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Nitrogen retention in natural Mediterranean wetlands affected by agricultural runoff

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Abstract

Nitrogen retention efficiency in natural Mediterranean wetlands affected by agricultural runoff was quantified and the effect of season and hydrological/chemical loading was examined from March 2007 to June 2008 in two wetland-streams located in Southeast Spain. Nitrate-N (NO_3^--N), ammonium-N (NH_4^+-N), total organic nitrogen-N (TON-N) and chloride (Cl^-) concentrations were analyzed to calculate nitrogen retention efficiencies. These wetlands consistently reduced water nitrogen concentration throughout the year with higher values for NO_3^--N (72.3%), even though the mean values of inflow NO_3^--N concentrations were above 20 mg l^{-1}. Additionally, they usually acted as sinks for TON-N (45.4%), but as sources for NH_4^+-N. Over the entire study period, the Taray and Parra wetlands were capable of removing a mean value of 1.6 and 0.8 kg NO_3^--N a day^{-1}, respectively. Retention efficiencies were not affected by temperature variation and did not follow a seasonal pattern. The temporal variability for NO_3^--N retention efficiency was positively and negatively explained by the net hydrologic retention and the inflow NO_3^--N concentration ($R^2_{adj}=0.832$, $p<0.001$), respectively. TON-N retention efficiency was only positively explained by the net hydrologic retention ($R^2_{adj}=0.1997$, $p<0.05$). No significant regression model was found for NH_4^+-N. Finally, the conservation of these Mediterranean wetland-streams may act as a tool to not only improves the surface water quality in agricultural catchments, but to also achieve a good ecological status for surface waters, this being the Water Framework Directive's ultimate purpose.

1 Introduction

Nitrogen is an essential nutrient for aquatic ecosystem functioning. Its variation influences community structure, microbial activity and primary production (Pringle, 1990; Peterson et al., 2001; Dodds et al., 2002). In recent years however, nitrogen concentrations have increased in many areas as a result of human activities and have important negative effects on natural ecosystems (Vitousek et al., 1997; Townsend et al., 2003; Niyogi et al., 2004). Therefore, a great deal of attention has been paid to the movement (fluxes) and transformation of nitrogen, especially in streams (Peterson et al., 2001; Kemp and Dodds, 2002; Campbell et al., 2004; Gücker and Boëchat, 2004).

Agricultural runoff is an important source of non point pollution of aquatic ecosystems, causing eutrophication through nutrient load enrichment (Peterjohn and Correll, 1984; Downing et al., 1999; Kemp and Dodds, 2001; Mitsch et al., 2005). Unlike point source pollution, diffuse pollution cannot be easily controlled and its reduction can only be achieved by appropriate land management techniques.

Over the last few decades, much interest has been manifested in specific natural systems, such as riparian zones which are able to reduce or buffer the flux of nitrogen from terrestrial to aquatic ecosystems (Lowrance et al., 1984; Pinay and Decamps, 1988; Groffman et al., 1992; Sabater et al., 2003). In general, wetlands can improve water quality through physical, chemical and biological processes that remove nitrogen from water (Howard and Williams, 1985). This is possible because they have zones of high primary productivity in surface environments and decomposition in sediments that create coupled aerobic and anaerobic transformations of nitrogen molecules that pass through them (Kaplan et al., 1979; Bowden, 1987; Denny, 1987; Reddy et al., 1989). The role of wetlands in removing nitrogen from runoff surface waters is globally recognized (Lowrance et al., 1984; Fisher and Acreman, 2004), but the extreme variability of biological and hydrological processes make it difficult to predict the efficiency of nitrogen retention of the different types of wetlands.

Nitrogen retention efficiency in constructed wetlands has been extensively studied for wetlands to be used for agricultural drainage and wastewater treatment purposes (Spieles and Mitsch, 2000; Carleton et al., 2001; White and Bayley, 2001). However, few studies have analyzed nutrient retention efficiencies in natural wetlands (Jordan et al., 2003; Vellidis et al., 2003; Fisher and Acreman, 2004; Balestrini et al., 2008; Knox et al., 2008), despite some studies demonstrating their utility in water quality control on the catchment scale (Mitsch, 1992; Mitsch et al., 2005; Chavan et al., 2008). Indeed, the European Framework Directive (2000/60/EC) emphasizes the role of wetlands as significant elements of the hydrological networks required to obtain a “good water status” for surface and ground waters (Wetlands Horizontal Guidance, 2003).

In the Southeast Iberian Peninsula (Spain), the presence of small wetland-streams is a typical feature of the Mediterranean landscape of sedimentary catchments (Gómez et al., 2005). These wetlands, which are associated with stream drainage systems, intercept the runoff waters originating from the agricultural catchments in which they are located. This spatial arrangement converts wetlands into natural tools to control non point pollution.

Apart from the studies on nitrogen retention in Mediterranean streams (Martí and Sabater, 1996; Sabater et al., 2000; Martí et al., 2004; Von Schiller et al., 2008), there are virtually no studies related with Mediterranean wetlands.

Unlike temperate wetlands, a feature of Mediterranean wetlands and other arid and semi-arid aquatic systems is the hydrological intermittency (Gasith and Resh, 1999; Acuña et al., 2005) which strongly influences the structure and functioning of aquatic ecosystems, including nitrogen dynamic (Dahm et al., 2003; Bernal et al., 2005; Von Schiller et al., 2008; Gómez et al., 2009). Moreover, the nitrogen concentration and water discharge in aquatic systems affected by agricultural runoff inflow likely show wide temporal fluctuations, mainly due to crop irrigation practices. Over longer time scales, the nature and extent of nitrogen input into wetlands will likely affect attenuation processes. By way of example, riparian zones that have been subject to long-term nitrate inputs may have attenuation capacities that differ from non nitrate enriched areas (Groffman et al., 1992). Many studies reported a negative effect of high nitrogen concentrations and discharges on nitrogen retention efficiency in wetlands (Emmett et al., 1994; Spieles and Mitsch, 2000; Knox et al., 2008). In fact, high nitrogen concentrations may have a saturation effect on nitrogen microbial and plant uptake (Sabater et al., 2003; Bernot and Dodds, 2005). On the other hand, high water discharges provide short retention times and low surface areas for nitrogen exchange per unit volume of water (Peterson et al., 2001; Pinay et al., 2002).

