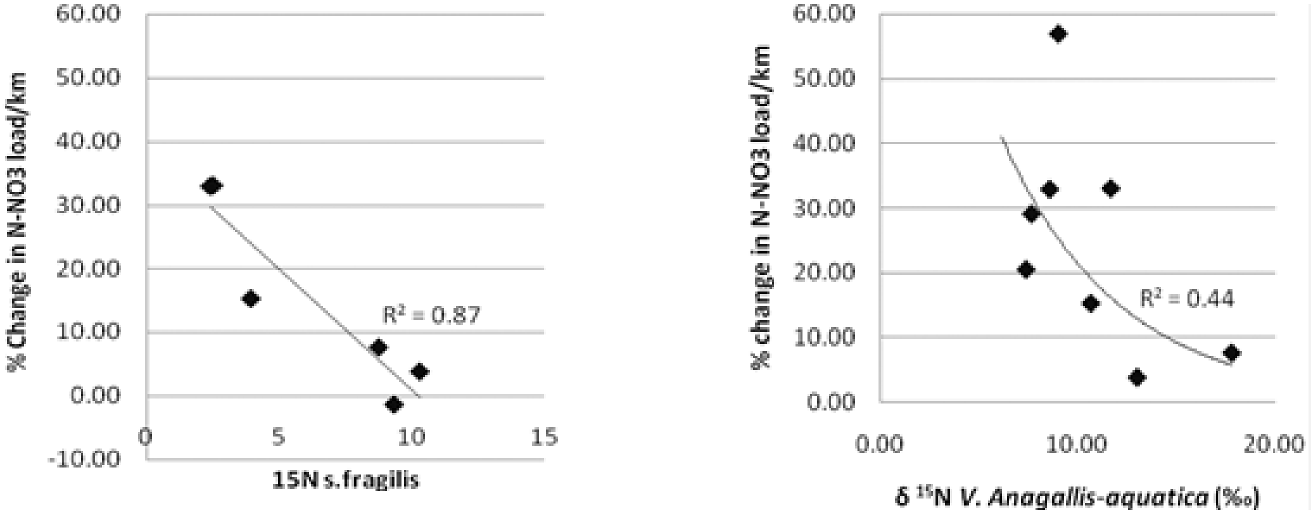

FIGURE 6. Relationship between $\delta^{15}N$ in *Salix fragilis* (A) and in *Veronica anagallis-aquatica* (B) and percentage of NO_3^- load change per km of stream.

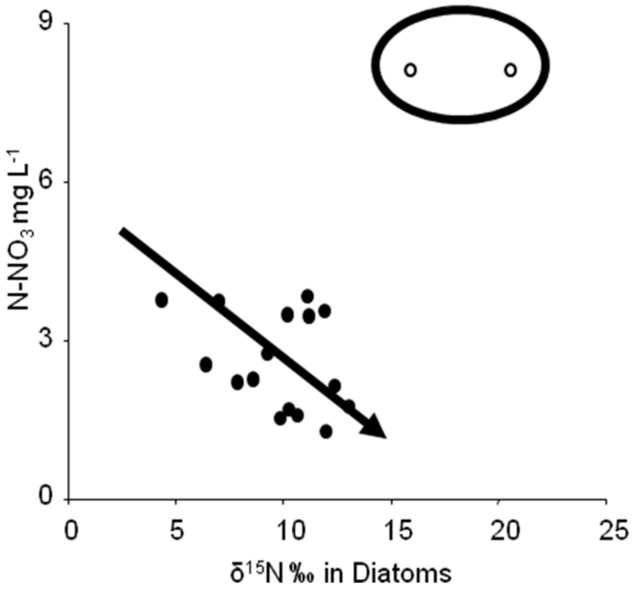

FIGURE 7. Relationship between stream NO_3^- concentration in the Arrow stream network and $\delta^{15}N$ in diatoms. The two open circles correspond to sampling sited downstream from urban wastewater treatment plants (Furey, 2010).

the positive relationship was demonstrated between the percentage of agricultural land cover in catchments and NO_3^- fluxes at their outlets. At the same time, it was demonstrated that riparian zones along streams could buffer diffuse N fluxes. Yet, their evaluation at the drainage basin scale is still a challenge due to a substantial local heterogeneity of farming activities. Isotopic signatures of ^{15}N ($\delta^{15}N$) in aquatic and riparian vegetation were found to be valuable indicators for determining sites of biogeochemical N transformation. These results confirm also the importance of in- and near-stream N buffering capacity along small agricultural catchments using $\delta^{15}N$ as a proxy for denitrification activity.

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Denitrifying Bioreactors: Opportunities and Challenges for Managing Offsite Nitrogen Losses

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ABSTRACT

In watersheds that deliver elevated levels of agricultural nitrogen (N), denitrifying bioreactors — often simple trenches or denitrification walls filled with a solid carbon (C) substrate — hold great promise for treating non-point discharges of nitrate-rich water. These systems have been developed largely in the temperate zone for high-input, high-production croplands and nitrified waste streams. A wide range of nitrate removal rates (0.014–22 g $N \cdot m^{-3} \cdot d^{-1}$) have been reported in field-based bioreactor studies generally reflecting differences in C substrates, hydrologic setting, temperature, seasonal/site variation in N loading and hydraulic residence time. The use of stable N isotopes has been critical for determining that denitrification is the process most responsible for observed declines in nitrate loads. Further, investigations with N isotopes provide insights into factors that can inform placement and design to minimize the extent of nitrous oxide (N_2O) and methane (CH_4) emissions from this type of management practice.

Key words: *nitrogen, nitrate, bioreactor, denitrification, denitrification wall.*

INTRODUCTION

To address the food security needs of a growing global population in a changing climate, agricultural lands in many areas may receive more intensive management, including additional nitrogen (N) fertilization, irrigation and artificial drainage. Each of these practices can exacerbate offsite losses of N, which can lead to surface water degradation. In addition, reactive N can undergo transformations that generate nitrous oxide (N_2O), a potent greenhouse gas.

Denitrifying bioreactors (Figure 1) hold great promise for reducing edge-of-field N losses through denitrification (Schipper *et al*., 2010). Denitrifying bioreactors are filled with a solid carbon (C) source, such as wood chips or corn cobs. Under saturated conditions, such as found in groundwater or from pipe flow and channelized discharges, this plant material degrades slowly, creating anaerobic conditions and labile C that can foster microbial denitrification. These bioreactors are being incorporated into many different types of settings and designs, but optimizing their value requires site-specific information on hydrology, temperature and nitrate (NO_3^-) loading rates. In addition, there are a number of important research questions that warrant further testing and mechanistic study, many of which would benefit from the use of isotopic techniques.

