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**Seasonal variability of denitrification efficiency in northern salt
marshes: An example from the St. Lawrence Estuary**

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Abstract

In coastal ecosystems, denitrification is a key process in removing excess dissolved nitrogen oxides and participating in the control of eutrophication process. Little is known about the role of salt marshes on nitrogen budgets in cold weather coastal areas. Although coastal salt marshes are important sites for organic matter degradation and nutrient regeneration, bacterial-mediated nitrogen cycling processes, such as denitrification, remain unknown in northern and sub-arctic regions, especially under winter conditions. Using labelled nitrogen (^{15}N), denitrification rates were measured in an eastern Canadian salt marsh in August, October and December 2005. Freshly sampled undisturbed sediment cores were incubated over 8 h and maintained at their sampling temperatures to evaluate the influence of low temperatures on the denitrification rate. From 2 to 12 °C, average denitrification rate and dissolved oxygen consumption increased from 9.6 to 25.5 $\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ and from 1.3 to 1.8 $\text{mmol O}_2 \text{ m}^{-2} \text{ h}^{-1}$, respectively, with no statistical dependence of temperature ($p > 0.05$). Nitrification has been identified as the major nitrate source for denitrification, supplying more than 80% of the nitrate demand. Because no more than 31 % of the nitrate removed by sediment is estimated to be denitrified, the presence of a major nitrate sink in sediment is suspected. Among possible nitrate consumption mechanisms, dissimilatory reduction of nitrate to ammonium (DNRA), metal and organic matter oxidation processes are discussed. Providing the first measurements of denitrification rate in a St. Lawrence Estuary salt marsh, this study evidences the necessity of preserving and restoring marshes. They constitute an efficient geochemical filter against an excess of nitrate dispersion to coastal waters even under cold northern conditions.

Keywords: Biogeochemical cycle, Denitrification, Ice, Nutrients, Salt marshes, Sediments, Stable isotopes.

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Introduction

Denitrification is the dissimilatory reduction of nitrogen oxides (NO_2^- ; NO_3^-) to gaseous nitrogen (N_2). A large group of anaerobic bacteria of the genus *Pseudomonas*, synthesizing different types of reductases, can use reduced nitrogen oxides as electron acceptors in the absence of oxygen (Knowles, 1981). Denitrification is recognised as the key process to maintain nitrogen limitation in coastal waters (Howarth, 1988). It removes excess dissolved inorganic nitrogen loads (Seitzinger, 1988), decreasing the amount of fixed nitrogen available to the primary producers (Nixon, 1981). As a consequence, denitrification is important in controlling the eutrophication level in coastal environments (eg. Nowicki *et al.*, 1997) that are increasingly affected by anthropogenic nutrient inputs (Cloern, 2001). The exposure of terrestrial organic matter and nutrient inputs to estuaries (Gearing and Pocklington, 1990) leads to high primary productivity and high organic matter deposition, and therefore results in high bacterial mineralization, which causes a depletion of oxygen supplies in the sedimentary compartment (Duarte, 1995).

Formed in the upper littoral zone of mid and high latitudes, coastal salt marshes are known as a major feature of macrotidal estuaries (Jickells and Rae, 1997). Affected strongly by tidal flooding and by riverine runoff, marsh areas act as an important bioprocessor of nitrogen species (Aziz and Nedwell, 1986) which play many critical ecological and economic roles (Boorman, 1990). Although the nitrogen cycle in North-West Atlantic Coast and Western Europe temperate salt marshes (Kaplan *et al.*, 1979; Aziz and Nedwell, 1986; Koch *et al.*, 1992; Thompson, 1995; Eriksson *et al.*, 2003) has been studied extensively, our understanding of the dynamic of sub-arctic marsh environments is still incomplete, specially during winter time when sea ice covers littoral

areas. There is still lack of knowledge about biogeochemical processes in these icy environments, especially the nitrogen cycle and the rate of microbial-mediated nitrogen transformations such as denitrification. As the first step toward predicting decennial behaviour of cold coastal ecosystems under the actual scenario of global coastal eutrophication (Cloern, 2001; Jickells, 2005), it is essential to determine rates and pathways by which fixed nitrogen is metabolised by bacteria.

The main objective of this study is to evaluate seasonal denitrification rates in a northern salt marsh subject to frozen conditions for four months of year. Using labelled nitrate ($^{15}\text{NO}_3^-$) (Nielsen, 1992), denitrification rates were measured in Pointe-au-Père salt marsh sediment (St. Lawrence Estuary, Québec, Canada) in August, October and December 2005; with weather conditions corresponding to summer, fall and winter, respectively. Freshly sampled intact cores were incubated under *in situ* temperatures to evaluate the influence of temperature on N_2 , dissolved inorganic nitrogen (DIN) and O_2 fluxes resulting from denitrification and mineralization processes. During the late experiment in December, sediment cores were collected under a thin ice cover to quantify denitrification rates under the coldest conditions occurring in this coastal region. The quantitative significance of denitrification as well as relative contribution of biochemical processes, such as organic matter mineralization to the cold salt marsh nitrogen cycle, has been discussed. These are the first direct measurements of the denitrification rates in a St. Lawrence Estuary salt marsh and provide the first estimates of the relative importance of denitrification as a nitrate removal process in northern estuaries.

Materials and methods

Studied site

The Pointe-au-Père salt marsh (48° 30' 30''N, 68° 28' 30''W) is located on the south shore of the St. Lawrence Estuary in the city of Rimouski (Québec, Canada) (Fig. 1). This marsh has been part of the Pointe-au-Père National Wildlife Area protected by Canadian Wildlife Service (Environment Canada) since September 2002. Confined in an elongated basin parallel to the main Estuary axis and sheltered from wave action by a longitudinal Palaeozoic structure, this 22.6 ha marsh is dominated by areas with homogenous emergent macrophyte (*Spartina alterniflora*) communities surrounded by vegetation-free network creeks. Due to its low slope, the floodwater complexly spreads over marsh area during semi-diurnal cyclic tidal excursion; tidal water enters by a large inlet at the western border, progresses laterally and smoothly over mud flats, as energy of the incoming tide is dissipated by friction on the inner bay. Located in a partly urbanised watershed, this marsh receives nitrogenous inputs in micro-molar concentrations from both agricultural and urban runoff ($A_v \pm SD$; $7.29 \pm 16.43 \text{ kg DIN d}^{-1}$). This freshwater runoff enters the salt marsh by two main drainage channels along the south-east border ($0.28 \pm 0.59 \text{ m}^3 \text{ s}^{-1}$). In addition, the St. Lawrence coastal zone is subject to important seasonal variations, which affects water temperature and salinity in response to heat flux and freshwater discharge. One of the main features of Saint-Lawrence cold salt marshes is the formation of sea ice that begins in early December and persists until April. This ice cover plays an important role in littoral ecosystems. Although sea ice erodes tidal flats, it

protects the intertidal zone from wave action and generates singular sedimentary structures (Dionne, 1998; Drapeau, 1992; Serodes and Dubé, 1983).