The two objectives of this study were to quantify the nitrogen (NO_3^--N, NH_4^+-N and TON-N) retention efficiency in Mediterranean wetland-streams affected by agricultural runoff and to examine the effect of season and hydrological/chemical loading on nitrogen retention.

To gain an understanding of the nitrogen retention capacity of the Mediterranean wetland-streams receiving agricultural runoff is important for several reasons: it may help to determine the key factors driving nitrogen retention in these systems; it allows better predictions of how nitrogen retention in wetlands will vary in response to fluctuations of hydrologic/chemical loading; it allows researchers and managers to design better management plans to control non point pollution in agricultural catchments.

2 Materials and methods

2.1 Study site

The study was carried out in two natural wetland-streams, the Taray and Parra wetlands, located in the Murcia Region in Southeast Spain (Fig. 1). The climate of the study area is semiarid Mediterranean with temperate winters and hot, dry summers. Average annual precipitation is 300 mm and the average annual temperature is close to 18°C.

Wetlands are situated at the base of small catchments (the mean altitudes are 207 and 172 m over sea level for the Taray and Parra wetlands, respectively) and collect runoff waters from agricultural lands and natural surrounding areas (Fig. 1). Surface water flows through the Taray and Parra wetlands and finally, water leaves them via an intermittent channel that flows into the Salada and Parra streams, respectively (Fig. 1). Both wetlands are temporal. The hydrologic parameters are shown in Tables 1 and 2.

The wetlands' catchments are characterized by impermeable sedimentary marls (from the Miocene) with a considerable gypsum content (calcium sulfate) and halite (sodium chloride). As a result of this lithology, water conductivity is very high (Table 2) and wetland sediments have a considerable clay and silt content. Natural vegetation in catchments is scarce and dominated by Mediterranean shrubs, including species like *Stippa tenacissima*, *Lygeum spartum* and *Thymus hyemalis*. Wetland plant communities are composed of helophitic species like *Phragmites australis* and *Juncus maritimus,* and halophytic species like *Suaeda vera*, *Arthrocnemum macrostachyum* and *Sarcocornia fruticosa*, in the lower flooded areas. *P. australis* is located in the upper-part of the wetlands with a plant cover that ranges from 47.2% to 58.7% for the Taray and Parra wetlands, respectively. *J. maritimus* only appears in small patches in the lower part of the Taray wetland. With the exception of small patches of *Vaucheria dichotoma*, aquatic macrophytes are absent. Periphyton communities are frequent on fine substrates.

2.2 Methods

To determine the wetland retention efficiencies for NO_3^--N, NH_4^+-N and TON-N, four sampling transects were located on each wetland, perpendicularly to the water flow direction and with a separation of 100 m (Fig. 2). Sampling transects were opened through vegetation areas to reach the surface water. Surface water samples were collected once a month from the different transects, from March 2007 to March 2008 (13 sampling dates) in the Taray wetland and from April 2007 to June 2008 (15 sampling dates) in the Parra wetland (Fig. 2). The four transects of Parra wetland were dry from July to September 2007, while in the Taray wetland surface water disappeared only in the transect 3 during August and September 2007 (Fig. 2). Surface water samples were collected with plastic syringes (100 ml) as the water was so shallow, and were stored in previously acid-washed polyethylene bottles (500 ml) under dark and cold conditions until they were analyzed at the laboratory. The number of samples per transect varied between 1 and 4, depending on the water sheet width (Fig. 2). The total number of samples per sampling date ranged from 7 to 11 and from 10 to 13 for the Taray and Parra wetlands, respectively. Air and water temperatures, salinity and conductivity (conductivity meter Tetracon 325; WTW, Munich, Germany) and the presence of macrophytes species or periphyton communities, were also recorded at each transect.

The discharge was estimated for both wetlands as the product of the average water velocity (current meter MiniAir2; Schiltknecht Co, Zürich, Switzerland) and the cross-sectional area at the wetland outlets (Transect 4, Fig. 2). It was not possible to measure the inlet discharge because of the diffuse surface water inputs to the wetlands.

The surface areas of the wetlands' catchments were delimited and calculated using a Digital Terrain Model (DTM 10×10 m, Instituto Geográfico Nacional, Centro Nacional de Información Geográfica, Spain) with the ArcView GIS 3.2 software (ESRI, Redlands, California, USA). The percentages of the different land uses were calculated by intersecting the Corine Land Cover 2000 Programme (Instituto Geográfico Nacional, Centro Nacional de Información Geográfica, Spain) with the surface areas of the wetlands' catchments (Table 1). Land use information was checked during the preliminary catchment inspections. The wetland surface areas and the percentages of plant cover were calculated with the measurements collected in the field with a GPS (GeoXT, Trimble GeoExplorer, USA) and also with the ArcView GIS 3.2 software.

2.3 Chemical analyses

Water samples were analyzed for nitrogen dissolved forms within 24 h of collection. They were filtered through glass-fiber filters (Whatman GF/C, 1.2 μm nominal pore size; Whatman International Ltd., Maidstone, England). NO_3^--N concentration was measured by a colorimetric method following cadmium reduction to NO_2^--N (Wood et al., 1967). Nitrite-N concentration (NO_2^--N) was analyzed by diazotization (Strickland and Parsons, 1972). NO_3^--N concentration was estimated by subtracting the NO_2^--N concentration obtained by diazotization. NH_4^+-N concentration was measured by the phenol-hypochlorite colorimetric method (Solorzano, 1969). Dissolved inorganic nitrogen (DIN) was calculated as the sum of the NO_3^--N, NO_2^--N and NH_4^+-N concentrations.