DENITRIFYING BIOREACTORS

The simplest denitrifying bioreactors are denitrification beds (Figure 1). These beds are often a lined container filled with particulate C. Nitrogen-bearing water is fed in at one end and discharged at the other. In general, these beds are used to treat NO_3^- rich discharges from conveyance systems, e.g. tile drainage or effluents (Figure 2a; e.g. Schipper *et al*., 2010; Woli *et al*., 2010). Denitrification beds have been adapted to other environments, such as in a stream bed (Figure 2b; Robertson and Merkely, 2009) to treat drainage once it enters the stream.

Denitrification walls (Figure 3) are an adaption to treat non-point discharges of NO_3^- rich ground water before it reaches surface water or tile drains. A trench of soil is excavated perpendicular to ground water flow and back-filled with a solid C source.

Rates of removal and controlling factors

Schipper *et al.* (2010) calculated a geometric mean of N removal across a range of denitrifying bioreactors as 3.4 $g \cdot N \cdot m^{-3} \cdot d^{-1}$ (where m^{-3} refers to a volume of the bioreactor). An informal review of published papers since 2010, indicates that the average N removal in denitrifying bioreactors may be closer to 5–7.5 $g \cdot N \cdot m^{-3} \cdot d^{-1}$ (Schipper, 2012) when focusing on systems that were not limited by NO_3^- concentrations.

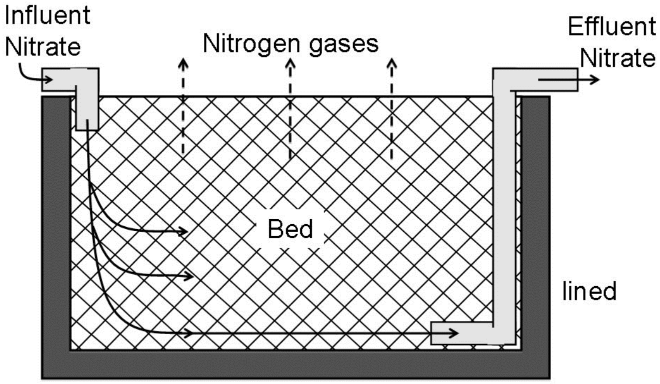

FIGURE 1. Denitrification beds are lined denitrifying bioreactors filled with a solid carbon source receiving pipe flow of N-enriched water.

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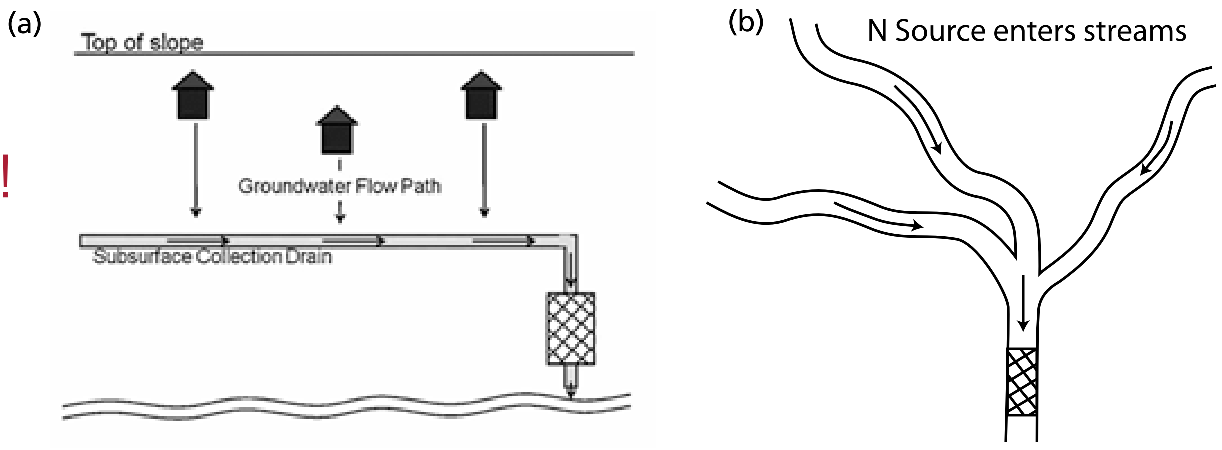

FIGURE 2. Denitrification beds can be placed in sequence to treat tile drainage (a), within a stream to treat stream water (b), or in a trench in the ground to intercept and treat ground water. (From Schipper *et al*., 2010).

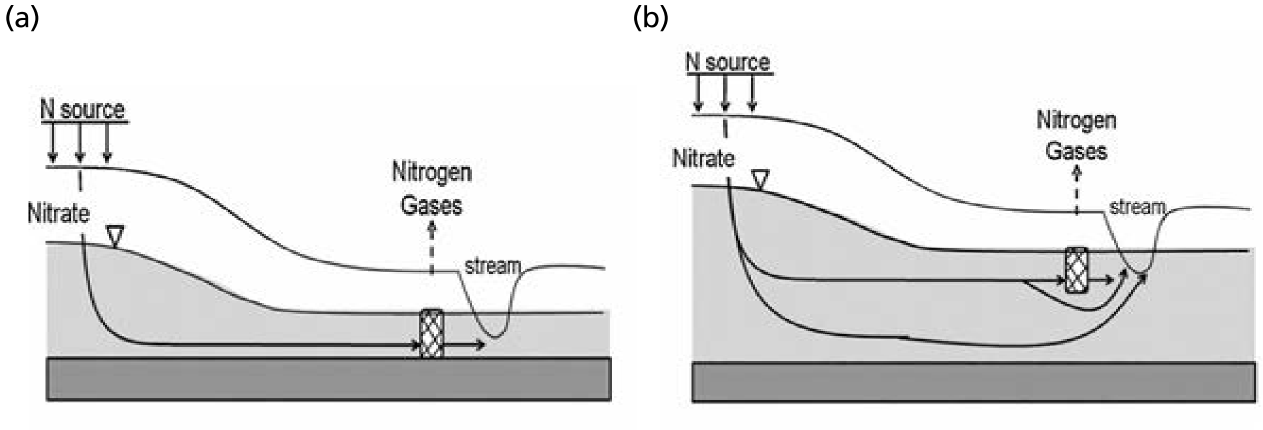

FIGURE 3. Denitrification walls are passive hydrologic systems that intercept NO_3^- enriched ground water. Inception and treatment of groundwater is enhanced when walls are placed close to the source or where a shallow confining layer (a) forces ground water through the wall. In deep aquifers (b), substantial flux of NO_3^- enriched ground water can by-pass the wall minimizing its effectiveness (From Schipper *et al*., 2010).

