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Spatial variations in the N₂O emissions and denitrification potential of riparian buffer strips in a contaminated urban river

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Spatial variations in the N_2O emissions and denitrification potential of riparian buffer strips (RBS) in a polluted river were examined. The river received large pollutant inputs from urban runoff and wastewater discharge, resulting in impaired water quality in the river and downstream reservoir. The potential for nitrogen removal by RBS was evaluated by measuring *in situ* N_2O emission fluxes in static closed chambers and sediment denitrification potentials with acetylene inhibition techniques. The results showed that N_2O emission fluxes decreased from the upstream ($16.39\,\mu g/(m^2 \cdot h)$) to downstream ($0.30\,\mu g/(m^2 \cdot h)$) sites and from the water body to upland sites. The trend in decreasing N_2O emission fluxes in the downstream direction was mainly associated with sediment/soil textures (clay loam → sandy soil) and sediment/soil water contents and was also related to the vegetation along the RBS and nutrients in the sediments/soils. The correlation coefficient was highest ($r = 0.769$) between the N_2O emission flux and sediment/soil water content. Sediment/soil denitrification potentials under N-amended and ambient conditions were higher (highest $32.86\,mg/(kg \cdot h)$) for the upstream sites, which were consistent with *in situ* N_2O flux rates.

Keywords: N_2O emission; denitrification potential; riparian buffer strips (RBS); nitrate removal

1. Introduction

Riparian buffer strips (RBS) are defined as vegetated areas adjacent to streams, rivers, lakes, and other waterways that protect aquatic environments from excessive sedimentation, surface runoff pollutants, and contaminant inputs from groundwater.[1] The RBS's role in water purification has been stressed before, but according to many studies, its purification efficiency is less favourable than its contribution to global warming potential (GWP). Most recent research has focused on large RBS emissions of greenhouse gases (GHG) such as CH_4, CO_2, N_2O and N_2O, which appeared to be the most significant gases in many studies.[2] Because both aerobic and anaerobic environments alternately occur within RBS, these regions create a unique environment for coupled nitrification and denitrification processes,[3,4] which are necessary for N_2O production. N_2O emissions ranged from $-1.8\,kg/ha\,yr$ in riparian mixed forest-grass to $6390\,kg/ha\,yr$ in managed riparian New Zealand grassland.[2] Denitrification occurs in the presence of microbially labile organic matter and under low-oxygen conditions. This process is strongly influenced

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by the spatial and temporal variability of groundwater nitrate concentrations.[5,6] Many factors affect N_2O emission fluxes, including temperature, water content, oxygen content, and nitrate and organic matter concentrations.[7–9] The size of the RBS has a large impact on its nutrient removal efficiency.[10] Adjacent land use, rainfall and water table characteristics, as well as vegetation type, growth and dormancy seasons can influence pollutant removal effectiveness.[11] RBS can remove pollutants and greatly enhance water quality, but their N_2O production makes a $\sim$298 times greater contribution to global warming than carbon dioxide.[12]

For aquatic ecosystems and riparian zones, the pollutants associated with wastewater discharge may affect nitrogen transformation processes (e.g., mineralisation, nitrification and denitrification). High ammonia concentrations inhibit the oxidation of nitrite (NO_2^-) to nitrate (NO_3^-) in hypereutrophic lakes.[13] Similarly, the denitrification rate increased as the N-load of wastewater increased, but it increased only up to a threshold value.[9,14] Long-term and continuously high nutrient loading in riparian stands would increase N_2 and N_2O emissions and affect the N_2:N_2O ratio; higher groundwater levels could significantly increase the N_2 and N_2O emission values.[15] However, an inverse relationship was shown between denitrification rates in sediments and water salinity (NaCl) level.[16] Zhao reported that low concentrations of heavy metals (e.g., Cu, Pb, As, and Cd) can increase the activity of denitrifying soil microbe enzymes, and high heavy metal concentrations inhibit denitrifying enzyme activities.[17]

Water bodies in the Pearl River Delta of China have recently experienced serious water pollution problems, and several rivers and reservoirs face severe eutrophication and hypoxia because of nitrogen, phosphorus and organic pollutants. In spite of an intensive 10-year water quality restoration project, the surface water quality of the Pearl River Delta has not improved.[18] As a result, water shortages resulting from quality degradation plague many cities in this region.[19]