Total nitrogen concentration (TN) was measured on unfiltered and frozen samples. These samples were digested to NO_3^--N using potassium persulfate (D'Elia, 1977) and were analyzed by cadmium reduction using an automated ion analyzer (EasyChem Plus, Systea Analytical Technologies, Italy). TON-N concentration was estimated by subtracting the DIN concentration from the TN concentration. Cl^- concentration was analyzed within 48 h of collection by the silver nitrate volumetric method (APHA, 1985).

2.4 Retention calculations

Chloride was used to calculate nitrogen retention in the wetlands. As a conservative solute, Cl^- undergoes dispersion, dilution and diffusion, but is not significantly removed from solutions and consequently, its movements largely track water flow. Thus, the variations in Cl^- concentration allow the detection of possible dilution (by lateral water inputs) or solute concentration (by evapotranspiration) that also affects nitrogen forms. Retention efficiency (%R) was calculated for the different nitrogen forms (NO_3^--N, NH_4^+-N and TON-N) on each sampling date by considering, Eq. (1), used by Trudell et al. (1986):

$$\%R = (1 - (N/Cl^-_{out}/N/Cl^-_{in})) \times 100 \tag{1}$$

N/Cl^-_{in} and N/Cl^-_{out} are the concentration ratios of both solutes in the inlet and outlet of both wetlands, respectively. %R is the percentage of the nitrogen removed by the wetlands in relation to the inflow of nitrogen. A negative retention value indicates that the outflow nitrogen/chloride ratio was higher than the inflow nitrogen/chloride ratio. The mean nitrogen retention values were calculated considering negative values to be 0% of retention efficiency. The outflow nitrogen load ($mg\,N\,day^{-1}$) was calculated as the product of outflow nitrogen concentration ($mg\,l^{-1}$) by discharge ($l\,s^{-1}$). The percentage of retention (%R) was applied to the outflow nitrogen load to estimate the inflow nitrogen load ($mg\,N\,day^{-1}$). The nitrogen net removal was calculated as follows:

$$\text{Nitrogen net removal} = \text{inflow nitrogen load} - \text{outflow nitrogen load} \tag{2}$$

Finally, the net hydrologic retention for each sampling date in both wetlands was calculated by considering, Eq. (3), used by Stanley and Ward (1997):

$$\text{Net hydrologic retention} = (\text{inlet discharge} - \text{outlet discharge})/\text{inlet discharge} \qquad (3)$$

The inlet discharge ($\text{l}\,\text{s}^{-1}$) for each sampling date was calculated as the product of the outlet discharge by the ratio $\text{Cl}^{-}_{\text{in}}/\text{Cl}^{-}_{\text{out}}$.

2.5 Statistical analyses

The coefficient of variation (*CV*) for inflow nitrogen concentrations and retention efficiencies was used as an indicator of their temporal variability throughout study period. The relationship between nitrogen retention efficiency and the physical, chemical and hydrological parameters was evaluated using Spearman correlations with the SPSS software rel.15.0.1 for Windows (SPSS Incorporated, Chicago, Illinois). Multiple linear regression analyses were used to calculate the best fitting regression model that explains the nitrogen retention in Mediterranean wetland-streams. The multiple linear regression analyses and simulation models were performed with R rel.2.6.0 for Windows (R Development Core Team, Vienna, Austria).

3 Results

3.1 Inflow water characterization

Figure 3 shows the variation of total daily precipitation and the inlet discharge in both wetlands during the study period. Although the temporal variability of total daily precipitation was high, the maximum values were registered mainly in months of spring and fall (March, April, May and October). The highest and lowest precipitation values did not always reflect increases or decreases in the inlet discharges, respectively. In fact, the inlet discharge differed vastly between study months (*CV*=114% and 147% in the Taray and Parra wetlands, respectively) and did not show a seasonal pattern.

Despite the high temporal variability of the low inlet discharges, the mean values in both wetlands were similar (Table 2).

Table 2 compiles the physicochemical characterization of the inflow water in the wetlands during the study period. The relative contribution of nitrogen forms in the inflow water was similar in both wetlands (90.4%, 9.5%, 0.1% and 92.6%, 7.3%, 0.1% as NO_3^--N, TON-N and NH_4^+-N, respectively). Although the mean values for nitrogen in both wetlands were similar, they differed in the range of solute concentrations. The highest variability in the range of inflow nitrogen concentrations throughout the study period corresponded to the Parra wetland, especially for NO_3^--N.

The inflow NO_3^--N concentrations in the Taray wetland were consistently similar throughout the study period (CV=8.6%, n=13), while a higher seasonal variability was noted for the Parra wetland (CV=37.1%, n=12) (Fig. 4). This difference between both wetlands was mainly influenced by the significant increase of inflow NO_3^--N concentrations registered from March to June 2008 (30–43 mg l^{-1}) in the Parra wetland (Fig. 4). The inflow TON-N and NH_4^+-N concentrations varied considerably among the study months (Fig. 4). The CV values for TON-N were 58.0% (n=13) and 131.3% (n=12), and the CV values for NH_4^+-N were 83.6% (n=13) and 117.2% (n=12) for the Taray and Parra wetlands, respectively.

3.2 Nitrogen retention efficiencies

Both wetlands showed the highest retention efficiency for NO_3^--N, followed by TON-N and NH_4^+-N (Table 3). When all the sampling data from both wetlands were considered, the mean retention efficiency for NO_3^--N was 72.3% (n=25) (ranging from 31.7% to 100%). However, the mean retention efficiency and net removal (mean inflow load – mean outflow load) for NO_3^--N was consistently higher in the Taray wetland than in the Parra wetland (Table 3).

The mean retention efficiency for TON-N was 45.4% (n=25) and ranged from –437% to 99.5%. The mean retention efficiency and net removal was also higher in the Taray wetland than in Parra wetland (Table 3). There was no removal of TON-N from the water of both wetlands on 6 of the 25 sampling dates (Fig. 5). On these occasions, the TON-N/Cl^- ratio was higher at the outlet than at the inlet of both wetlands.