The factors that control NO_3^- removal rates and denitrification in these systems are temperature, C source, and absence of oxygen. Stable isotope studies with ^{15}N-labelled NO_3^- point to denitrification as the dominant NO_3^- removal process within denitrifying bioreactors (Greenan *et al*., 2009; Warneke *et al*., 2011a). Greenan *et al.* (2009) indicated that in column studies of wood chip material, minimal N_2O was produced. This suggested that N_2 gas production may be a predominant product of denitrification instead of nitrous oxide (N_2O), a potent greenhouse gas. Further studies using N-15 techniques (either natural abundance or enriched) are needed to refine estimates of N_2O production from bioreactors.

Warneke *et al.* (2011a) compared four approaches to measure denitrification rates in a denitrification bed treating hydroponic glasshouse effluent (Figure 4a). The *in vitro* acetylene inhibition method yielded highly variable rates and overestimated the NO_3^- removal rate. Denitrification rates were also obtained from two groundwater push-pull tests based on the production of ^{15}N enriched N gases from ^{15}N-labelled NO_3^- amendments. The denitrification rates from the natural abundance stable isotopic method, when coupled with estimates of retention time, corresponded well with the decline in $NO_3^-$and with the changes in dissolved N_2 concentration along the length of the bed (Figure 4b).

Seasonal and annual temperature differences between regions are likely to account for some of the variability observed in bioreactor performance. In general, biological reaction rates positively correlate with temperature. In the Schipper *et al.* (2010) review of non-NO_3^- limiting bioreactors, a general trend of increasing denitrification rates with increasing average annual temperature was noted. However, some studies suggest that long-term N removal may be lowered in warmer climates since the C substrate may decompose more rapidly (Cameron and Schipper, 2010). In general, as temperature increases by 10°C, the denitrification rates in bioreactors increase two-fold (Figure 5). Cameron and Schipper (2011) found that it was possible to increase pilot-scale bioreactor's temperature by 3–4°C using passive solar heating.

Denitrifying bioreactors will only continue denitrification as long as there is available labile C. Until recently, it was not clear how long denitrifying bioreactors would continue to remove NO_3^- but three studies have now demonstrated that bioreactors constructed with woodchips or sawdust will remove NO_3^- for nine yr or more (Moorman *et al*., 2010; Roberston *et al.*, 2010; Long, Schipper and Bruesewitz, 2011). These studies also estimated the future performance of denitrifying bioreactors by examining decay rates of wood material in denitrification walls and estimated bioreactor material half-life as between 4.6 and 37 yr in Iowa depending on sample depth (Moor-

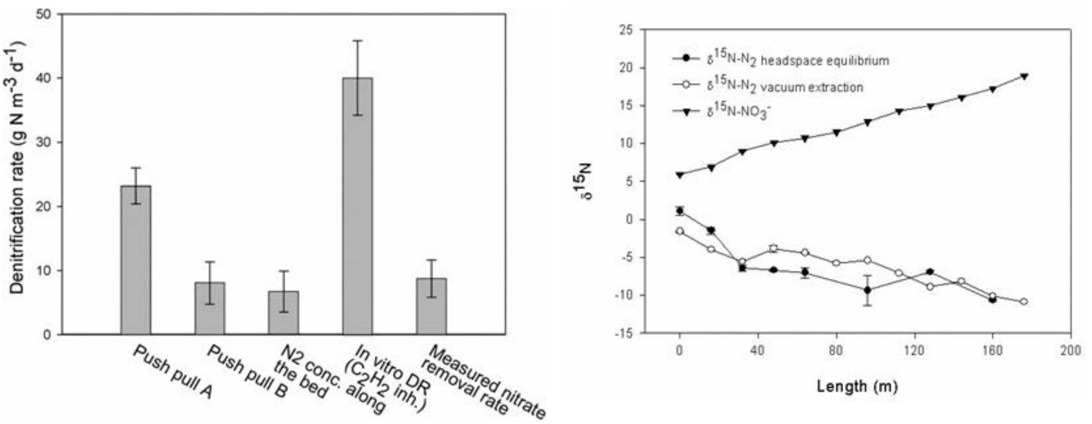

FIGURE 4. (a) Denitrification (estimated by a variety of methods; push-pull using ^{15}N- NO_3^- additions and N_2 concentrations along bed using ^{15}N natural abundance) and NO_3^- removal rates within a denitrification bed indicating the importance of denitrification to NO_3^- removal. (b) Using the natural abundance technique, N_2 was found to decline along the length of the denitrification bed. From Warneke *et al.* (2011a).

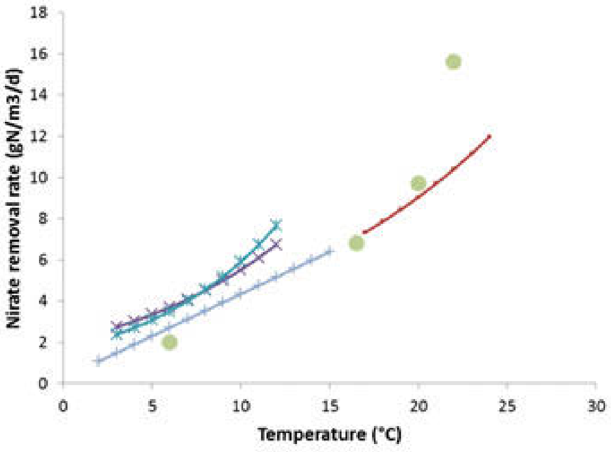

FIGURE 5. Response of nitrate-N removal rates in denitrifying bioreactors to temperature. Adapted from Schipper *et al.* (2010).