The Tongsha Reservoir is located in Dongguan City of Guangdong Province, P. R. China. The water quality of this reservoir is not acceptable to drink and cannot be used as a backup water supply for Dongguan City, and can only meet requirements for agricultural and landscape use. The Huangsha River flows through the urban area of Dongguan, and it is the main stream entering the Tongsha Reservoir. The objectives of this research were to:

(1) evaluate how nutrients such as N can be reduced and how to recover the water quality of the Tongsha Reservoir [20];
(2) investigate N_2O emissions and nitrate removal by RBS using an *in situ* static closed chamber;
(3) evaluate sediment/soil characteristics affecting N_2O emission fluxes;
(4) detect the nitrate removal efficiency and denitrification potential of RBS under non-nitrate-limiting conditions using acetylene (C_2H_2) inhibition assays in the laboratory.

2. Materials and methods

2.1. *Establishment of sampling plan*

Sampling sites were established along the east bank of the downstream part of Huangsha River, next to the Tongsha Reservoir in Dongguan City, Guangdong province, P. R. China (Figure 1). The Huangsha River watershed has an area of $63.9\,km^2$ and enters the Tongsha Reservoir, a backup water supply for Dongguan City. Dongguan City has experienced rapid growth in the past three decades and has become the most developed area in China, which contributes to serious water pollution along the Huangsha River. Wastewater and urban runoff within the watershed contains high biological oxygen demand (BOD) and chemical oxygen demand (COD) concentrations, total suspended sediments (TSS), total phosphorus (TP), total nitrogen (TN), ammonium-N (NH_4-N) and heavy metals, which have deteriorated the reservoir water quality.[4,21]

Figure 1.   Sampling sites along the Huangsha River.

Table 1.   Selected sampling site characteristics.

Sites	Longitude & latitude	Water body	Sediment texture	Vegetation	Surrounding land use
S1 (Upstream)	22°56′10.5″ N, 113°49′49.2″E	Poor fluidity, black colour	Loam and clay	Meadow and orchard	Residential area and entrance of wastewater
S2 (Upper Middle)	22°56′17.3″N, 113°49′36.5″ E	Covered by water hyacinths	Loam	Meadow and vegetable field	Farmlands
S3 (Lower-Middle)	22°56′28.7″ N, 113°49′19.0″ E	Covered by reed & water hyacinths	Loam and sandy soil	Meadow and orchard	Pond and road
S4 (Downstream)	22°56′41.1″ N, 113°49′07.3″ E	Covered by reed & water hyacinths	Sandy soil	Meadow and fish pond	Farmland and road
S5 (Entrance of the reservoir)	22°56′58.8″ N, 113°48′45″ E	Higher transparency	Sandy soil	Meadow and bare area	Forest and road

Five sampling sites based on the topography and land use along the Huangsha River (S1-S5) were established along a ∼3 km section of the water flowpath to characterise the spatial variation of N_2O emission fluxes and sediment denitrification potential from riparian buffer strips (Figure 1). The sampling site characteristics are described in Table 1. S1 and S2 were located in the upstream part of our study area and were surrounded by a residential area and farmland. They were polluted by wastewater discharge and non-point source pollution. The sediment/soil textures were loams to clays, giving them a higher capacity to retain water, organic materials and nutrients. S3, S4 and S5 were located in the middle to downstream part of the study area and were mainly surrounded by farmland and forest. The sediment or soil textures of these segments were sandy alluvial deposits with a low capacity to retain water, organic materials and nutrients.

A sampling campaign was undertaken on 18 September 2010. Static closed chambers were used to measure N_2O emission fluxes. Three sampling locations were selected at each site [7]: location-0 m represented the interface between the RBS and river water, and it was flooded most of the time (0 m away from the river); location-5 m represented the transition area between the river

and dry land, which flooded only at high river flows during the rainy season (at approximately 5 m away from the river water); and location-10 m represented the dry upland area that has never experiencing flooding at any time of year (at approximately 10 m away from the river).