Sampling procedure

For each experiment (carried out in August, October and December 2005), 18 sediment cores (5 to 10 cm long x 9.8 cm i.d.) were collected at low tide in the same 10 m² area showing homogenous and specific surface characteristics (Fig. 1) using a tubular aluminium corer (100 cm long x 9.8 cm i.d.). To minimize perturbation of superficial sediment, the corer was slowly pushed into the sediment and the core was recovered using a small shovel. Each sediment core was delicately truncated at 3 cm below the sediment surface, to obtain a 3-cm long x 9.8 cm i.d. core, and was carefully transferred to a Plexiglas tube (14.5 cm long x 9.8 cm i.d.) later used as incubation chambers. Tubes with cores were transported to the laboratory within 30 minutes to minimize alteration of natural biogeochemical equilibria, and wrapped in aluminium foil to avoid photochemical reactions. In addition, 50 L of surface sea water was collected from the Pointe-au-Père biological station pier (Fig. 1) and stored in an acid pre-cleaned polypropylene bottle to perform incubation; whose salinity, dissolved oxygen and nitrate level is 25 ± 2 , 10 ± 2 mg l⁻¹ and 1.8 µM (August) ~ 14.7 µM (December), respectively.

Laboratory incubations

In the laboratory, tubes were placed in a temperature controlled room set at the temperature measured in sediment cores at the sampling site (i.e. 12, 6, and 2 °C for August, October and December, respectively). The tubes were labelled from 1 to 18 and

sealed at the bottom with rubber stoppers. Tubes 1 to 8 were used for denitrification measurements, tubes 9 to 12 were used for nitrate (NO_3^-) and ammonium (NH_4^+) flux measurements whereas tubes 13 to 16 were used for dissolved oxygen (O_2) flux measurements. These 16 capped tubes (named incubation chambers) were incubated in the dark, using a large temperature-controlled water bath equipped with a stirring system (shaking table type), set at the temperature corresponding to the sampling season. The incubation period was fixed at 8 h to avoid expected development of hypoxic conditions ($[\text{O}_2] < 2 \text{ mg l}^{-1}$) in the overlying water layer, since preliminary data obtained over the last three years showed that Pointe-au-Père salt marsh water column is year around well oxygenated. The remaining two sediment cores, kept in tubes 17 to 18, were freeze-dried and homogenised for determination of sediment characteristics, including carbon and nitrogen element, particle size, trace metal and total hydrolysable amino acid (THAA).

Denitrification activity

For the denitrification rate determination, seawater (500 ml) enriched with 35 to 45 μM K^{15}NO_3 (98 atom % $^{15}\text{NO}_3$, Aldrich) was transferred in tubes 1 to 8, giving a water layer of about 7 cm height and an air head-space of ~2 cm (281 ml). The concentration of NO_3^- in typically impacted salt marsh water was ~20 μM . Tubes were capped with rubber stoppers equipped with gas-tight sampling ports and stirred for 10 min using a stirring table set at ~60 RPM to ensure homogenization of spiked nitrate. Then, a 5-ml water sample was sampled and replaced by ambient air (using 5-ml gas-tight syringe) to measure the initial concentration of NO_3^- and therefore the initial concentration of $^{15}\text{NO}_3^-$ was calculated. Tube air head-space was sampled (using a 10 μl

gas-tight syringe) to measure the initial N_2 isotopic composition. After an 8-h incubation period, sediment cores were manually shaken for 2 min in order to equilibrate pore water gases with the overlying water. Air head-space of each chamber was sampled once again to measure final N_2 isotopic composition. Before each sampling, the gas-tight syringe and the GC-IRMS injection port were flushed with helium. After collection, air samples were immediately introduced in the GC gas port for isotopic composition determination to avoid a gas storage step and contamination risks.

Nitrogen species and dissolved oxygen fluxes

The procedure described previously was applied to the 8 remaining incubation tubes, but labelled $K^{15}NO_3$ was replaced by unlabelled KNO_3 . These chambers were incubated without gas head-space and were sampled hourly during the 8-h incubation, using 5 and 25 ml gas-tight syringes. For NO_3^- flux measurements, water samples (5 ml) were taken from tubes 9 to 12, transferred into 5-ml cryovials and stored at $-80^\circ C$ for further analysis. The same procedure was applied to measure NH_4^+ fluxes except that water samples were analysed immediately after sampling. The remaining four chambers (13 to 16) were used for O_2 flux measurements as 25-ml water samples were transferred in volumetric glass bottles and analysed without delay. To avoid depressurisation in chambers, sampled water was replaced by an identical volume of ambient air.

Using denitrification rate measurement via direct determination of air head-space N_2 isotopic enrichment from immersed sediments (Nielsen, 1992) can avoid some of the problems associated with indirect approaches (e.g. Sorensen, 1978). However, despite their advantages, the labelled N_2 flux technique suffers of some artefacts mainly caused

by the non-equilibrium conditions imposed by closed chambers (Hamersley and Howes, 2005), particularly for O₂. Since sediment cores were incubated without considering diurnal tidal inundation and dewatering cycle, photosynthetic O₂ production as well as atmospheric advection, sedimentary O₂ supply was blocked. This artefact could alter chamber chemical conditions (affecting the redox structure of sediment core and the equilibrium between dissolved ionic compounds in the pore water and onto sedimentary particles), and affect the balance between aerobic and anaerobic heterotrophy as well as the overall measured nitrification-denitrification rates (Risgaard-Petersen, 2003). By opting for an experimental design including short incubation period, relatively large gas headspace and water thicknesses, we minimised measurement errors and artefacts linked to closed incubation chambers.