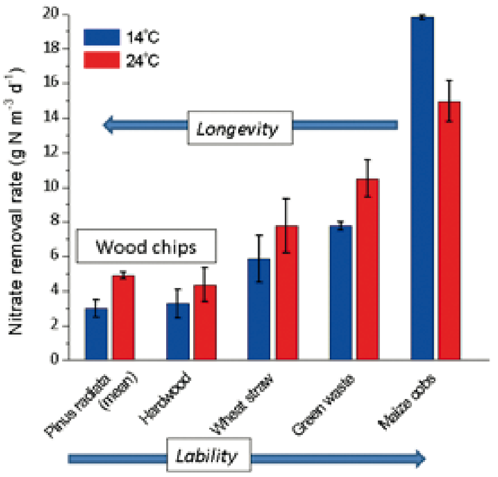

FIGURE 6. Nitrate-N removal rates in denitrifying bioreactors with different carbon sources. Adapted from Cameron and Schipper (2010).

man *et al*., 2010) and as 11 yr in New Zealand (Long, Schipper and Bruesewitz, 2011). Warneke *et al*. (2011b) measured total losses of C from a large denitrification bed and estimated a life time of up to 39 years. Use of material with higher lability such as maize cobs, may compromise the longevity of the denitrifying bioreactor (Figure 6; Cameron and Schipper, 2010). These studies suggest that NO_3^- removal will be sustained for decades once the bioreactors are constructed, although with a likely declining efficiency through time.

Hydrologic considerations and isotopic approaches for siting denitrifying bioreactor

Hydrologic site conditions are critical in designing a bioreactor. Denitrification walls (Figure 3) are passive systems, restricted by construction practicalities to the upper 1–2 m of groundwater. They have the greatest potential to intercept NO_3^- enriched groundwater in shallow aquifers, where the confining layer is within several meters of the surface. In deep aquifers, where the denitrification wall is not installed to the confining layer depth, flow paths may go below the wall restricting the extent of treatment. Because groundwater flow paths are often relatively shallow within 15–50 m of the site of infiltration, placing walls relatively close to a "hotspot" or elevated source of NO_3^- inputs can enhance the likelihood of intercepting and treating groundwater that is contaminated with NO_3^- . Assessing groundwater flowpaths and aquifer characteristics can be a costly and time-consuming enterprise. Isotopic methods can assist in the selection and strategic placement of denitrification walls. The abundance of stable isotopic signatures of oxygen-18 and hydrogen-2 (δ^{18}O and δ^{2}H) in ground water provides a finger print of the source water (Craig, 1961; Ingraham and Taylor, 1991). Local, shallow groundwater tends to be isotopically heavier (^{18}O enriched). Enrichment of ^{18}O in base flows of streams may serve as a positive indicator for the use of denitrification walls where they will intercept shallow groundwater flow.

Because bioreactor beds are positioned to intercept channelized flow or tile drainage, the extent of removal within these designs can be limited by hydraulic residence time and N loading. Sizing bioreactor beds warrants careful understanding of void space volume as well as the temporal variations in flow and spatial variation of inputs. Design criteria for beds need to optimize costs vs. performance when considering seasonal variation and storm generated pulses of hydrologic input.

Environmental trade-offs

Uncertainty surrounds the extent of unintended environmental trade-offs. Initial leaching of dissolved labile C from the solid carbon source within the bioreactor can temporarily affect dissolved oxygen concentrations of receiving waters. However, careful start-up procedures may be able to minimize losses of dissolved C, such as pre-leaching of wood chips.

Bioreactors may produce other unwanted pollutants, such as N_2O and methane (CH_4), both potent greenhouse gases, from either incomplete denitrification or prolonged retention times that promote highly reducing conditions within the bioreactor. When NO_3^- loading is high and retention times are limited, there is the potential for more N_2O to be produced since denitrifiers reduce nitrate to N_2O and not completely to N_2 (Elgood *et al.,* 2010). On the other hand, under conditions of low NO_3^- loading and extended retention periods (as can occur during low flow seasons), highly reduced conditions can be generated within the C bioreactors. Controlling NO_3^- losses without generating substantial greenhouse gas emissions will likely depend on scaling bioreactors to ensure that the N concentrations within the bioreactor are poised to ensure complete denitrification while preventing CH_4 production from methanogenesis (Warneke *et al*., 2011b).

A further reason for optimizing the size of denitrification bioreactors is management of the production of methyl mercury which can be released by sulphate under reducing conditions (Shih *et al*., 2011). When NO_3^- concentrations are high, sulphate reduction is suppressed and toxic methyl mercury is not formed (Shih *et al*., 2011). Again, proper design will require consideration of NO_3^- loading and retention to promote complete denitrification, minimize methanogenesis and suppress methyl mercury production.

Costs

Based on a functional life time of 20 yr, Schipper *et al*. (2010) estimated a removal cost of between US$2.39 and US$15.17 per kg N, which compares well with other agricultural management techniques such as controlled drainage, soil testing, wetlands and autumn cover crops. Estimates from later studies have suggested more constrained and lower costs of between US$3.67 and $4.72 (Schmidt and Clark, 2012). The lower costs were achieved when local resources, including the wood chips, lining and flow structures and equipment to dig were available.

Strategic placement

Geospatial analysis has been used to integrate data layers at various scales to allow for the spatial targeting and interpretation of BMP implementation. The efficacy of bioreactors is dependent on spatially and temporally variable factors such as physiography, seasonality of drainage, aquifer properties, soils, precipitation and temperature. At regional scales, geospatial analysis can therefore provide broad guidelines for bioreactor BMP implementation, based on variations due to climatic and generalized physiographic characteristics. This type of regional analysis has been applied to demonstrate differences in riparian buffer efficacy for pollution abatement across nine physiographic provinces in the Chesapeake Bay watershed (Lowrance *et al*., 1997). In that analysis, the effectiveness, optimum design and management of buffer systems were linked to differences in hydrologic connections associated with different physiographic provinces. Similarly, there would be benefits for regional geospatial analysis that provide broad interpretations for bioreactor BMP implementation based on variations due to temperature, seasonal runoff patterns and farming practices. Physiographic provinces are also important considerations for these artificial sinks; for example, agricultural regions dominated by artificially drained soils are likely locations for denitrification beds rather than walls.

Geospatial data are also useful for design and siting at more localized scales. County-level soil survey data and associated interpretations have a long history of guiding conservation practices. Design and placement of denitrifying bioreactors would benefit from soil survey data on depth to restrictive layers, seasonal water table elevations and hydraulic conductivity. Stream gauging networks can afford extensive, spatially explicit datasets on area-normalized flow that provide insight into expected magnitudes and seasonality of flow (Armstrong, Parker and Richards, 2004).

Given our understanding of bioreactors, to optimize NO_3^- removal they should be located in areas with the greatest NO_3^- loads to surface waters (Crumpton *et al.,* 2008). David, Drinkwater and McIsaac (2010) showed locations within the Mississippi River basin where artificial sinks such as denitrifying bioreactors would be strongly beneficial, based on the co-location of tile drainage combined with intensive agriculture in producing high winter and spring nitrate loads.