At the time of the gas sampling, sediment/soil samples were collected adjacent to each gas sampling location using 1 kg of mixed sediment/soil sample (10 cm depth) for each location. Samples were placed on ice and maintained at 3°C until analysis (<3 days). The river water samples at each site were collected in triplicate in polyethylene bottles (23 April, 16 May and 18 September) to characterise the river water quality.

Sediment/soil samples were tested for TOC, NO_3-N, NH_4-N, water ratios and pH using standard methods.[22] Water samples were analysed for NO_3-N, NH_4-N, NO_2-N, TN, TP, TSS and COD_{Cr} within 48 h using standard methods for surface water.[23]

2.2.   *Determination of N_2O emission flux*

Perspex chambers (inner diameter 20 cm; outer diameter 20.5 cm; height 30 cm) were inserted 5 cm deep with minimal disturbance to the soil beneath the chamber (which was covered by aluminium foil to minimise heating). A small hole at the top of the chamber was fitted with a septum for gas sampling. The chamber was deployed for 1.5 h, with sampling at 30, 60 and 90 min. A gas-tight syringe was used to a take the gas samples from the chamber, and 1 mL of each gas sample was taken and injected into a vial (Labco Limited, High Wycombe UK, 5.9 mL). Sample vials were stored in a dry environment at room temperature and in the absence of light (the measurements were completed within one month).

The N_2O concentration was quantified using gas chromatography with a [63]Ni electron capture detector (7890 II, Techcomp). The instrument specifications include the following: stainless steel pre-column and analytical column (3 m × 2 mm) with Porapak Q (80–100 mesh); column, inlet and detector temperatures of 45°C, 130°C and 280°C, respectively; N_2 carrier gas (purity > 99.99%, flow rate: 30 mL·min^{-1}, retention time: 8.5 min); and sample gas concentration were quantified using peak areas against a standard curve ($R^2 = 0.9997$).

The N_2O emission flux was determined from N_2O concentrations measured over time in the static closed chambers using the following formula:

$$F = \frac{\Delta m}{A \times \Delta t} = \frac{m_2 - m_1}{A \times \Delta t}$$

where F is the N_2O emission flux ($\mu g/(m^2 \cdot h)$), A is the basal area of the static closed chamber (m^2), V is the inner volume of the chamber (m^3), m_1 and m_2 are the masses of N_2O at the beginning and end of gas sampling (μg), and Δt is the time interval between the beginning and end of gas sampling (h).

2.3.   *Measurements of sediment/soil denitrification potential*

The acetylene (C_2H_2) inhibition technique was used to determine sediment/soil sample denitrification potential rates in the laboratory. In brief, fresh duplicate 25 g sediment/soil samples were placed in a culture bottle (250 mL modified conical flasks). The following two treatments were assessed: amended with 25 mL of distilled water and N-amended samples with 25 mL of 0.014 mol/L KNO_3 solution. The bottles were capped with septa stoppers, evacuated, and flushed with nitrogen gas at a flow rate of 1.5,L/min for two minutes. Fifteen mL of pure acetylene was injected into each bottle with a syringe. After the acetylene addition, the samples were incubated at room temperature (22–25°C) on an orbital shaker at 120 rpm. Head-space gas samples were

collected every 30 min over 1.5 h using a 1 mL gas-tight syringe and the gas samples were stored in vials prior to N_2O analysis by GC (as described above).

2.4. *Data analyses*

All statistical analyses were performed with SPSS 17.0. Correlation coefficients between N_2O emissions and sediment/soil parameters were calculated using Spearman's rho test ($p < 0.05$). One-way ANOVA, LSD and Student-Newman-Keuls tests were used to determine the statistical significance of the differences between the mean water and sediment/soil parameter values, as well as the mean fluxes of 3 locations and denitrification potentials; the significance level was set at $p < 0.05$. ArcGIS and Origin 6.0 were used for graphics.

3. Results

3.1. *Physicochemical properties of water and sediment/soil samples*

Surface water samples were taken and analysed at each site (S1–S5) along the Huangsha River three times during the study (Table 2). The results indicate that the Huangsha River above the Tongsha Reservoir was highly polluted. Most of the factors including TN, TP, COD_{Cr} and NH_4^+-N concentrations exceeded China's national surface water quality standard level III, which is the minimum acceptable level for use as a drinking water source, aquaculture and swimming. The COD_{Cr} and TSS concentrations decreased downstream along the water flowpath, while NH_4-N, NO_3-N, NO_2-N and TP concentrations showed no distinct longitudinal trends. The TN concentrations were considerably higher than the sum of the mineral N concentrations (NH_4-N + NO_3-N + NO_2-N), which indicates that the majority of the TN fraction was composed of organic nitrogen (76–91%).

