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Nitrate removal and potential soil N_2O emissions in eutrophic salt marshes with and without *Phragmites australis*

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ABSTRACT

Wetlands are highly effective systems mitigating the negative effects of N excess, but at the same time they contribute to global warming through greenhouse gas emissions. The present study aimed to ascertain the role of *Phragmites australis* in N transformations in eutrophic semiarid salt marshes, under low ($NO_3^- = 20$ mg L^{-1}) and high ($NO_3^- = 200$ mg L^{-1}) nutrient level and alternating flooding-drying phases. Methacrylate mesocosms were filled with a saline soil, with and without the presence of *Phragmites* stands, and subjected to alternating flooding-drying conditions. For 44 weeks the soil Eh was regularly monitored at two depths and the N-NO_3^- and N-NH_4^+ concentration in pore water and drainage and the potential soil N-N_2O emissions to the atmosphere measured. In the surface soil layers, more than the 80% of N-NO_3^- was removed regardless of the presence of plants, the nutrient level and the season of the year. Denitrification seemed to be the main responsible of this. In the subsurface soil layers N-NO_3^- decreased an average of ~83% in presence of *Phragmites* and ~32% without plants during the warmer period (soil temp. ~15 to ~30 °C), but the effectiveness was reduced to <10% during the colder period (soil temp. ~10 to ~15 °C). The N-NH_4^+ increased during the flooding phases (reaching 2–6 mg L^{-1}), and the results indicated that it was nitrified during the following drying phases. A tendency to lower potential soil N-N_2O emissions was observed in treatments with *Phragmites* during drying phases, pointing that the plants absorbed this newly formed N-NO_3^-. Hence, we propose harvesting *Phragmites* stands at the beginning of the summer, but after a lag time to permit N-NO_3^- absorption by plants before the complete drying of the watercourses.

1. Introduction

The massive anthropogenic production of fertilizers has led to the degradation of numerous valuable ecosystems worldwide, increasing the eutrophication risk of water bodies (Di and Cameron, 2002; Robertson et al., 2013). This is of particular importance in catchments with high proportion of agricultural use because their effluents are often enriched by nitrogen (N), mainly in form of nitrate (NO_3^-) derived from fertilizers (Moss, 2008) which is not fixed to the exchangeable soil complex. Wetlands have been highlighted as valuable ecosystems to mitigate the negative effects of NO_3^- excess due to their capacity to act as green filters (Hoffmann et al., 2012; Lind et al., 2013). Hence, the diversion of N-rich effluents towards natural and constructed wetlands has been indicated as a suitable strategy to depurate eutrophic water. However, the latter strategy may be questioned in the current scenario of climate change due to the increasing emissions of greenhouse gasses (GHG) such as nitrous oxide (N_2O) (Hefting et al., 2013; Audet et al., 2014; Jacobs and Harrison, 2014).

The fate of N in wetlands is influenced by several complex inter-connected processes including mineralization, nitrification-denitrification, plant absorption, fixation and dissimilatory nitrate reduction (DNRA) (Tiedje, 1998; Saeed and Sun, 2012). One of the main mechanisms for N removal is the reduction of NO_3^- to the gaseous end product N_2O or dinitrogen (N_2) via denitrification process (van Oostrom and Russell, 1994; Xue et al., 1999; Vymazal, 2007). DNRA is another important NO_3^- reduction pathway, but in this process N is conserved in the system as ammonium (NH_4^+) which may pose threats to aquatic organisms since high NH_4^+ concentrations might be toxic (Ip et al., 2001; Maa and Aelion, 2005).

Denitrification may have important consequences for the atmosphere because N_2O is a potent GHG with a global warming potential

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298 times stronger than CO_2 over a 100 yrs time horizon (IPCC, 2007). However, even if more attention has been paid to the emissions of N_2O from different sources (Yang et al., 2012), some studies suggest that the advantages of the environmental benefits of water purification could outweigh the risks of GHG emissions (Hefting et al., 2013).