Ammonium-N was not removed from water, but was exported instead on the majority of the sampling dates (13 of 25) (Fig. 5). The mean retention efficiency was 34.7% (n=25), ranging from −1537.5% to 96.0%. As for NO_3^--N and TON-N, the highest retention efficiency and net removal of NH_4^+-N was detected in the Taray wetland (Table 3).

3.3 Temporal variability of nitrogen retention efficiencies

The temporal variability of the retention efficiencies for NO_3^--N was higher in the Parra wetland than in the other; CV=42.7% (n=12) and CV=8.2% (n=13), respectively (Fig. 5). During the summer (June–September), retention efficiencies for NO_3^--N tended to increase in both wetlands. However, this increase was observed only in June in the Parra wetland (it was dry during the rest of the summer) (Fig. 5). The maximum NO_3^--N retention values (99.9% and 96.0%) were recorded in August and October in the Taray and Parra wetlands, respectively (Fig. 5).

The temporal variability of the retention efficiency for TON-N was higher than that for NO_3^--N (CV=158.8%, n=13 and CV=502.9%, n=12 in the Taray and Parra wetlands, respectively), and no clear seasonal pattern was seen (Fig. 5). Retention efficiency ranged from −140% to 99.5% and from −437% to 95% in the Taray and Parra wetlands, respectively (Fig. 5).

The NH_4^+-N retention efficiencies varied considerably throughout the study period (CV=779.4%, n=13 and CV=209.7%, n=12 in the Taray and Parra wetlands, respectively) and no seasonal pattern was observed (Fig. 5). Negative NH_4^+-N retention values were recorded in many months, particularly in the Parra wetland (Fig. 5).

3.4 Effect of environmental factors on nitrogen retention efficiencies

Table 4 shows the results of the Spearman correlations done to evaluate the relationship between nitrogen retention efficiency and different environmental factors: inlet discharge, net hydrologic retention, inflow nitrogen concentration, inflow load, and water and air temperatures.

The strongest relationship found was between NO_3^--N retention efficiency and net hydrologic retention ([discharge in – discharge out]/discharge in), which was positive (Table 4). In contrast, the TON-N and NH_4^+-N retention efficiencies were not correlated with this variable (Table 4).

Nitrate-N retention efficiency was negatively correlated with the inflow NO_3^--N concentration and the inlet discharge, whereas TON-N retention efficiency was positively correlated with the inflow TON-N concentration (Table 4).

Finally, the multiple linear regression analysis showed that 83.0% of seasonal variability for the NO_3^--N retention efficiency was explained by the net hydrologic retention and the inflow NO_3^--N concentration (Fig. 6). This model was positive for the net hydrologic retention and negative for the inflow NO_3^--N concentration with a high level of significance (R^2_{adj}=0.832, $p<0.001$, n=25). The regression model that explained the temporal variability for the TON-N retention efficiency was significant and positive for net hydrologic retention, but this factor only explained 20% of the variation (R^2_{adj}=0.1997, $p<0.05$, n=25). A significant regression model was not obtained for NH_4^+-N.

4 Discussions

4.1 Nitrogen retention efficiencies

This study shows that Mediterranean wetland-streams affected by agricultural runoff prove efficient to remove nitrogen from water. The retention efficiency was strongly influenced by nitrogen speciation in agreement with previous studies (Kovacic et al., 2000; Spieles and Mitsch, 2000; Vellidis et al., 2003; Knox et al., 2008; Balestrini et al., 2008).

Wetlands have proved most efficient for removing NO_3^--N from water, the dominant nitrogen form, but were less efficient for the removal of TON-N and NH_4^+-N. Several studies have shown the ability of wetlands to remove NO_3^--N from water. Knox et al. (2008) found a mean retention efficiency for NO_3^--N of 60.0% in a natural flow-through wetland of California with a Mediterranean climate that collected agricultural runoff whose mean NO_3^--N concentration was 0.2 mg l^{-1}. Jordan et al. (2003) showed that a restored wetland removed 52.0% of the NO_3^--N received from agricultural runoffs whose usual NO_3^--N concentration values were <1 mg l^{-1}. In the studied wetlands, the mean retention efficiency for NO_3^--N (72.3%) was higher than that found in these aforementioned studies, even though the mean inflow concentrations for NO_3^--N were above 20 mg l^{-1}. Besides, other studies performed in constructed wetlands generally show lower retention efficiencies for NO_3^--N than our results (Hammer and Knight, 1994; Spieles and Mitsch, 2000; Braskerud, 2002; Mitsch et al., 2005). By considering both the annual mean inflow load of NO_3^--N and the annual mean retention efficiency, the Taray and Parra wetlands proved capable of removing mean values of 1.6 and 0.8 kg of NO_3^--N a day^{-1}, respectively.

Although nitrogen removal processes have not been studied in these wetlands, their high NO_3^--N retention efficiency values are mainly attributed to high denitrification rates. Denitrification, biological uptake, and microbial immobilization are the main mechanisms for NO_3^--N removal in wetlands (Reddy and Patrick, 1984; Bowden, 1987; Groffman et al., 1992). However, several authors have reported that denitrification may be potentially important in aquatic systems dominated by fine sediments, high NO_3^--N and organic carbon availability, a low redox potential of sediments, and warm water temperature (Smith and De Laune, 1983; Faulkner and Richardson, 1989; García-Ruiz et al., 1998; Inwood et al., 2007; Pinay et al., 2007). Unlike organic matter (and nitrogen) accumulation, which conserves nitrogen within the wetland, denitrification represents a permanent nitrogen loss from the system. Natural wetland sediments are chemically reduced and frequently contain ample organic carbon. Therefore, denitrification in wetlands is generally limited by nitrate availability (Ambus and Lowrance, 1991). Nonetheless, this is not the case of the wetlands affected by agricultural runoff. Therefore, although denitrification was not estimated in the studied wetlands, this process is proposed to be an important pathway for NO_3^--N loss because its occurrence is consistent with wetland environmental characteristics (high NO_3^--N availability, high water temperature and anoxic-black sediments).