The physicochemical properties of sediment/soil samples from three locations along the RBS transect are listed in Table 3. The sediment/soil texture ranged from loam to clay from S1 to S2, and from loam to sand among sites S3–S5. The sample pHs ranged between 6.9 and 7.9. At each of the five sampling sites, the location-0 m (submerged) had the highest water content (20.5–36.4%) followed by location-5 m (transitional zone; 16.2–24.8%) and location-10 m (dry upland; 14.7–24.6%). The contents of TOC, NO_3-N and NH_4-N were related to the land use of the area surrounding the sample sites. Along the river flow path (from S1 to S5), the TOC decreased

Table 2. Selected water quality characteristics for overlying water along the Huangsha River (mean value, $n = 3^{a}$) (mg/L).

Sites	TSS	TN	NH_4-N	NO_3-N	NO_2-N	TP	COD_{Cr}
S1	82.4a	15.3a	1.05a	0.19a	0.18a	0.14a	45.9a
	(83.7∼81.2)	(18.0∼12.2)	(1.74∼0.35)	(0.30∼0.08)	(0.20∼0.17)	(0.74∼0.07)	(62.2∼38.0)
S2	25.1b	21.3a	4.32a	1.50a	0.15a	0.23a	54.1a
	(39.7∼11.6)	(29.0∼11.7)	(8.85∼0.24)	(4.20∼0.08)	(0.22∼0.09)	(0.46∼0.08)	(82.8∼8.29)
S3	39.8b	17.4a	1.08a	0.78a	0.07b	0.11a	42.2a
	(59.6∼23.3)	(23.0∼9.1)	(3.87∼0.26)	(1.85∼0.04)	(0.09∼0.03)	(0.15∼0.08)	(82.0∼17.3)
S4	25.6b	20. 7a	1.01a	1.41a	0.14a	0.23a	37.6a
	(59.6∼22.2)	(29.5∼12.0)	(1.81∼0.25)	(3.85∼0.06)	(0.16∼0.11)	(0.47∼0.06)	(44.2∼34.2)
S5	21.8b	21. 8a	3.60a	1.44a	0.16a	0.13a	23.0a
	(32.1∼14.4)	(29.9∼13.5)	(6.46∼0.22)	(4.04∼0.08)	(0.23∼0.12)	(0.19∼0.04)	(24.7∼20.7)

[a]Mean value for the following 3 time periods: April 23, May 16 and September 18. The values in brackets indicate the maximum and minimum values of each site. A statistical analysis using one-way ANOVA, LSD and Student-Newman-Keuls tests at the $p < 0.05$ level of significance; different letters mean there was a significant difference between sites, and the same letters mean the difference was not significant.

Table 3. Physicochemical properties of sediments/soils.

Sampling locations	NH$_4^+$-N (mg/kg)	NO$_3^-$-N (mg/kg)	TOC (g/kg)	Water ratio (%)	pH
S1-0 m	0.36	0.02a	31.8	36.4a	7.4
−5 m	0.47	0.25b	38.1	24.8b	7.5
−10 m	0.48	0.35c	39.1	24.6b	7.2
S2-0 m	0.61	0.03a	18.1a	30.3a	7.6
−5 m	0.50	0.06a	19.2a	19.7b	7.4
−10 m	0.49	0.11b	33.0b	14.9c	7.1
S3-0 m	0.53a	0.02	9.8	25.8a	7.3
−5 m	0.47a	<0.01	14.5	22.6ab	6.9
−10 m	0.21b	<0.01	13.6	19.8b	7.2
S4-0 m	0.29	0.02	7.3	20.5a	7.5
−5 m	0.35	<0.01	13.9	16.2b	7.3
−10 m	0.28	0.01	13.3	14.7b	7.3
S5-0 m	0.35a	0.01	6.0	30.1a	7.9
−5 m	0.43a	<0.01	7.9	18.7b	7.4
−10 m	0.20ab	<0.04	6.8	17.3b	7.8