Analyses

Isotopic composition of air head-space N₂ (¹⁴N¹⁴N, ¹⁴N¹⁵N and ¹⁵N¹⁵N) was determined using a gas chromatograph/combustion/isotope ratio mass spectrometer system (GC/C/IRMS Delta XP Plus[®], Thermo Finnigan equipped with a ConFlo III interface). Gas samples (10 µl) were injected manually in the GC inlet and nitrogen species were separated isothermally at 125 °C by gas chromatography using a DB5 30 m capillary column (0.25 mm i.d.) with helium as the vector gas and were combusted in an oxidation and reduction furnace at 850 and 650 °C respectively. The gas samples were then passed through a cryogenic trap (liquid nitrogen) to remove water vapour and condensable gases followed by the alternative introduction of pure N₂ reference gas and N₂ samples into the mass spectrometer for ¹⁴N¹⁴N, ¹⁴N¹⁵N and ¹⁵N¹⁵N peaks area

determination. The retention time for N₂ was 150 sec and mass peaks were integrated over 120 sec.

Dissolved O₂ was measured using the standard Winkler titration method (Strickland and Parson, 1968), NO₃⁻ dosages were made by classical colorimetric technique (Strickland and Parson, 1968) using an automated analytic Bran+Luebbe AA3[®] platform whereas NH₄⁺ concentrations were determined using a micro-plate base fluorometric technique (Poulin and Pelletier, 2006). Sediment core elementary analyses for carbon and nitrogen (C_{org}/N_{tot}) were performed with a ECS 4010 Costech[®] instrument equipped with a zero blank auto sampler, using certified sediment sample (n = 10) NIST-1941b as a reference, whereas granulometric analyses were done with Coulter[®] counter model LS13320C. Trace metals (Mn and Fe) were measured in 0.5 g dry sediment samples according to Anschutz *et al.*(2000). Extraction was carried with 35 ml of 1 N HCl for 6 h. The solutions were centrifuged, supernatant was diluted in 1 % HCl and analysed in normal mode with an inductively coupled plasma mass spectrometer (ICP-MS Agilent[®] 7500c) equipped with a micro-nebulizer. Metals were quantified with an external linear calibration curve established from standard solutions (Multielements standards solution IV, Fluka Chemie, Sigma-Aldrich). Total hydrolysable amino acids (THAA) were measured in 0.5 g freeze-dried, homogenised sediment samples. After hydrolysis with 10 ml of 6 N HCl at 100 °C for 24 h, the supernatant acid solution was centrifuged, diluted and neutralized with 2 N NaOH. The solutions were analysed on a Shimadzu[®] LC 10AD VP HPLC system using a Agilent[®] C-18 column (4.6 X 250 mm, 5 µm) and a Water[®] 470 fluorescence detector (λ_{ex} = 230 nm, λ_{em} = 445 nm) after derivatisation with o-phthaldialdehyde and 2-mercaptoethanol (Lindroth and Mopper,

1979) using phosphate buffer and methanol gradient. Individual amino acids were identified and quantified using amino acid standard solution (Sigma®) which contained 21 amino acids and ammonium chloride.

Calculations

Total denitrification rates (Dt) were calculated from chamber air-space ^{15}N enrichment according to Nielsen (1992). The labelled ^{15}N concentration was estimated by multiplying its isotopic ratios ($^{14}\text{N}^{15}\text{N}/\text{total N}_2$ and $^{15}\text{N}^{15}\text{N}/\text{total N}_2$) by the calculated N_2 concentration in the air trapped in the head-space and in water layer knowing the distribution coefficient of N_2 in sea water as a function of temperature (Weiss, 1970). NO_3^- denitrification rates coming from overlying water (Dw) and denitrification rates of NO_3^- produced within the sediment by nitrification (Dn) were calculated using equations below. These equations require three main assumptions: 1) the total amount of $^{14}\text{N}^{14}\text{N}$ inside the incubation chamber does not change during the sample collection period, 2) the ^{15}N labelling of the NO_3^- in the sediment is uniform, 3) $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}^{15}\text{N}$ constitute 0.7299 % and 0.001 % of total N_2 in the air (Nielsen, 1992).

$$D15 = (^{14}\text{N}^{15}\text{N}) + 2(^{15}\text{N}^{15}\text{N}) \quad (1)$$

$$D14 = D15 \times (^{14}\text{N}^{15}\text{N}) / 2(^{15}\text{N}^{15}\text{N}) \quad (2)$$

$$Dw = D15 \times [^{14}\text{NO}_3^-] / [^{15}\text{NO}_3^-] \quad (3)$$

$$D_t = D_{15} + D_{14} \quad (4)$$

$$D_n = D_t - D_w \quad (5)$$

The $^{14}\text{NO}_3^-$ concentrations were determined in overlying water in incubation chambers before $^{15}\text{NO}_3^-$ addition whereas $^{15}\text{NO}_3^-$ concentrations were measured as a concentration increase in water after the addition.

Diagenetic alteration of sedimentary amino acids was assessed using the Degradation Index (DI) developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999). This index is based on the first axis of a Principal Component Analysis (PCA) of the amino acid composition and summarizes, in one variable, the relative cumulative variation of 14 amino acids (aspartic acid, glutamic acid, serine, histidine, thréonine, arginine, glycine, tyrosine, alanine, méthionine, valine, phenylalanine, isoleucine and leucine). DI values were calculated from amino acids average molar concentration, standard deviation and predetermined coefficient factors (i.e. first axis of the Principal Component Analysis from the comprehensive data set of Dauwe et al., 1999). The DI sign indicates a depletion (-) or an enrichment (+) of labile organic nitrogen protein in sediment.

Pearson correlations were performed in first instance to assess the relationship between pairs of variables considering correlation significance at $p < 0.05$ level. Thereafter a One-Way Analysis of Variance (ANOVA) was performed to test the significant effect of a fixed factor (temperature) on dependant variables (denitrification, oxygen and nitrate consumptions and ammonification). To isolate groups that differed

from the others, a Tukey post-hoc test was performed. When ANOVA assumptions were not respected, a Kruskal-Wallis One-Way Analysis of Variance on Ranks was performed followed by a Dunn's post-hoc test. Differences between groups were considered significant at the $p < 0.05$ level. Comparisons of means were performed with Sigma Stat[®] version 3.11 from SyStat Software Inc.