On the other hand, processes involved in NO_3^--N cycling are influenced by the hydrologic conditions of wetlands (De Laune et al., 1981; Bowden, 1987; Pinay et al., 2007). In the studied wetlands, NO_3^--N retention efficiency was negatively correlated with the inlet discharge and positively correlated with net hydrologic retention, thus suggesting that longer water residence times allow a longer time for NO_3^--N removal from surface water. Nutrient retention in wetlands is governed not only by changes in the hydrographs, but also by both the flow-through (velocity) and water residence time rates (Howard-Williams, 1985). If water moves through a wetland at a quicker rate than that of nitrogen retention processes (denitrification or biological uptake), then considerable flow-through of nitrogen will take place. Peverly (1982) found that wetlands retained nutrients only when flow-through rates were low, while Stanley and Ward (1997) observed that net retention for all the nitrogen forms was strongly correlated with hydrological retention in the Talladega Wetland Ecosystem (TWE, Alabama, USA).

The loading capacity of wetlands varies seasonally, particularly in temperate regions where biological activity diminishes in winter (Howard-Williams, 1985; Groffman et al., 1992). Despite NO_3^--N retention efficiency tends to increase in summer months, no significant seasonal pattern in the NO_3^--N removal efficiency was detected in the studied wetlands. This lack of seasonality in the NO_3^--N retention efficiency is in agreement with those results obtained in constructed wetlands (Reddy and Patrick, 1984; Vymazal, 2006; Spieles and Mitsch, 2000) and may be explained by the absence of a seasonal pattern for inlet discharge (Fig. 3). The Taray and Parra wetlands are influenced by agricultural runoff inputs; therefore, increases in inlet discharges are in relation with crop irrigation practices. The fact that the temporal variability of the inlet discharge and the daily precipitation are not related supports this idea (Fig. 3). Another further suggestion to explain the lack of seasonality of the NO_3^--N retention efficiency in the studied wetlands is that the warm temperate climate of the study area enables the continuous operation of the essential biogeochemical processes involved in NO_3^--N removal. According to this suggestion, Sabater et al. (2003) to explain the lack of seasonality in nitrogen removal rates in riparian buffers from Europe suggested that the two main removal processes (denitrification and plant uptake) operate either simultaneously or in isolation, depending on the hydrological and temperature conditions. This result contrasts with those obtained in studies performed in temperate areas where NO_3^--N retention efficiency was controlled mainly by the temperature (Hill, 1988; Spieles and Mitsch, 2000; Chavan et al., 2008). This apparent lack of seasonality reinforces the fact that Mediterranean wetlands can significantly remove nitrogen input.

Wetlands also acted as sinks for TON-N during most of the study period. In fact, when comparing our results with those from previous studies, a relatively high fraction of TON-N (45.4%) had been removed in the studied wetlands (the Taray and Parra wetlands removed mean values of 160 and 50 g a day^{-1} of TON-N, respectively). For example, Jordan et al. (2003) reported TON-N retention efficiencies ranging from –15.0% to 39.0%, and also indicated that a restored wetland could be a source of TON-N. Braskerud (2002) found a mean retention efficiency value for TON-N of 22.0%, ranging from 11.0% to 32.0%, in four surface-flow constructed wetlands in Norway.

TON-N retention could be greater than the values obtained by input-output balance. Leaching and decomposition of autochthonous particulate organic matter is an additional source of organic nitrogen and decreases net TON-N retention. Decomposition of litter is probably the major source of TON-N in our wetlands, as other studies reported (Triska et al., 1984; Howard-Williams, 1985; Bowden, 1987; Chapman et al., 2001). In fact, some of these studies show that TON-N concentrations are generally higher in summer and fall and suggest increases relate to the autochthonous litter decomposition or to primary production. In contrast, no seasonal pattern was observed in our wetlands study. Bernal et al. (2005) also reported the absence of such a pattern in TON-N retention for an intermittent Mediterranean stream.

As same as previous studies, the TON-N retention efficiency was positively correlated with the inflow TON-N concentration (Braskerud, 2002).

The studied wetlands were usually net sources of NH_4^+-N over the study period. However, when wetlands occasionally retained NH_4^+-N, their retention values were relatively high in comparison with those of previous studies. For example, Braskerud (2002) showed a mean retention value of 1.0% in small constructed wetlands that treat agricultural non-point source pollution. We suggest that litter decomposition and mineralization are the main autochthonous sources of NH_4^+-N in wetlands. Once wetland vegetation has died, a large and complex series of nutrient transformations emerges, all of which are associated with the leaching of detritus and simultaneous decomposition (Howard-Williams, 1985). Several studies have demonstrated that plant detritus processing may be an important source of nutrients (Howarth and Fisher, 1976; MacLean and Wein, 1978). Kinetic mineralization of TON-N probably proceeds more rapidly than nitrification, thus NH_4^+-N concentration increases in surface water (Kadlec and Knight, 1996; Braskerud, 2002).

On the other hand, NH_4^+-N is more sensitive than NO_3^--N to slight changes of local conditions (chemical, physical and biological variables) (Hill, 1996; Butturini and Sabater, 1998, 2002; Gücker and Boëchat, 2004), which also change as flow discharge does (Martí et al., 1997; Fisher et al., 1998; Dent and Grimm, 1999; Dahm et al., 2003; Von Schiller et al., 2008). Furthermore, NH_4^+-N reacts abiotically via adsorption/desorption reactions, and displays processing lengths that reflect the nature of the sediments and the chemical environment (Triska et al., 1994). Both properties are spatially heterogeneous in wetlands, and this variability increases as flow discharge decreases (Gücker and Boëchat, 2004), which also occurs close to wetland outlets. Thus, slight changes in the sediment redox potential may not only affect the exchange of NH_4^+-N at the water-sediment interface, but may also influence the NH_4^+-N concentration in surface water (De Laune et al., 1981; Bowden, 1987). The fact that NH_4^+-N retention efficiency was lower than that for NO_3^--N, and that it was even exported from wetlands, is consistent with this idea.