Denitrifying bioreactors hold considerable promise for reducing nitrate export from agricultural catchment. These systems have been developed largely in the temperate zone for high-input, high-production croplands and nitrified waste streams. As agricultural practices continue to intensify in developing countries with different climatic regimes and different cropping systems, there is a need for denitrifying bioreactors to be tailored to these conditions. Future designs may include incorporation into constructed wetlands where food and fibre can be generated.

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Large Scale Evaluation of Water Conservation Zones for Water Quality Improvements and Biomass Production in Northern Iran

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ABSTRACT

Water scarcity and uneven distribution of rainfall are the most important limiting factors for the development of agriculture in Iran. In order to assess water quality, quantity and characterize seasonal variation in isotopic signatures of oxyge-18 ($\delta^{18}O$) and hydrogen–2 (δD), a study was conducted during 2010 to 2011 in 30 different ponds in the north of Iran (Ab–bandans). Water samples were collected in winter, spring and summer of 2010 and 2011 and analysed for chemical and isotopic compositions. Data showed that highest $\delta^{18}O$ and δD were recorded in summer (–1.15‰ and –12.11‰ for $\delta^{18}O$ and δD) and the lowest $\delta^{18}O$ and δD were recorded in winter (–7.50‰ and –47.32‰ for $\delta^{18}O$ and δD), respectively. The $\delta^{18}O$ and δD signatures showed that the water at the Ab–bandons were enriched from spring (–3.57 and –27.72‰) to summer (–1.15 and –12.12‰), respectively. The relationship between $\delta^{18}O$ and δD for pond water and local/global precipitation showed that rainfall and snowmelt can be a major source of water for these Ab-bandans. Water and nutrient balance based on input, output and storage showed that on average 7.6 million cubic meters of water along with 86 tonnes of nitrogen (N) and 17 tonnes of phosphorus (P) were captured and stored by these ponds and are available for irrigating downstream rice crops. Flood irrigation of this water at a rate of 10 000 m^3/ha over the growing season (April to September) was able to produce rice in an area of 730 ha with a yield of 3.5 t/ha. However, changing the irrigation method from flood to an eight-day irrigation interval was able to cultivate 1500 ha with similar yield and significantly increased water use efficiency by 53%. The results of the study are useful to identify the sources of water in the pond and to improve land and water management practices to optimize the capture and storage of water and nutrients for downstream irrigation.

Key words: *Ab-bandans, ponds, $\delta^{18}O$, δD, northern Iran, water quality, water reservoir*

INTRODUCTION

In Iran, water scarcity is one of the main limiting factors for low agricultural productivity. Although irrigation agriculture generally provides 2 to 3 times more crop yield than rainfed agriculture, crop yields are still on the lower end (2 tonnes/ha) by international standards (Smedema, 2003). Although arid and semi-arid climate with low rainfall (annual average of <250 mm) covers over two third of Iran, a narrow part between the Caspian Sea and the Alborz mountains could provide humid climate with average annual rainfall between 1 200 to 1 800 mm (varies along the coastline). In this respect, constructed or man-made wetlands and ponds can be suitable options to capture, store and use water and nutrients in these areas to improve agricultural productivity and environmental quality.

In the southern Caspian lowlands, one of the most important types of wetlands is the "Ab-bandans", a number of small, manufactured ponds. These shallow water ponds (sometimes also called as wetlands), varying in size from 3 ha to 1 000 ha, most were originally built as temporary water storage providing water for irrigation of rice fields during summer growing seasons (Teif Saz Sabz, 2004). Recent surveys by Department of the Environment, Islamic Republic of Iran have showed that there are still about 2160 ponds in the Guilan Province, Northern Iran covering an area of 8 353 ha. These ponds are one of the major sources of water for agriculture in Caspian low lands.

Scientific knowledge of all available water resources, including sources and fluxes is vital for the optimal utilization of scarce water resources in arid and semi-arid areas (Leontiadis, Vergis and Christodoulou, 1996). The use of oxygen-18 and hydrogen-2 stable isotopes as naturally occurring tracers is a valuable tool to identify water sources and fluxes to and from rivers and lakes in catchments (Bowen, 2010). Studies have shown that the evaporation of surface water increases the isotopic signatures of oxygen-18 ($\delta^{18}O$) and hydrogen-2 (δD) in the remaining water and deviate linearly from the local meteoritic water line (LMWL). However, such studies are often restricted to local scale water dynamics (Vandenschricka *et al.*, 2002). Wassenaar *et al.* (2011) used isotopic signatures of oxygen-18 and deuterium ($\delta^{18}O$ and δD) to assess water sources of different lakes in western Canada. They showed that the $\delta^{18}O$ and δD of surface waters were more positive than mean annual precipitation, indicating the basin-scale evaporation of surface waters. With isotopic mass-balance modelling, they also found that about 35% of inflow to the lake watershed was lost to evaporation. Jonsson *et al.* (2009) compared isotope signature of the sub-Arctic lakes in northern Sweden and showed that lake waters showed a range of isotopic

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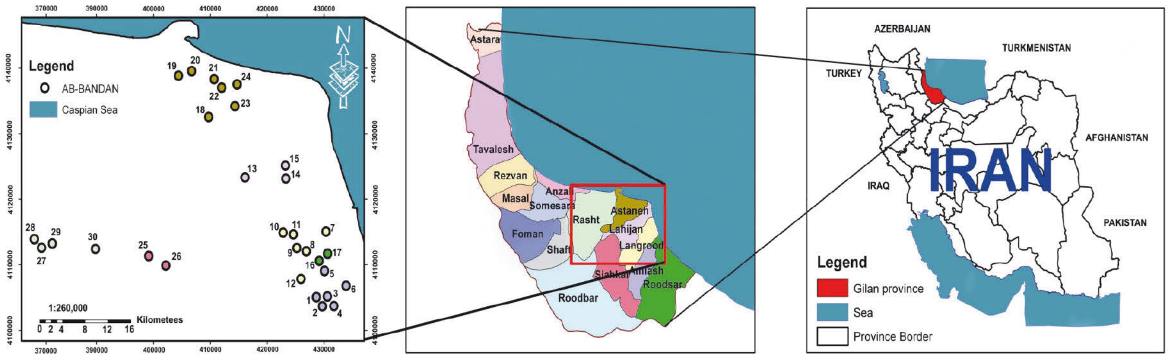

FIGURE 1. Locations of 30 Ab-bandans in northern Iran.