Results

Sediment analysis revealed that all cores exhibited quite uniform characteristics with organic carbon abundance ranging from 6.5 to 9.0 %, C/N values ranging from 13.2 to 19.4, average particle size ranging from 109 to 198 μm , manganese and iron concentrations ranging from 0.04 to 0.08 $\mu\text{mol g}^{-1}$ (d.w.) and from 4.17 to 4.84 $\mu\text{mol g}^{-1}$ (d.w.), respectively (Table 1).

Total denitrification rates ($D_t = D_w + D_n$) measured in Pointe-au-Père salt marsh sediment varied from 5.73 to 15.01 $\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ at 2 °C, from 11.18 to 24.62 $\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ at 6 °C, and from 18.36 to 42.24 $\mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$ at 12 °C. Measured D_t rates increased with temperature but this trend is not statistically significant ($p > 0.05$) (Fig. 2) due to a large range of values observed for each series of measurements. For the same initial nitrate addition, D_t rates remained important even under the lowest temperature since the average rate at 2 °C was only 2.6 fold lower than the one determined at 12 °C. Denitrification coming from overlying water (D_w) averaged 15, 6 and 2 % of D_t rates at 2, 6 and 12 °C, respectively. Although representing a minor contribution to D_t rates, D_w values were statistically correlated to temperature ($p = 0.001$). Denitrification produced within the sediment by nitrification (D_n) represented the main contribution to D_t rates.

Statistically correlated to temperature ($p = 0.038$), Dn contributed for 85, 94 and 98 % of Dt rates at 2, 6 and 12 °C, respectively.

Dissolved oxygen sediment consumption rates also showed an increasing trend with temperature, which ranged from 1.25 to 1.43 mmol O₂ m⁻² h⁻¹ at 2°C, from 1.59 to 1.70 mmol O₂ m⁻² h⁻¹ at 6 °C, and from 1.63 to 1.94 mmol O₂ m⁻² h⁻¹ at 12 °C; but this was not statistically significant ($p > 0.05$) (Fig. 3). However, sediment nitrate consumption and ammonium generation rates were both statistically correlated to temperature ($p = 0.001$ and 0.04, respectively). Between 2 and 6 °C, nitrate and ammonium fluxes remained statistically identical (ranging from 59.25 to 139.41 μmol NO₃⁻ m⁻² h⁻¹ and 2.61 to 69.70 μmol NH₄⁺ m⁻² h⁻¹) whereas they significantly increased at 12 °C (215.52 to 296.79 μmol NO₃⁻ m⁻² h⁻¹ and 205.56 to 248.62 μmol NH₄⁺ m⁻² h⁻¹) (Fig. 4). This observation is expected to be closely linked to the increase of microbial activity with the temperature (Sundback *et al.*, 2000). In addition, a significant linear correlation was observed between nitrate consumption and ammonium generation rates ($r = 0.90$), which indicated a possible mechanistic relationship between these two processes in salt marsh sediment.

A typical HPLC profile of total hydrolysable amino acids (THAA) is given in figure 5 showing the dominance of aspartic and glutamic acids, serine, threonine and alanine in salt marsh sediment. THAA concentrations measured in triplicate on one core sampled during summer time (early in August 2005), reached 55.71 ± 5.61 μmol g⁻¹ ($n = 3$). The average DI value calculated for Pointe-au-Père salt marsh sediment (-0.67 ± 0.02 ; $n = 3$) was below the range of values usually obtained for coastal sediments (from -0.35

to 1.01) as reported by Dauwe *et al.*, (1999) indicating that organic matter in sediment was in an advanced state of decomposition (Table 1).

Discussion

A large body of information is available on factors influencing denitrification in coastal marine environments (see review by Herbert, 1999). The three main factors influencing benthic denitrification are temperature, supplies of NO_3^- and availability of organic carbon (Smith *et al.*, 1985; Yoon and Benner, 1992; Tuominen *et al.*, 1998). Despite these factors, denitrification rates values measured in our cold salt marsh sediments are comparable with those obtained by other workers along the North-West Atlantic Coast and in Western Europe temperate salt marshes (e.g. Great Sippewissett Marsh (New England, USA) $0\text{--}357 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, Kaplan *et al.*, 1979; Colne Point Marsh (England) $2.6\text{--}6.4 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, Aziz and Nedwell, 1986; Torridge Marsh (England) $2.51\text{--}59.0 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, Koch *et al.*, 1992; New Port Marsh (North Carolina, USA) $0\text{--}14.6 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, Thompson., 1995; Lagoon of Venise (Italia) $0\text{--}160 \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$, Eriksson *et al.*, 2003). Although a part of the variation in published denitrification rates could be related to differences in experimental designs, values reported here indicate that the denitrifying process is efficient in cold salt marsh sediments, even under winter conditions. Due to the lack of a significant relationship between mean Dt rate and temperature of incubation, the direct effect of temperature was difficult to assess when dissolved oxygen and nutrient concentration variations in the overlying water were taken into account. Temperature effects were weak since mean Dt rate at 2°C was only 2.6 fold lower than during incubation at 12°C (Fig. 2). Although the

high variability of measured denitrification rates needs to be considered to explain the lack of significant relationship between mean D_t rates and temperature, the incidence of coupled bacterial processes and favourable chemical conditions such as high NO_3^- availability should be considered. In addition, this result could indicate the combined contribution of a cold-adapted microbial population, which dominated winter time moderate denitrification activity, with a higher temperature optimum population being active during summer (Blackburn and Sorensen, 1988). However, no information is available on bacterial population succession in the study area.