The temporal variability of the NH_4^+-N retention was very high in this study and was not correlated with any measured environmental factor. However, Sabater et al. (2000) showed that 83.0% of the seasonal variation in the NH_4^+-N retention efficiency in a Mediterranean stream without riparian vegetation is explained by water temperature. The lack of correlation between environmental factors and NH_4^+-N retention in the studied wetlands may be explained by the high sensitivity to slight changes of the local conditions, as we previously suggested.

4.2 Influence of the net hydrologic retention and the inflow nitrogen concentration on the nitrogen retention efficiency

The main factors controlling the NO_3^--N retention efficiency in the studied wetlands are the net hydrologic retention and the inflow NO_3^--N concentration (Fig. 6).

Net hydrologic retention is used as a measurement of the water residence time in wetlands. This factor often influences the nitrogen retention in aquatic systems because a longer contact time between surface water and sediment implies that the total amount of processed nitrogen increases (Peterson et al., 2001; Gücker and Boëchat, 2004). Furthermore, the net hydrologic retention explained 20.0% of the temporal variability in TON-N retention efficiency in the studied wetlands. Several studies report that long hydraulic residence times are necessary to transform and remove TON-N in wetlands (Hammer and Knight, 1994; Kadlec and Knight, 1996; Chavan et al., 2008). However, the low variance explained by the hydraulic resident time indicates that other factors must be involved in TON-N removal in the studied wetlands.

Inflow NO_3^--N concentration is the second factor controlling the NO_3^--N retention in the studied wetlands (Fig. 6). Other studies, in both riparian buffers and natural/constructed wetlands, report a similar relationship between both variables (Spieles and Mitsch, 2000; Sabater et al., 2003). In addition, these authors suggest a saturation effect by a high NO_3^--N load which exceeds the buffering capacity of these systems. Although the inflow NO_3^--N concentrations registered during the study period were high, they never exceeded the loading capacity of the wetlands, as high NO_3^--N retention rates indicated.

5 Conclusions

Our study in the Taray and Parra wetlands clearly demonstrates the crucial role of Mediterranean wetland-streams in the control of the nitrogen flux from agricultural landscapes to aquatic ecosystems located downstream. The studied wetlands consistently reduce the concentration of nitrogen forms, in such a way that the water leaving the wetlands is always of more quality than that entering them. In some countries, surface flow wetlands are highly valued for their high nutrient retention potential and their unique biodiversity. However, despite the high efficiency of the Mediterranean wetland-streams to improve surface water quality, they are often desiccated for agricultural purposes. Presently, there are an increasing number of activities aimed at restoring these sites as multifunctional landscape entities. In fact, there are studies which focus on identifying the most suitable areas for the restoration of surface flow wetlands to improve the water quality of a given catchment (Mitsch, 1992; Trepel and Palmeri, 2002; Moreno et al., 2007). The wide distribution and strategic location of the Mediterranean wetland-streams in upstream reaches of basins makes them more interesting as natural tool for the control of non point pollution at the landscape scale. Our results emphasize the high efficiency of Mediterranean wetland-streams as nitrogen sinks all year round. This feature is influenced by low water discharges and, probably, by the warm temperate climate, both of which are key factors that make Mediterranean wetland-streams especially interesting in terms of respecting temperate wetlands. Our results highlight the conservation interest of Mediterranean wetland-streams to improve the surface water quality in agricultural catchments in accordance with WFD's objective (2000/60/EC).

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Von Schiller, D., Martí, E., Riera, J. L., Ribot, M., Argerich, A., Fonollá, P., and Sabater, F.: Interannual, annual and seasonal variation of P and N retention in a perennial and an intermittent stream, Ecosystems, 11, 670–687, 2008.

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Table 1. Surface land uses at wetland catchments, and the hydrologic parameters recorded in the wetlands during the study period. [a] = Irrigated lands included fruit trees and vegetables (with irrigation and fertilizer inputs). [b] = Dry lands included almond and olive trees (without irrigation and fertilizer inputs).

	Taray	Parra
Wetland catchment		
Total area (ha)	74.5	33.2
Irrigated lands (%)[a]	24.1	10.8
Dry lands (%)[b]	13	24.6
Natural vegetation (%)	60.5	61.8
Roads and artificial ponds (%)	2.4	2.8
Wetland		
Total area (ha)	0.5	0.7
Surface flow length (m)	300	300
Surface flow width (m)	3.4–7.1	2.3–13.4
Surface flow depth (cm)	0.5–10	0.5–10

Table 2. Mean, minimum and maximum values for solute concentrations, conductivity and temperature of inflow water to wetlands. The mean values of the inlet and outlet discharges are also shown. The mean values are calculated with data of all the sampling dates: n=13 and n=12 in the Taray and Parra wetlands, respectively. ^{a}=(n=11).

	Taray wetland			Parra wetland		
	Mean	Min.	Max.	Mean	Min.	Max.
NO_3^--N (mg l^{-1})	21.5	17.8	24.5	27.4	10.3	43
TON-N (mg l^{-1})	2.4	0.4	5.1	2.3	0.1	7.6
NH_4^+-N (mg l^{-1})	0.01	0.001	0.04	0.01	<0.001	0.06
Cl^- (g l^{-1})	3.2	2.9	3.5	3.5	2.5	4.4
Conductivity (mS cm^{-1})	17.3	15.2	18.6	15.6	13.2	18.6
Water temperature (°C)	15.8	9.5	22.2	14.7	10.2	17.5
Inlet discharge (l s^{-1})	1^a	0.1^a	2.7^a	0.8	0.1	1.4
Outlet discharge (l s^{-1})	0.6^a	0.02^a	1.4^a	0.7	0.1	1.4

Table 3. Concentration, load, net removal, and retention efficiency for NO_3^--N, TON-N, and NH_4^+-N registered at inflows and outflows of the wetlands. Values are the mean ± standard deviation based on the data collected over the study period (n=13 and n=12 in the Taray and Parra wetlands, respectively). ^{a}=(n=11).