The magnitude of N_2O emissions from wetlands are mediated by a number of abiotic and biotic factors including sulfide and oxygen availability and plant and microbial community composition (Picek et al., 2007; Ma et al., 2008; Jacobs and Harrison, 2014). Also, there is a variety of results about the influence of different types of wetlands in N_2O emissions. Mander et al. (2014) reviewed GHG emissions from different types of constructed wetlands and concluded that the hydric regime, wastewater loading and presence of aerenchymal plants are key aspects for their behavior. Hefting et al. (2003) emphasized the substantial emission of N_2O from a NO_3^- loaded riparian buffer zone. Moseman-Valtierra et al. (2011) demonstrated that anthropogenic additions of NO_3^- to a coastal salt marsh incremented N_2O fluxes, with the highest emissions occurring during the warmer season. In other cases, the conclusions about N_2O emissions were uncertain due to the large variability obtained (e.g. Jørgensen et al., 2012; Audet et al., 2013). The latter was observed by Jørgensen et al. (2012) who studied temporal trends in N_2O fluxes in a wetland vegetated with *Phalaris arundinacea*. These authors found that N_2O fluxes were related with the O_2 concentration, water level, mineral-N availability, but also with light intensity. The importance of the last factor was linked to its influence on the plant activity which facilitated the N_2O transport from the root zone to the atmosphere. The complexity of the phenomena and the variety of influencing factors make necessary studies contributing to a better understanding of the processes involved in the reduction of NO_3^- and the emission of N_2O and to quantify the potential contribution of eutrophic wetlands to the global warming.

The Mar Menor lagoon (135 km^2, SE Spain; Fig. S1, Supplementary Material) and the surrounding agricultural lands (Campo de Cartagena) are among the most affected areas by eutrophication in Europe due to anthropogenic activities. In fact, the lagoon was declared a sensitive area subject to eutrophication in June 2001 under the European Directive 91/271/EEC and the Campo de Cartagena vulnerable to NO_3^- from agricultural origin in December 2002 under the Directive 91/676/EEC (Velasco et al., 2006; Conesa and Jiménez-Cárceles, 2007). The changes in crop production and/or the repeated production cycles during the year promote strong variations in the pulses of N-rich effluents flowing from the agricultural fields (Álvarez-Rogel et al., 2006). Large amounts of NO_3^--enriched water flows to the lagoon and coastal salt marshes during flash flood events, due to the short but intense storms typical of the area (García-Pintado et al., 2007; González-Alcaraz et al., 2012). This leads to the flooding of extensive areas of these salt marshes followed by drying periods due to the prevalence of high temperatures and the absence of precipitations. According to the global warming predictions, intense droughts and more irregular precipitation patterns are expected (IPCC, 2007). This may affect the response of these marshes against eutrophication, leading to changes in potential GHG emissions.

This paper is part of a wider study in which soils and plants collected from a coastal salt marsh of the Mar Menor lagoon were used to simulate the effects of eutrophic water pulses in these systems at mesocosms scale. In a previous paper Tercero et al. (2015) showed that the presence of *Phragmites australis* (Cav.) Trin ex Steud (common reed) and the nutrient level in the flooding water affected differently the evolution of the physico-chemical and microbiological soil properties at different depths, and this was modulated by changes in the soil temperature and the physiological activity of the plants throughout the year.

The aim of the present study was to ascertain the role of *Phragmites* in N transformations in eutrophic salt marshes throughout the seasons of the year, and to evaluate the potential soil N-N_2O emissions. To achieve this goal, a 1-year mesocosms experiment was performed with alternating flooding-drying conditions with eutrophic water enriched in N, phosphorus (P) and organic carbon at two concentration levels and with the presence and absence of common reed plants. During 44 weeks, the concentrations of N-NO_3^- and N-NH_4^+ in the soil solution and the potential soil N-N_2O emissions were regularly measured. Based on previous field studies (Álvarez-Rogel et al., 2006; González-Alcaraz et al., 2012) in which it was observed that the eutrophic water flowing throughout the Marina del Carmolí salt marsh was depurated, we hypothesized that the soil-plant system of this salt marsh can be highly effective in NO_3^- removal and that denitrification plays a main role in this process.