TABLE 1. Geographical and climate characteristics of pond catchments

No	Catchment area (ha)	Maximum elevation of catchment (m a.s.l)*	Minimum elevation of catchment (m a.s.l)	Average annual rainfall (mm)	Average ET (mm/year)
1	831	261	11	1218	763
2	831	261	11	1218	763
3	831	261	11	1218	763
4	831	261	11	1218	763
5	172	5	0	1218	763
6	112	6	0	1218	763
7	140	–17	–22	1431	792
8	370	243	–7	1431	792
9	370	243	–9	1431	792
10	315	430	–5	1431	792
11	190	383	–13	1431	792
12	247	100	25	1431	792
13	2542	–3	–16	1431	792
14	1332	–10	–19	1431	792
15	1332	–10	–19	1431	792
16	106	6	–4	1218	763
17	72	–1	–8	1218	763
18	440	–6	–20	1359	831
19	171	–16	–23	1359	831
20	231	–17	–24	1359	831
21	418	–15	–20	1359	831
22	1704	–8	–20	1359	831
23	304	–7	–23	1359	831
24	153	–20	–20	1359	831
25	105	122	46.1	1146	788
26	59	114	53.2	1146	788
27	120	177	41	1369	831
28	105	169	41	1369	831
29	34	138	70.2	1369	831
30	115	103	41.5	1369	831

*meters above sea level (m.a.s.l)

signatures between different sites as effected by catchment elevation and timing of snow-melt. Until now no comprehensive assessment of water fluxes in ponds was undertaken. In this respect, an assessment of water quality, quantity and water and nutrient balance in relation to upland activities and land use practices is important for developing strategies for effective management of water for agricultural use.

The objective of this paper was to assess the dynamics of water using isotopic signatures of oxygen-18, hydrogen-2, and nutrients of water ponds in Northern Iran in order to optimize the capture and storage of water and nutrients in these ponds.

MATERIALS AND METHODS

The study was carried out during 2010–2011 in Guilan province, close to the Caspian Sea, Northern Iran bounded by geographical co-ordination of X: 368376 to 43358 and Y: 4104370 to 4139522 (Figure 1). The hydrological regime for the area is a seasonal water cycle with maximum input to the ponds in autumn and winter due to precipitation (rainfall and snow) and minimum input in summer. The water data used in the study were collected from 30 man-made ponds. These ponds have a range of surface area, volume and depth. Surface area of ponds and their usage were taken in to consideration when selecting these 30 ponds. The major losses of water from the pond are evapotranspiration and discharge for irrigation during the crop growing season. The elevation ranges for the ponds were classified by Digital Elevation Model (DEM) of watersheds. Catchment area, elevation, and long term average rainfall and evapotranspiration are provided in Table 1. Land use, soil types, topography and climate for the catchment were characterized and details were provided elsewhere (Teif Saz Sabz, 2004). As shown in Table 1, the ponds were grouped based on drainage area, and elevation.

Measurements

Climate, hydrology and physiographical data were collected from the selected weather stations covering all 30 ponds. Water samples were collected during three different seasons, (i) at the beginning of the irrigation period (June 2010), (ii) at the end of the irrigation period (August 2010), and (iii) at the end of precipitation season (March 2011). Water samples were analyzed for chemical compositions (pH, CO_3^{2-}, Cl^-, SO_4^{2-} TDS, Na^-, Ca^{2+}, Mg^{2+}, NO_3^-, NH_4^+ and P), $\delta^{18}O$ and δD during spring and summer 2010 and winter 2011. The amount of water, nitrogen (NH_4-N +NO_3-N) and phosphorus (P) captured in the ponds, the change in $\delta^{18}O$ and δD of water and other hydro chemical properties of water were measured during this period. Nitrogen and P budget for all ponds were estimated based on the amount of water in the ponds and the concentration of N and P in the water. Statistical analyses for the chemical compositions were carried out using multivariate analysis (Johnson and Wichern, 2002).

The stable isotopic signatures of O-18 and D are expressed in δ-values representing deviations in per mil (‰) from the standard for O-18 and D such as

$$\delta^2{}_{\text{sample}}(‰) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} - 1\right) \times 1000$$

where R is the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ration in sample and standard. The $\delta^{18}O$ and δD values for water samples were plotted by linear regressions to obtain its relationship with Global Meteoric Water Lines (GNWL). From this relationship, the deuterium excess (d-excess) which provides information about changes in seasonal precipitation or moisture sources in the region (Saulnier-Talbot *et al.*, 2007).

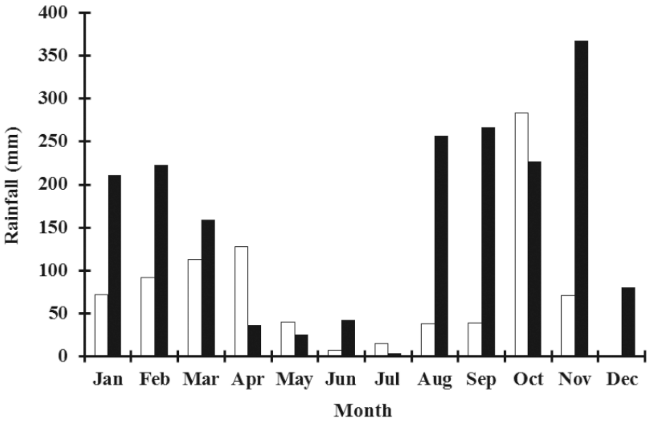

FIGURE 2. Rainfall in the catchment in 2010 (□) and 2011 (■).

RESULTS AND DISCUSSION

Annual rainfall

The 2010 and 2011 annual rainfall for the catchment is provided in Figure 2. The total rainfall for 2010 (900 mm) is lower than the long-term average (1330 mm). However, total rainfall in 2011 (1 900 mm) is much higher than both the long-term and the year 2010. Eventually there was more water available in pond in 2011 than 2010. As characterised by the hydrological cycle, most rainfall occurred in autumn and winter of both years with less rainfall during spring and summer. As a result of higher rainfall during 2011, the amount of water in these ponds increased by more than 30%.