	Concentration (mg l^{-1})		Load (mg m^{-2} d^{-1})			Retention efficiency (%)
	Inflow	Outflow	Inflow	Outflow	Net removal	
Taray wetland						
NO_3^--N	21.5±1.9	3.8±2.7	378±321^a	54±58^a	324±269^a	90.4±7.4
TON-N	2.4±1.4	1.6±1.1	49.6±68^a	18±28^a	31.6±48^a	59.2±35
NH_4^+-N	0.013±0.01	0.02±0.02	0.12±0.08^a	0.08±0.08^a	0.04±0.05^a	34.7±36
Parra wetland						
NO_3^--N	27.4±10.2	15.4±9.4	287.4±237	171.6±162	115.8±79	52.8±22.6
TON-N	2.3±3	1.6±2	22.1±29	14.9±22	7.2±14	30.4±33.6
NH_4^+-N	0.013±0.016	0.016±0.008	0.18±0.25	0.13±0.11	0.06±0.2	12±25

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Table 4. Results of Spearman correlations between the retention efficiencies (%*R*) of the different nitrogen forms and the environmental factors by considering the dataset registered during the study period in both wetlands. * Significant at the 0.05 probability level. ** Significant at the 0.01 probability level.

	NO_3^--N %*R*		TON-N %*R*		NH_4^+-N %*R*	
	r	*p*	*r*	*p*	*r*	*p*
Inlet discharge ($l\,s^{-1}$)	−0.419*	0.047	−0.098	0.655	0.104	0.636
Net hydrologic retention	0.834**	0.000	0.412	0.051	0.283	0.191
Inflow NO_3^--N concentration ($mg\,l^{-1}$)	−0.655**	0.000				
Inflow TON-N concentration ($mg\,l^{-1}$)			0.513**	0.009		
Inflow NH_4^+-N concentration ($mg\,l^{-1}$)					0.345	0.091
Inflow NO_3^--N load ($mg\,m^{-2}\,d^{-1}$)	−0.370	0.082				
Inflow TON-N load ($mg\,m^{-2}\,d^{-1}$)			0.100	0.650		
Inflow NH_4^+-N load ($mg\,m^{-2}\,d^{-1}$)						
Water temperature (°C)	0.256	0.216	−0.219	0.293	−0.116	0.582
Air temperature (°C)	0.125	0.561	−0.160	0.454	−0.217	0.309

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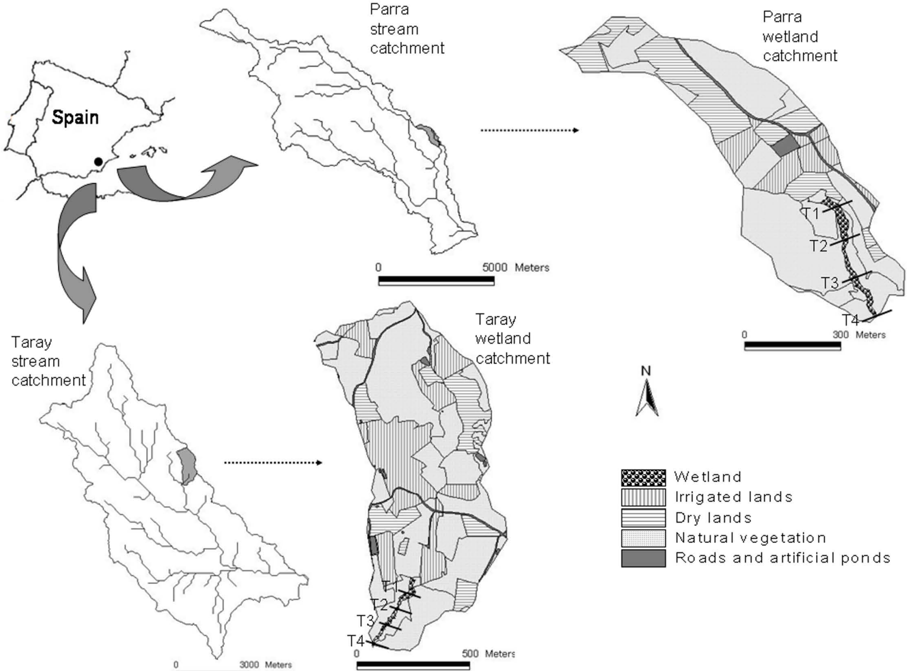

Fig. 1. Location of the studied wetlands and their catchments. Black lines represent the four transects on each wetland where samples were collected.