Denitrification is recognised to be limited by NO_3^- supplies and hence by nitrification in coastal sediments (Jenkins and Kemp, 1984). In our study, nitrification is the main source of NO_3^- for denitrification, with an average D_n rate contribution reaching 98 % of D_t rate at 12 °C. Since D_n was statistically correlated to temperature, this result suggests that the coupling between nitrification and denitrification is thermo-dependant and consequently could be more important under summer than winter conditions in a cold salt marsh environment. The relative contribution of D_w to D_t could therefore explain the observed seasonal trend of denitrification rates. D_w rates, expected to increase with the *in situ* NO_3^- concentration, was negatively related to temperature ($p = 0.001$). Because *in situ* NO_3^- concentration was higher in December (14.7 μM) than in August (1.8 μM) in the St. Lawrence Estuary surface water, due to the incidence of sea ice on primary producers (data not shown), D_w contribution to D_t tends to mask seasonal denitrification variation (since the same $^{15}\text{NO}_3^-$ amendment was used for each experiment). These results indicate a control of D_w by NO_3^- concentrations and suggest that NO_3^- could play a substantial role in D_t limitation in cold salt marsh environment.

Aerobic respiration is related to temperature in coastal sediment (Thamdrup *et al.*, 1998; Silverberg *et al.*, 2000). However, no statistical relationship can be demonstrated ($p > 0.05$) between oxygen consumption rates and temperature in our study (Fig. 3). We hypothesize that aerobic microbial mineralization processes, predominantly responsible for oxygen consumption, are affected mainly by the quality and quantity of sedimentary organic matter and much less by temperature. Even if elementary analysis revealed no significant trend in organic carbon content with seasons (Table 1), more organic matter is available in salt marsh sediment during fall than at the end of summer (Valiela *et al.*, 1976). Since available organic matter may increase during autumn period when dead vegetation is added to marsh, it could have increased the overall sediment oxygen consumption during incubation carried in October as well as in December. Thus, carbon availability is low in summer but potential oxygen consumption rates are high because of warmer temperatures, while in fall/winter, carbon availability is high but potential rates are limited by colder temperatures. Alternatively, a greater proportion of carbon degradation could take place during the warmer months via alternative oxidation pathways such as sulphate, iron or manganese reduction.

Average NO_3^- consumption (molecular ratio) represented 46, 42 and 86 % of O_2 respiration rates at 2, 6 and 12 °C, respectively, showing that NO_3^- plays a determining role as a terminal electron acceptor for organic matter mineralization. On the other hand, we estimated that no more than 31 % of NO_3^- removed by salt marsh sediment at 6°C was subsequently denitrified (based upon the highest Dt/NO_3^- consumption ratio). Because nitrate consumption largely exceeded denitrification, alternative NO_3^- reduction pathways in sediment are suspected. Dissimilatory NO_3^- reduction to NH_4^+ (DNRA) by

heterotrophic bacteria has been reported as very important NO_3^- reduction pathway in shallow coastal environments (An and Gardner, 2002). On a molar ratio basis, NH_4^+ average flux reached 89 % at 12 °C and 29 % at 6 and 2 °C of the average NO_3^- consumption (Fig. 4). This result and the observed significant positive correlation between nitrate consumption and ammonium generation rates ($r = 0.90$) could indicate that a coupling exists between these two processes in cold salt marsh sediment. However, before considering this coupling, we need to evaluate the relative contribution of both ammonification processes (NH_4^+ bacterial production from organic matter and DNRA processes) on NH_4^+ generation rates. Although we did not measure $^{15}\text{NH}_4^+$ enrichment from $^{15}\text{NO}_3^-$ amendment in this study (to determine DNRA rates), the calculated DI (-0.67) from THAA measurement as well as the C/N ratio (13.2-19.4) of organic matter suggest that marsh sediment possessed only a small amount of labile organic material readily available for biologic mineralization (Table 1).

Mainly related to bacterial, phytoplanktonic and zooplanktonic cell plasma material (Dauwe and Middelburg, 1998), aspartic acid, glutamic acid, serine, threonine and alanine stand for this labile organic matter pool (Fig. 5). Although amino acids from proteins are the major organic nitrogen source to microbial ammonification (Pantoja and Lee, 2003), the quantitative mineralization of THAA present in marsh sediment ($55.71 \pm 5.61 \mu\text{mol g}^{-1}$) can not be used to explain the observed NH_4^+ flux ($228.51 \pm 21.67 \mu\text{M NH}_4^+ \text{ m}^2 \text{ h}^{-1}$). Thus, we suggest DNRA constitute a significant nitrogen recycling process in this sedimentary environment. This assumption is supported by a study carried by King and Nedwell (1985) which shows that NO_3^- concentration contributed to determine either how much NO_3^- is lost to N_2 or preserved as NH_4^+ in anaerobic salt marsh sediment.

These authors demonstrated that a low NO_3^- concentration ($[\text{NO}_3^-] < 236 \mu\text{M}$) can enhance DNRA whereas a high NO_3^- concentration promoted denitrification. In addition, Joye and Hollibaugh, (1995) showed that sulphur compounds can inhibit denitrification and enhance DNRA. Since only a low $^{15}\text{NO}_3^-$ concentration was used in this study (corresponding to natural level) and particularly because the presence of sulphur compounds was suspected in our salt marsh samples (presence of hydrogen sulphide odour during sampling) DNRA should be investigated in cold salt marsh sediment as a key NO_3^- removal process.

Another NO_3^- sedimentary sink that can be invoked in this study is the NO_3^- reduction by Mn^{2+} . In anoxic sediment, dissolved oxidants present in pore water are recognised to be actively used by heterotrophic bacteria as terminal electron acceptor for OM oxidation, leading to the reduction of oxidized metals. Partially reduced metal, such as Mn^{2+} , can be re-oxidised to MnO_2 by NO_3^- in the absence of oxygen (Luther *et al.*, 1997). Although this abiotic process could contribute to nitrogen cycling, reduced Mn likely played a marginal contribution in measured NO_3^- flux considering low Mn^{2+} concentration ($0.04\text{-}0.08 \mu\text{mol g}^{-1}$) measured in salt marsh sediment (Table 1) compared to St. Lawrence Estuary surface sediment ($13.4\text{-}92.8 \mu\text{mol g}^{-1}$; Anschutz *et al.*, 2000).