Statistical analysis using one-way ANOVA, LSD and Student-Newman-Keuls tests at the $p < 0.05$ level of significance for each individual site; different letters indicate there was a significant difference between locations in each separate site, and the same letter means the difference was not significant. There are no significant differences if no letter follows the number.

from 31.8–39.1 g/kg at S1 to 6–7.9 g/kg at S5. The sediment/soil -extractable NO$_3$-N and NH$_4$-N were low in spite of the high nitrogen content of the river water. There were positive correlation coefficients among the NH$_4$-N, NO$_3$-N and TOC of sediment/soil samples, with values between the NH$_4$-N with TOC and NO$_3$-N with TOC of 0.64 and 0.55, respectively. The highest correlation coefficient was between NO$_3$-N and TOC ($r = 0.75$) (Table 4).

Table 4. Correlation coefficients (r) between N$_2$O emission and sediment/soil parameters.

Sediment variables	Correlation coefficient*
NH$_4^+$-N	0.483
NO$_3^-$-N	0.403
TOC	0.465
Water ratio	0.769

*$p < 0.05$ level of significance.

3.2. *N$_2$O emission fluxes*

The N$_2$O emission fluxes measured at the Huangsha RBS sampling sites along the Huangsha River are presented in Figure 2. All the sites were net sources of N$_2$O emissions, with values ranging from 0.30 μg/(m^2 · h) (S4-10 m) to 16.39 μg/(m^2 · h) (S1-0 m) (Figure 2). There was a remarkable reduction in the N$_2$O emission fluxes from upstream to downstream (S1–S5) (Table 5). For sites S1 to S3, location-0 m (submerged) had the highest N$_2$O emission flux compared to locations-5 m and-10 m, whereas sites S4 and S5 had lower N$_2$O emission fluxes and no significant difference among the locations within each site. The Huangsha River had appreciably higher N$_2$O emission fluxes with a general trend of decreasing N$_2$O emission fluxes from S1 to S5 (Figure 2). The correlation coefficients (r) between the N$_2$O emission fluxes and sediment/soil water content, ammonium, nitrate, and TOC were all positive.
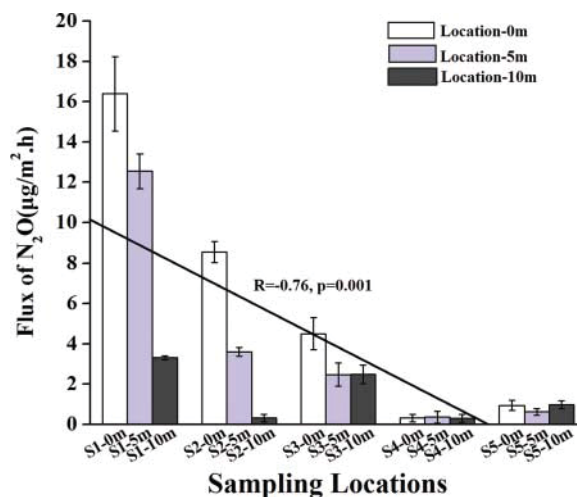
Figure 2.   N$_2$O emission flux for longitudinal sampling sites.

Table 5.   Mean N$_2$O fluxes of three locations at selected sites $-\mu g/(m^2 \cdot h)$.

Sites	Mean[a]
S1 (0, 5, 10 m)	10.75a
S2 (0, 5, 10 m)	4.15ab
S3 (0, 5, 10 m)	3.15ab
S4 (0, 5, 10 m)	0.33b
S5 (0, 5, 10 m)	0.84b

[a]Mean values with different letters are significantly different ($p < 0.05$), statistical analysis using one-way ANOVA, LSD and Student-Newman-Keuls tests at the $p < 0.05$ level of significance; different letters mean there was a significant difference between sites, and the same letter means the difference was not significant.