2. Materials and methods

2.1. Field sampling and soil characterization

Soils and plants were collected from the Marina del Carmoli salt marsh, located on the coast of the Mar Menor lagoon (SE Spain, N 37° 41′ 42″, W 0° 51′ 31″; Fig. S1, Supplementary Material). In this salt marsh, the typical soil profile consists on a surface loam to silty loam A layer overlaying a sandy C layer (Álvarez-Rogel et al., 2007). Several field studies have demonstrated that this salt marsh receives eutrophic water enriched in NO_3^- (e.g. Álvarez-Rogel et al., 2006; González-Alcaraz et al., 2012). Three types of samples were taken: 1) soil (top 25 cm) and the corresponding plants of *Phragmites* growing in it were collected from a stand of this species; 2) soil (top 25 cm) from a bare area next to the *Phragmites* stand; 3) sand from a dune system of the salt marsh located next to the two previous zones.

Aliquots (~300 g) of the soil and sand samples ($n = 5$) were air-dried and sieved through a 2-mm mesh for the initial characterization. The pH and electrical conductivity (EC) were measured in a 1:5 soil:water suspension after shaking for 2 h. Sieving (particles >50 μm) and the Robinson's pipette method (particles <50 μm) were used to determine particle size distribution, after organic matter oxidation with H_2O_2 and dispersion with $Na_6P_6O_{18}$. Total $CaCO_3$, total organic matter and total nitrogen were determined in powdered aliquots after grinding in an Agatha mortar as follows: total $CaCO_3$ by the Bernard calcimeter method (Muller and Gastner, 1971; Hulseman, 1996); total organic matter by loss on ignition (LOI) at 500 °C; and total nitrogen (TN) in an automatic LECO CHN analyzer.

The two soils collected were alkaline (pH ~ 7.9–8.1), with high content of total $CaCO_3$ (~28–31 g kg^{-1}) and fine textured (clay + silt content ~ 65%). The soil from the *Phragmites* stand showed higher content of organic matter (LOI ~ 6.8%) and TN (~0.19%) and it was slightly less saline (EC ~ 1.5 dS m^{-1}) than the soil from the bare area (LOI ~ 5.9%, TN ~ 0.14%, and EC ~ 3.2 dS m^{-1}). The sand was much less saline (EC ~ 0.2 dS m^{-1}), with higher pH (8.7) and total $CaCO_3$ content (59 g kg^{-1}), and lower content of organic matter (LOI ~ 3.5%) and TN (~0.08%).

2.2. Experimental set-up

The experiment was carried out in a greenhouse, in 12 methacrylate mesocosms (0.5 × 1.0 × 0.5 m^3; Fig. S2, Supplementary Material). The collected material was transported to the greenhouse in different containers and the mesocosms filled in the next two days as follows: the collected sand at the bottom (~15 cm, subsurface layer) and the collected soil above the sand (~25 cm, surface layer). This layering reproduces the typical soil profile of many areas of the Marina del Carmoli salt marsh (Álvarez-Rogel et al., 2007). Six mesocosms were filled with the soil + plants from the *Phragmites* stand, and six with the soil collected from the bare area. Each mesocosms had a drain cock at the bottom (Fig. S2, Supplementary Material).

The mesocosms were equipped, at each depth (surface and subsurface layers), with six Rhizon® type samplers (10 cm length, pore diameter 0.1 μm) and three redox potential (Eh) electrodes (Crison 50–55). The Rhizon® samplers were connected to plastic syringes to extract soil porewater samples for analyzing N-NO_3^- and N-NH_4^+. Two PVC