Results based on field and laboratory studies (Simek and Cooper, 2002) determined that denitrification processes measured in cold salt marshes would not be a significant source of N_2O . These authors showed that denitrification end products were mostly determined by sediment pH with low $\text{N}_2\text{O}/\text{N}_2$ production ratios in more neutral sediment. Because pH of flooding estuarine water in the Pointe-au-Père marsh varied from 6.5 to 8.5 (data not shown), denitrification should mostly produce N_2 . Although

both environments might be different, dinitrogen was the exclusive product of denitrification in the Tagus Estuary salt marsh sediment (Cartaxana and Lloyd, 1999). High organic content and low oxygen concentration were assumed to increase the demand for electron acceptors in salt marsh sediment, preventing N_2O emission by denitrification. In addition, a recent study on a coastal embayment located in Eastern Canada reported very low N_2O production from denitrification ranging from undetectable to $40 \text{ pmol N}_2\text{O l}^{-1} \text{ d}^{-1}$ (Punshon and Moore, 2004).

The relatively high microbial organic matter degradation propensity observed in salt marsh surface sediment (Table 1) coupled with high nitrate uptake capacity measured in this study argue for a significant role of salt marsh in estuarine annual N and C budget. The reduced vascular plant canopy and coarse salt marsh sediment favour the development of benthic microbial communities involved in N and C biochemical cycles (Aspen *et al.*, 2004). Nevertheless, since St. Lawrence Estuary marshes are affected strongly by erosion (Dionne, 1986), these areas actually might appear insignificant in regard to estuarine bottom sediment surface ($\sim 3000 \text{ km}^2$). While they represented only 90 km^2 in 1986 (Dionne, 1986), these marsh areas are becoming more vulnerable to increased erosive forces (Morissette, 2006). Thus, it is clear that marsh areas need restoration effort to recover a significant contribution to the whole St. Lawrence estuarine system because these ecosystems possess a strong nutrient regeneration potential. Concerning the nitrogen cycle, measured sedimentary denitrification and NO_3^- consumption rates on this study were, in average, ~ 6 times higher than rates measured in deep sediments of the St. Lawrence marine system ($1.8\text{-}3.3 \text{ } \mu\text{mol N}_2 \text{ m}^{-2} \text{ h}^{-1}$; and $13.9\text{-}25.5 \text{ } \mu\text{mol NO}_3^- \text{ m}^{-2} \text{ h}^{-1}$; Wang *et al.*, 2003). In addition, assuming that 2.4 mol of N_2 are

produced through the mineralization of 6 g of elemental carbon (Gottschalk, 1979), we can estimate the denitrification contribution to the carbon salt marsh cycle at $< 64 \mu\text{g C m}^{-2} \text{ h}^{-1}$ (using average summer time denitrification rate value). This carbon mineralization rate resulting from denitrification is 16 times higher than the one defined for the Laurentian Through by Wang *et al.* (2003) evaluated at $4.125 \mu\text{g C m}^{-2} \text{ h}^{-1}$ (based on a denitrification rate of $3.3 \mu\text{mol N m}^{-2} \text{ h}^{-1}$).

Because this study focused only on one specific site, we cannot extrapolate our results to the whole St-Lawrence Estuary intertidal system. On the other hand, these results combined with those of Wang *et al.*, (2003) support the idea that cold salt marsh environments appear to be an efficient year-round sinks for nitrate, which could contribute to the whole St. Lawrence estuarine denitrification capacity if actions are taken to increase substantially their surface. This study shows that denitrification accounts for a variable fraction of NO_3^- reducing processes and alternative pathways, such as DNRA, appear important in salt marsh sediment, especially during summer. Further investigations should be undertaken to explain the relative contribution of these two processes as well as seasonal changes in NO_3^- reducing bacterial population in this area. Considering that coastal wetlands are being lost worldwide (Boorman, 1999), our results highlight the importance of preserving and restoring northern salt marsh areas, as they are part of an efficient geochemical filter against nitrate dispersion to coastal waters.

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Table 1 : Geochemical characteristics (mean values) of sediment samples collected in St. Lawrence Estuary salt marsh in 2005.

Sample	Grain size	N	C	C/N	[Mn]	[Fe]	[AA]	DI
(y/m/d)	(μm)	(%)	(%)		($\mu\text{mol g}^{-1}$)	($\mu\text{mol g}^{-1}$)	($\mu\text{mol g}^{-1}$)	
2005-08-10	109.6	0.55	6.53	13.96	0.04	4.34	58.28	-0.66
2005-08-10	109.5	0.54	9.00	19.35	0.04	4.36	49.27	-0.69
2005-08-10	ND ¹	ND	ND	ND	ND	ND	59.58	-0.66
2005-10-04	198.5	0.61	6.91	13.19	0.07	4.17	ND	ND
2005-10-04	167.4	0.56	8.18	17.01	0.04	4.52	ND	ND
2005-12-06	156.5	0.55	6.96	14.86	0.08	4.63	ND	ND
2005-12-06	145.3	0.56	7.67	16.11	0.08	4.84	ND	ND

¹ not determined

Figure Captions

Figure 1 : Map of Pointe-au-Père salt marsh located along the St-Lawrence Estuary south shore in Rimouski. The white area represents the infra-littoral zone, dark grey area the inter-tidal zone and light grey area the supra-littoral zone. The black square represents the 10-m² sampling area.

Figure 2 : Contribution of denitrification rates produced within the sediment cores by nitrification (Dn in grey) and denitrification rates coming from overlying water (Dw in black) to total denitrification (Dt) as a function of incubation temperatures. Values represent mean $\pm$ SD (n = 8).

Figure 3 : Dissolved oxygen uptake rates as a function of incubation temperatures. Values represent mean $\pm$ SD (n = 4).

Figure 4 : Nitrate consumption rates (in grey) and ammonium production rates (black) as a function of incubation temperatures. Values represent mean $\pm$ SD (n = 4).

Figure 5 : Typical HPLC chromatogram of THAA extracted from Pointe-au-Père salt marsh sediment sampled in August 2005. main identified amino acids are aspartic acid (Asp), glutamic acid (Glu), serine (Ser), threonine (Thr) and alanine (Ala).