3.3.   *Denitrification potential of sediments/soils*

The sediment/soil denitrification potentials are shown in Figure 3 and Table 6. For the ambient samples treated with distilled water, the denitrification potentials ranged from <0.01 mg/(kg $\cdot$ h) to 2.02 mg/(kg $\cdot$ h). In general, the pattern for sediment denitrification potentials was similar to the *in situ* N$_2$O emission fluxes. When compared to the *in situ* results, denitrification potential values for NO$_3$-N-amended sediments/soils were higher, ranging from 0.05 mg/(kg $\cdot$ h) to 11.66 mg/(kg $\cdot$ h). The mean values of NO$_3$-N amended to ambient denitrification potential values were 4.9, 17.9, 3.9, 6.2 and 2.7 times greater for S1, S2, S3, S4 and S5, respectively. In contrast to the *in situ* N$_2$O emission fluxes, the NO$_3$-N amended denitrification potential of S2-0 m was higher than that of S1-0 m.

4.   Discussion

A survey of 22 drinking water reservoirs in Guangdong Province showed that eutrophication and heavy mental pollution (e.g., Cd, Zn, Pb) were the most serious water quality issues. Among the 22 reservoirs, Tongsha Reservoir had the highest NH$_4$-N and TN concentrations. Point source
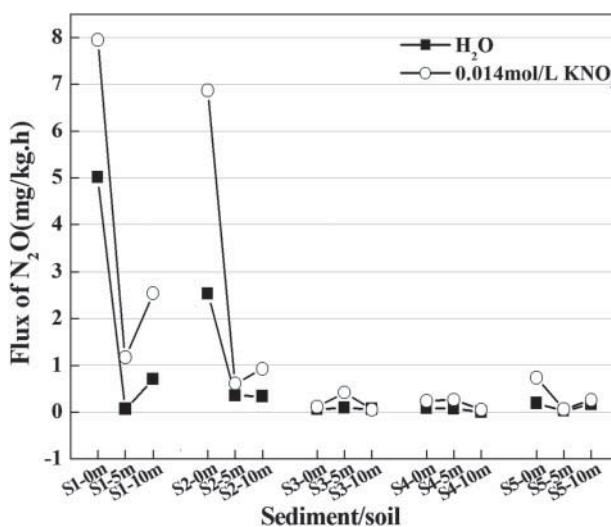
Figure 3.   Denitrification potential for sediments/soils determined in laboratory assay.

Table 6.   Mean denitrification potentials of 3 locations from laboratory experiment in mg $N_2O/(kg \cdot h)$.

Sites	Mean[a] (ambient)	Mean[a] (amendment)
S1 (0, 5, 10 m)	0.95a	4.66x
S2 (0, 5, 10 m)	0.25ab	4.39x
S3 (0, 5, 10 m)	0.05b	0.21y
S4 (0, 5, 10 m)	0.06b	0.35y
S5 (0, 5, 10 m)	0.15ab	0.40y

[a]Mean values with different letters are significantly different ($p < 0.05$), statistical analysis using one-way ANOVA, LSD and Student- Newman-Keuls tests at the $p < 0.05$ level of significance, a different letter means there was a significant difference between sites, and the same letter means the difference was not significant.

pollution from industry and domestic sewage along with non-point source pollution from storm runoff in urban and agricultural areas have resulted in the progressive worsening of Tongsha Reservoir water quality over time. In this study, there were negative correlations between TSS and TN, NH_4-N and NO_3-N ($r = -1, -0.6, -0.9$, respectively), which suggest that the high suspended solid contents in the water body may absorb more nitrogen pollutants.

Previous studies reported that adjacent land use had tremendous impact on surface sediment properties and that these properties were a principal indicator for the water quality of runoff discharged from adjacent lands to the stream.[24] For example, deeply buried organic matter in RBS can be a significant nitrogen source during water table drawdown that exposes the sediment layer to oxygen.[25] The high correlation between NO_3-N and TOC ($r = 0.75$) indicated that higher TOC content may result in higher NO_3-N, which in turn results in higher denitrification potential.

The highest correlation coefficient (0.769) between N_2O emissions and sediment/soil water content suggests that the sediment/soil water content was a key factor in N_2O emissions because of its effect on sediment oxygen concentrations. N_2O emission fluxes have been shown to increase with increasing soil water contents.[26] Balestrini and co-workers [11] found a significant linear relationship ($R^2 = 0.635, p < 0.0001$) between denitrification potential and organic carbon (OC)

content, and attributed this relationship to OC being the energy source for the heterotrophic microbial community that creates anoxic conditions by consuming O_2.[27]

NH_4-N and NO_3-N are the substrates for nitrification and denitrification, respectively. The level of extractable NH_4-N and NO_3-N in the sediments was low, which may result from coupled nitrification and denitrification processes. Variations in the sediment redox environment is necessary for nitrification (which is aerobic) and denitrification (which is anaerobic) to occur.