Pond characteristics

The highest water depths were recorded in the winter (average of 1.89 m) and the lowest were in the summer (average 0.38 m). The volume of water decreased from winter to summer (0.27 to 0.018 million cubic meters). On average, the reduction in water column depth and water volume from winter to spring were 26.9% and 5.3% and from spring to summer were 23.7%, and 3.1%, respectively. The main reason for this phenomenon is the demand of water for land preparation at the end of winter and irrigation during summer. All 30 ponds were being recharged during winter through rainfall, runoff and snow melt which increased the volume of water. With minimum rainfall and higher evapotranspiration losses and water discharged for irrigation, the amount of water available in these ponds decreased during summer.

Data obtained showed that water depth, pond area, and pH, CO_3^{2-}, Cl^-, SO_4^{2-}, Na^-, Ca^{2+}, Mg^{2+}, NO_3-N NH_4-N and P of pond water vary significantly ($p<0.01$ Duncan's test) during spring, summer and winter (not shown). The concentrations of anions and cations increased from spring to summer and then decreased over the period from summer to winter.

Nitrogen

The range and average concentrations of NO_3-N, NH_4-N and dissolved P of pond waters during winter, spring and summer are shown in Table 2. As seen, they are highly variable during the monitoring period which was also observed for other inland water bodies (Quirós, 2003). The average nitrate (NO_3-N) concentration was recorded during the winter (15.4 mg/L) and was greater than that

TABLE 2. Nitrate, ammonium and dissolved P concentrations (mg N or P/L) in different seasons

Variable		Winter	Spring	Summer
Nitrate-N	Range	1.0–30.0	0.2–13.7	1.2–33.8
	Average	15.4	2.2	8.8
Ammonium-N	Range	<0.1–1.38	0–7.4	0–25.6
	Average	0.14	2.2	2.0
Dissolved P	Range	0–18.1	1.5–4.5	1.5–5.3
	Average	1.4	3.2	3.2

recorded in summer (8.8 mg/L) and spring (2.18 mg/L). This may be due to greater NO_3-N input by runoff from the catchment to the pond during winter. In addition, reduced losses of NO_3-N from the pond during winter through plant uptake and microbial activity caused by low temperatures may also lead to the presence of high NO_3-N in the water during this period.

Average ammonium-N (NH_4-N) concentrations were lower than NO3-N concentrations for all three period (Table 2). Unlike NO_3-N, the NH_4-N concentrations of pond water were lower during winter than in spring and summer. Reasons for low NH_4-N concentrations during winter are not clear.

The average concentration of dissolved P was lower in winter compared to spring and summer seasons (Table 2). In this respect water samples during spring and summer were not significantly different (Table 2).

Water, nitrogen and phosphorus budget for the ponds

Water, N and P balance in the ponds over winter, spring and summer showed that on average of 7.6 million cubic meters of water is collected annually. However, in 2011 the volume of water collected

TABLE 3. Isotopic signatures of oxygen-18 and hydrogen-2 in all thirty ponds during winter, spring and summer

Pond No.	δ^{18}O‰ (vs SMOW)				δD‰ (vs SMOW)				d excess
	Max	Min	Mean	SD	Max	Min	Mean	SD	
1	0.45	−7.47	−3.21	4.0	−1.44	−45.96	−23.53	22.3	2.13
2	2.54	−7.26	−1.95	4.9	0.18	−46.57	−17.54	23.6	−1.93
3	−0.90	−7.11	−3.54	3.1	−8.97	−45.70	−25.66	18.4	2.69
4	−0.41	−7.78	−3.34	3.7	−4.57	−48.12	−23.71	21.8	3.02
5	−0.17	−7.11	−2.91	3.5	−3.53	−46.22	−22.58	21.4	0.73
6	−0.20	−7.71	−4.61	3.8	−3.97	−46.43	−29.70	21.4	7.17
7	−1.61	−7.62	−4.81	3.0	−17.25	−48.24	−33.78	15.5	4.68
8	5.26	−8.51	−1.44	6.9	18.57	−60.09	−19.27	39.3	−7.73
9	3.41	−6.52	−1.75	5.0	11.67	−42.96	−17.35	27.3	−3.39
10	−2.85	−7.75	−5.30	2.4	−17.26	−48.40	−33.26	15.6	9.14
11	−0.32	−5.57	−2.81	2.6	−12.26	−37.82	−24.23	12.8	−1.71
12	−1.24	−6.89	−4.82	2.9	−16.33	−43.55	−31.99	13.7	6.58
13	−0.01	−8.05	−2.98	4.1	−8.81	−49.65	−24.91	20.6	−1.06
14	1.02	−7.85	−2.31	4.5	−6.05	−48.50	−22.18	21.4	−3.68
15	−1.04	−8.54	−5.05	3.8	−16.09	−54.10	−36.10	19.0	4.26
16	1.26	−7.58	−3.44	4.4	1.71	−49.07	−25.69	25.4	1.81
17	1.35	−6.42	−3.40	3.9	2.37	−41.68	−24.08	22.2	3.15
18	−1.46	−7.42	−5.06	3.0	−17.51	−46.33	−35.22	14.5	5.26
19	−2.41	−8.08	−5.44	2.8	−20.47	−49.13	−36.32	14.4	7.21
20	−4.16	−6.93	−5.72	1.4	−29.44	−42.46	−37.62	6.6	8.12
21	−3.53	−7.36	−5.83	1.9	−26.72	−44.85	−38.19	9.2	8.42
22	−3.45	−8.15	−5.44	2.4	−26.38	−50.69	−37.04	12.2	6.51
23	−1.77	−7.25	−4.83	2.7	−18.68	−44.73	−33.70	13.1	4.91
24	−3.82	−6.03	−5.11	1.1	−27.24	−37.63	−34.05	5.3	6.79
25	−4.66	−8.14	−6.43	1.7	−33.76	−49.42	−40.33	7.9	11.12
26	−5.27	−8.12	−6.73	1.4	−32.41	−50.83	−42.16	9.2	11.71
27	−1.35	−6.42	−3.98	2.5	−14.87	−38.58	−27.35	11.9	4.45
28	−1.04	−7.67	−3.90	3.3	−5.58	−47.37	−25.39	20.9	5.82
29	1.83	−8.85	−3.46	5.3	2.02	−54.08	−25.34	28.1	2.37
30	1.69	−9.54	−2.86	5.6	5.82	−60.92	−23.34	33.5	−0.48