FIGURE 1

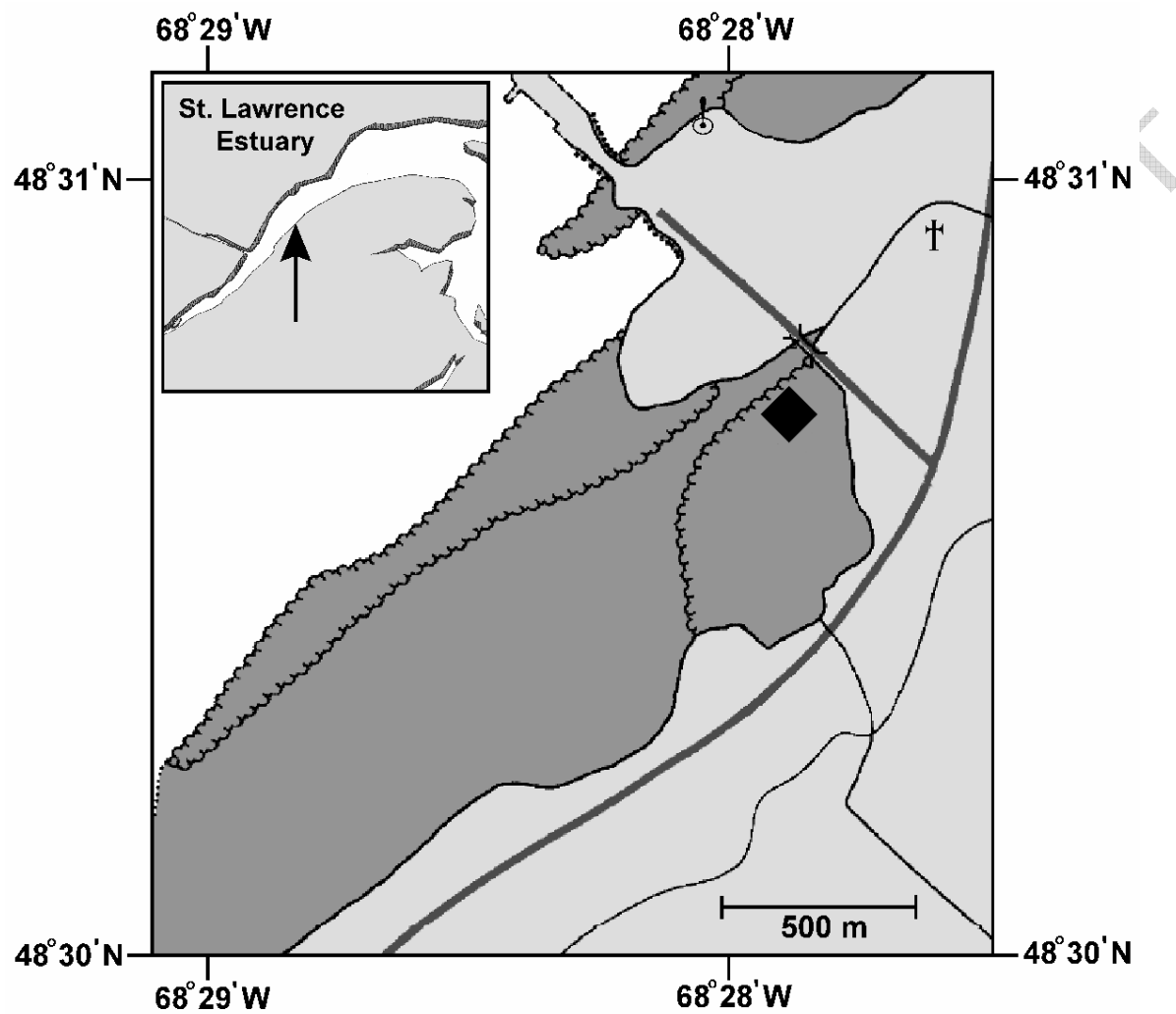


FIGURE 2

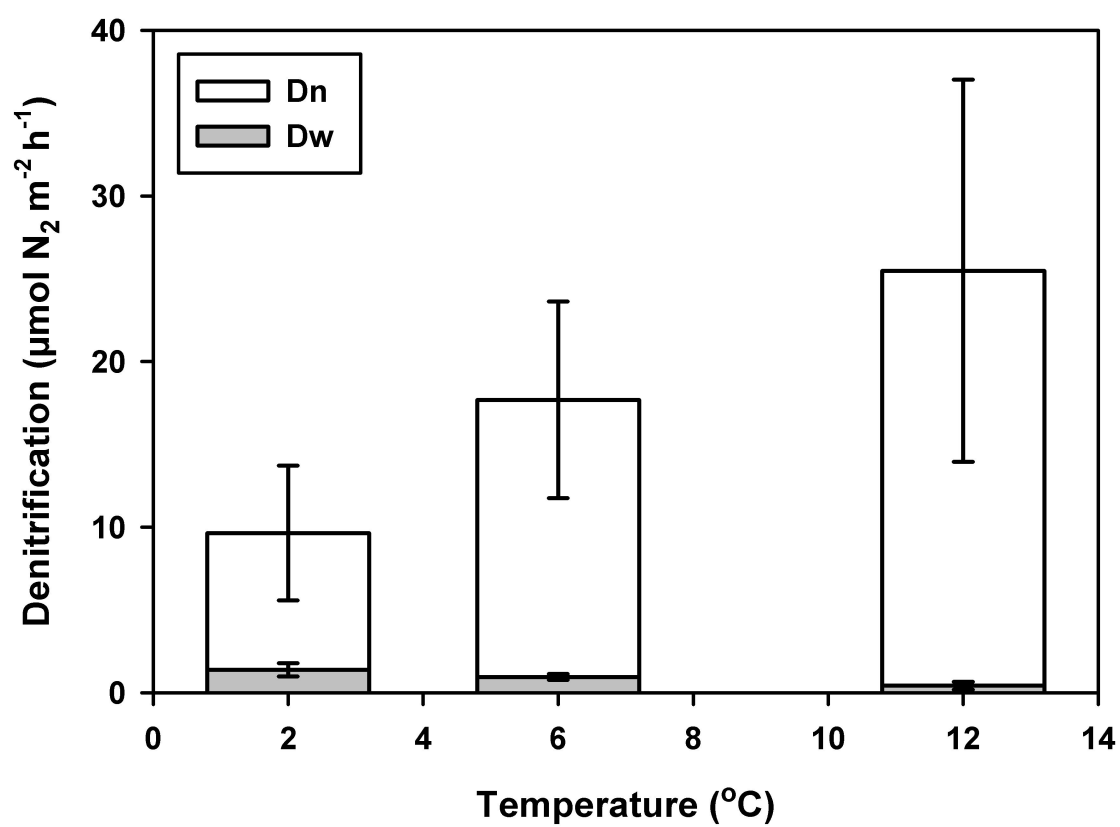