Mayer and co-workers [28] investigated the groundwater ecosystem of Minebank Run, and they found that subsurface sediments with high organic carbon have the capacity to denitrify NO_3-N. Above all, the denitrification and removal of NO_3-N in groundwater were limited by dissolved organic carbon (DOC) availability. The denitrification potential assays in our laboratory showed that the addition of NO_3-N greatly increased the denitrification potential, especially for sites S1-0 m and S2-0 m (submerged sites). Sediments/soils from these two locations had higher water, NH_4-N and TOC contents and thus presented a better environment for NO_3-N removal when additional NO_3-N was poured in, leading to stronger denitrifying activities in the sediments/soils. Figure 3 also indicates that the highest denitrification potentials occurred at the locations (location-0 m) that experienced the greatest submergence and presumably the most anaerobic conditions. Several studies have shown in created riverine wetlands with a pulsing regime had significantly lower N_2O emissions than those with fluctuating water tables.[15,29,30] However, some researchers have found that both intermittent loading regimes and fluctuating water tables could significantly enhance N_2O emissions. These results indicate that N_2O release may depend on the frequency and length of pulses (drainage–rewetting cycles), which means the freezing–thawing cycles in sediment/soil.[31] In this study, location-5 m experienced an oxidised environment most of the time, and this would change the N_2:N_2O emission ratio and lower the N_2O production in this area.

The NO_3-N removal capacity of RBS has been demonstrated over a wide range of environmental conditions.[32,33,35,36] Laboratory denitrification potential assays showed C_2H_2 could inhibit the transformation of N_2O to N_2, which caused all denitrification products to accumulate as N_2O. Thus, the N_2O emission flux could represent the denitrification potential and the relative nitrate removal efficiencies among RBS sediments/soils. Some researchers found that nitrate concentrations exceeding 50 mg/L in the groundwater entering RBS were decreased to less than 10 mg/L while moving across the RBS sediments/soils, yielding potential denitrification rates of 18.7 to 20.3 mg N kg^{-1}DW soil day^{-1}. However, it is difficult to extrapolate a single denitrification potential rate over longer time periods because sediment/soil conditions (e.g., temperature, dissolved oxygen, water content, nitrate concentrations, etc.) can change over short time periods (e.g., diurnal temperature and dissolved oxygen fluctuations). It is generally accepted that short-term microcosm tests usually overestimate denitrification capacity because they are typically conducted under optimal conditions.[34,37,38]

5. Conclusions

N_2O emission fluxes and denitrification potential rates decreased along the river flow path (from sites S1 to S5) and across from submerged sediment to dry soil because of the surrounding land use and sediment/soil characteristics. The adjacent land use and wastewater discharge had a great impact on the sediment/soil properties (e.g., sediment/soil texture and organic matter content). Sites (S1 and S2) near the residential area had finer sediment textures, higher organic matter concentrations, and higher inputs of wastewater discharge, and they also had the highest N_2O emission fluxes and denitrification potentials. In contrast, the other three sites (S3–S5) had sandy sediment/soil textures and lower wastewater discharge, resulting in much lower N_2O emission fluxes and denitrification potentials. In this study, the water content, TOC, nitrate and ammonium

contents were all positively correlated with N_2O emission fluxes and denitrification potentials. Among these parameters, the water content was most strongly correlated with N_2O emission fluxes and denitrification potentials within the five study sites, and the submerged locations nearest the river water had the highest N_2O emission fluxes. The RBS were effective in removing nitrogen by coupled transformation and denitrification processes. Thus, the incorporation of RBS along rivers and the optimisation of their performance, e.g., maintaining a gradient of aerobic to anaerobic conditions, may be effective in removing nitrogen from surface waters and increasing water quality. Further study should focus on the exact method of nitrogen removal, with more parameters affecting nitrification and denitrification.

Acknowledgements

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