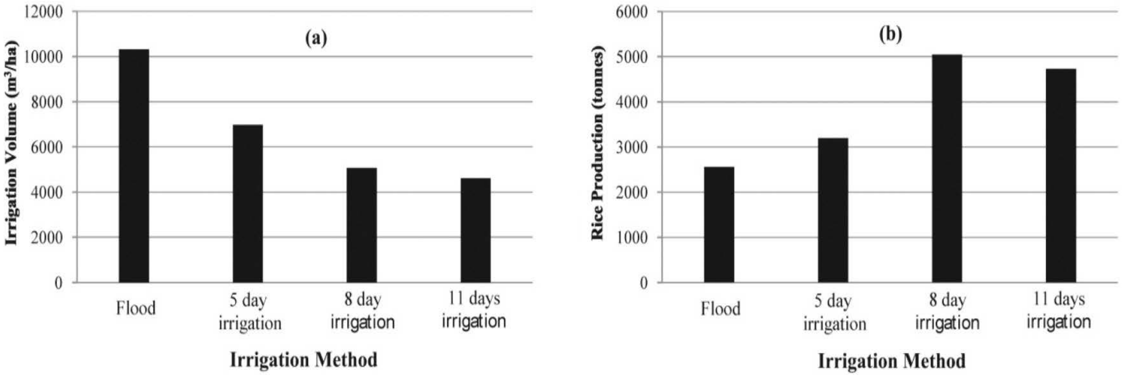

FIGURE 3. Influence of irrigation methods on amount of water used (a) and total rice production (b) of ponds.

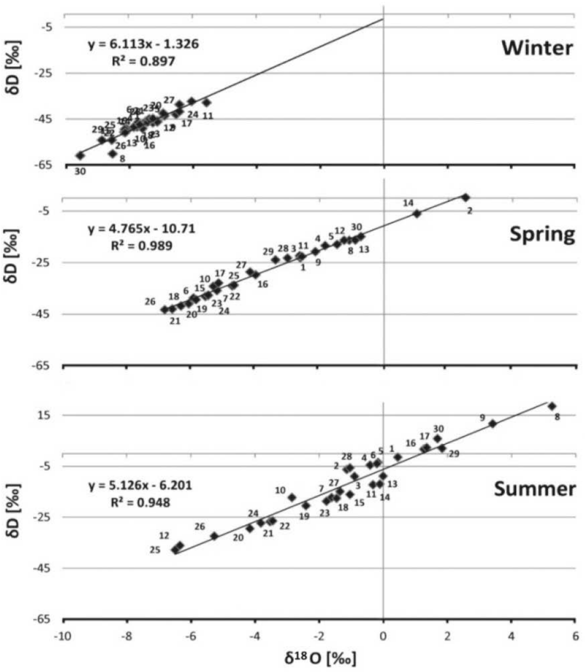

FIGURE 4. Relationship between δ^{18}O and δD signatures in pond water during winter, spring and summer seasons.

through runoff was about 40% more than the volume of water collected on an average year. Based on N and P concentrations of water about 86 tonnes of N and 17 tonnes of P were collected by these ponds and were available for rice crops.

Rice production related to the irrigation management

The water available in the pond can be used to irrigate an area up of 1500 ha producing 5000 tonnes of rice. Irrigation management practice had a major influence on the use of pond water for irrigation and rice yield (Figure 3). Flood irrigation at 10 000 m^3/ha of water over the growing season was able to irrigate an area of 730 ha and produced a total of 2 561 tonnes of rice. However, by changing the irrigation method from flood to 8 days irrigation (4 500 m^3/ha), an area of 1 500 ha was able to be used for rice cultivation with a total production of 5 050 tonnes of rice. This showed that cultivation area and rice production can be increased by more than 50% and 94%, respectively by changing irrigation practices. In addition, water use efficiency of rice production can be increased by more than 50%.

Isotope signatures of δ^{18}O and δ^{2}D and their seasonal variations

The maximum, minimum and the mean isotopic signatures of pond water measured during winter, spring and summer are shown in Table 3. These values are within the broad range of signatures observed for lakes in other agro-climatic conditions (Jasechko *et al*., 2013).

Data showed that ponds have a range of δ^{18}O (2.54‰ to –9.54‰) and δD (5.82‰ to –69.9‰) values and these isotopic signatures are influenced by local hydrology and different seasonal parameters (including rainfall, temperature and land use in the catchment). For any given pond, the δ^{18}O and δD signatures were dependent on water inputs (direct precipitation, groundwater, surface and stream inflows) and outputs (evaporation, groundwater loss, surface and stream outflows).

The relationship between isotopic signatures of δ^{18}O versus δ*D* in water during winter, spring and summer are shown in Figure 4. Isotopic signatures of pond waters during winter, spring and summer showed that most ponds in winter have light isotopic signature compared with other seasons (Figure 4).

The relationship between δ^{18}O and δD in rainfall is well understood on a global scale (Craig, 1961), known as the Global Meteoric Water Line (GMWL), and is given by the equation

$$\delta D = 8\delta^{18}O + 10‰ \quad (1)$$

For the local meteoric water line (LMWL), Vreča *et al.* (2006) obtained correlation for the relationship between δ^{18}O and δD in precipitation water and is provided by the equation

$$\delta D = 8\delta^{18}O + 10‰ \quad (2)$$

The slopes of the relationship between δ^{18}O and δD in water during winter (6.113), spring (4.765) and summer (5.126) are lower than that of both global and local meteoric water lines (Equations 1 and 2). Also the mean deuterium excess (d–excess) for water during winter (–1.326), spring (–10.71) and summer (–6.201) are lower than that of both global and local meteoric water lines. The value of d becomes higher as evaporation rates are high due to high temperature and low relative humidity in the atmosphere during the formation of water vapour. However, the significantly lower d-excess values (<10‰) of water sample from ponds may be indicative of water in the ponds was sourced from rainfall/runoff that are subjected to evaporation in a warm and dry atmosphere in the region.

CONCLUSION

The “Ab-bandans” in Northern Iran are an important source of water and nutrients for rice crop by capturing and storing rainfall and snowmelt during winter and spring. This water can be used to irrigate up to 1500 ha of cropland providing more than 5 000 t of rice. The $\delta^{18}O$ and δD signatures showed that the water in the Ab-bandons was enriched from spring (–3.57 and –27.72‰) to summer (–1.15 and –12.12‰), respectively. The seasonal variation of $\delta^{18}O$ and δD in pond water depended on the input of winter snowmelt (with light isotopes) during the early spring period and the enriched summer rainfall and evaporation in late summer. The linear relationship between $\delta^{18}O$ and δD, their slopes and d-excess showed that the pond water is mainly derived from rainfall/runoff and snow melt. The results also showed that most ponds in the north of Iran do not receive sufficient inputs (groundwater input or rainfall) of water during summer.

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