FIGURE 3

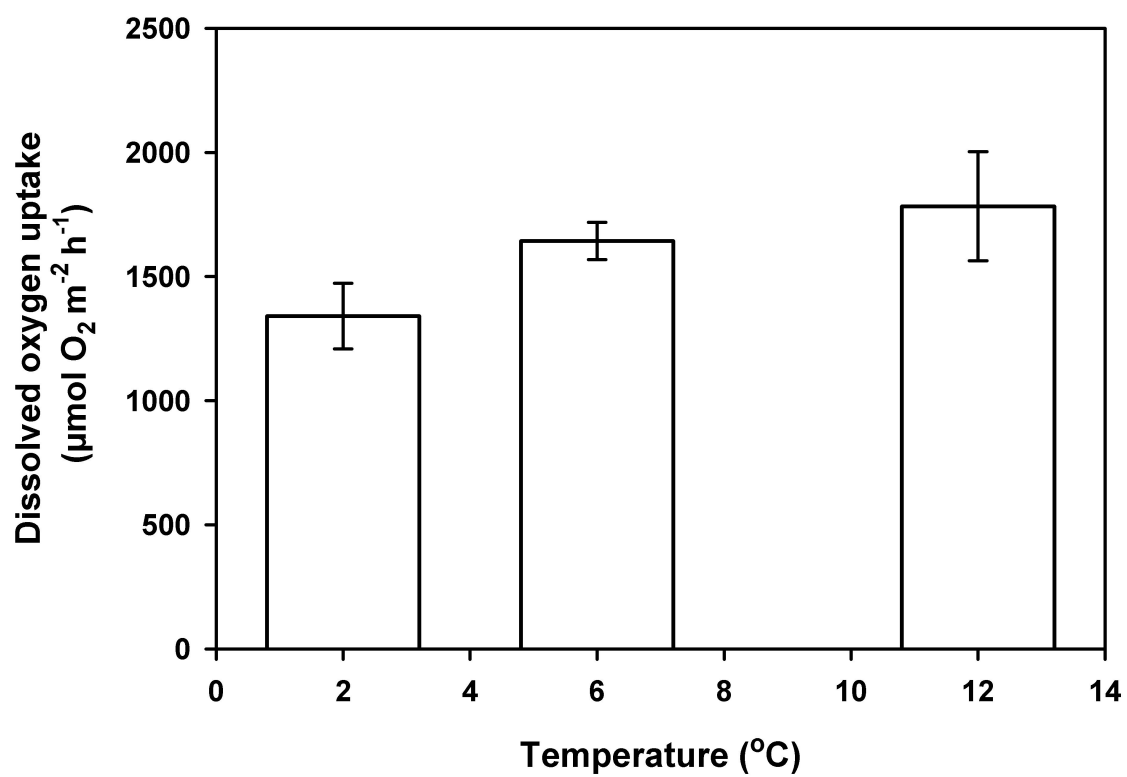


FIGURE 4

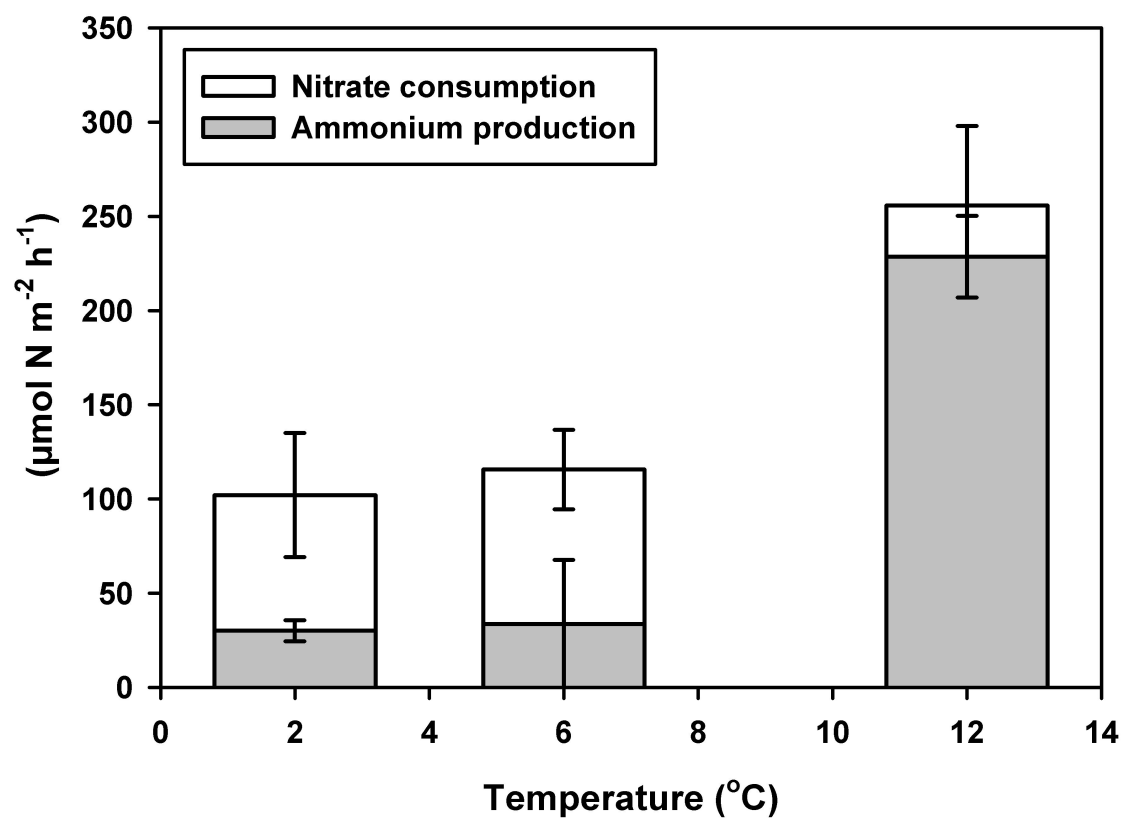


FIGURE 5