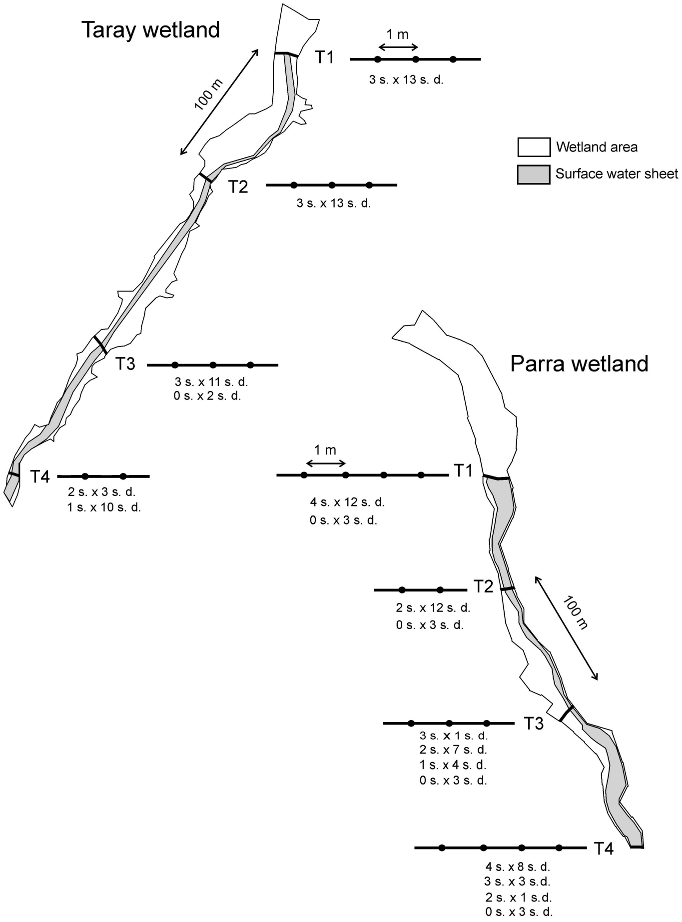

Fig. 2. Location of the four sampled transects in the studied wetlands. In each transect (black lines) the number of samples (s.) collected in the different sampling dates (s. d.) are shown. 0 samples mean that the transect was dry.

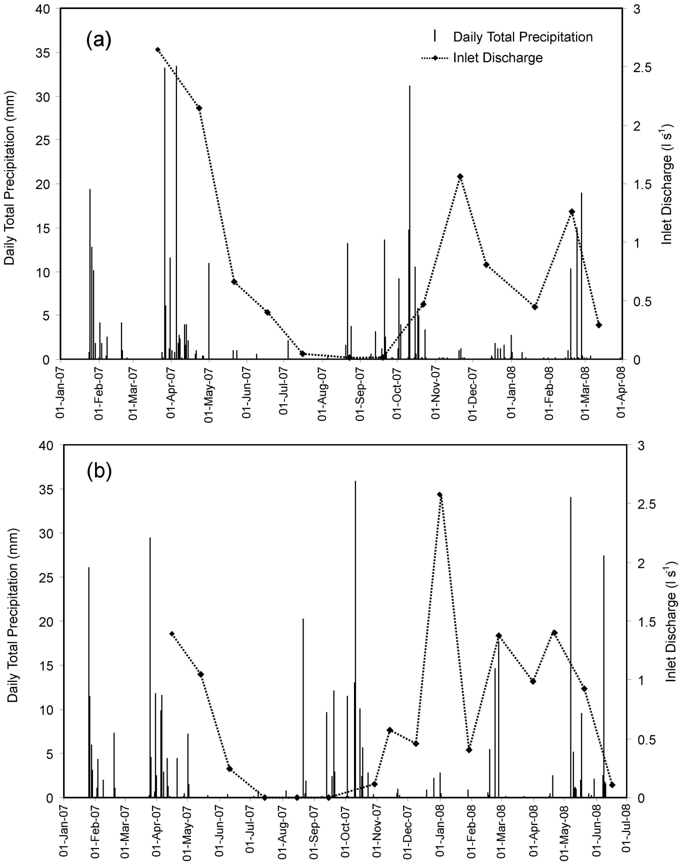

Fig. 3. Daily total precipitation and inlet discharge registered during the study period in the **(a)** Taray and **(b)** Parra wetlands. Precipitation values were obtained from the thermo-pluviometric stations located in the wetland catchments; Fortuna C.H. (Taray catchment) and Abanilla C.H. (Parra catchment).

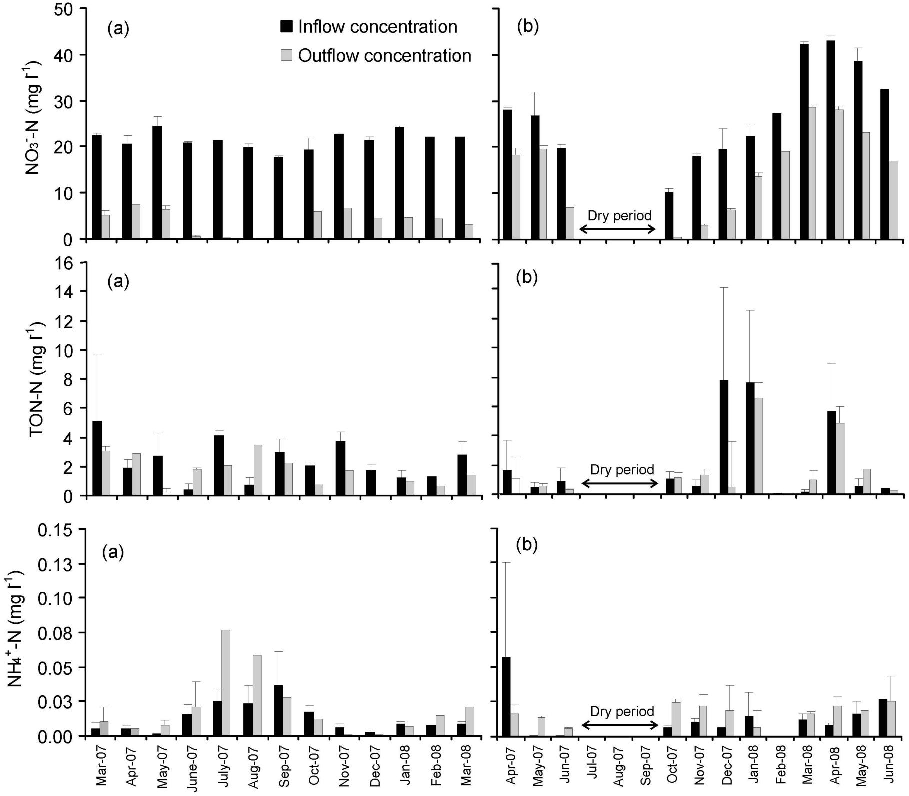

Fig. 4. Temporal variation of NO_3^--N, TON-N and NH_4^+-N mean concentrations of inflowing and out-flowing water in the **(a)** Taray and **(b)** Parra wetlands, over the study period. Standard deviations bars (+SD) are shown.

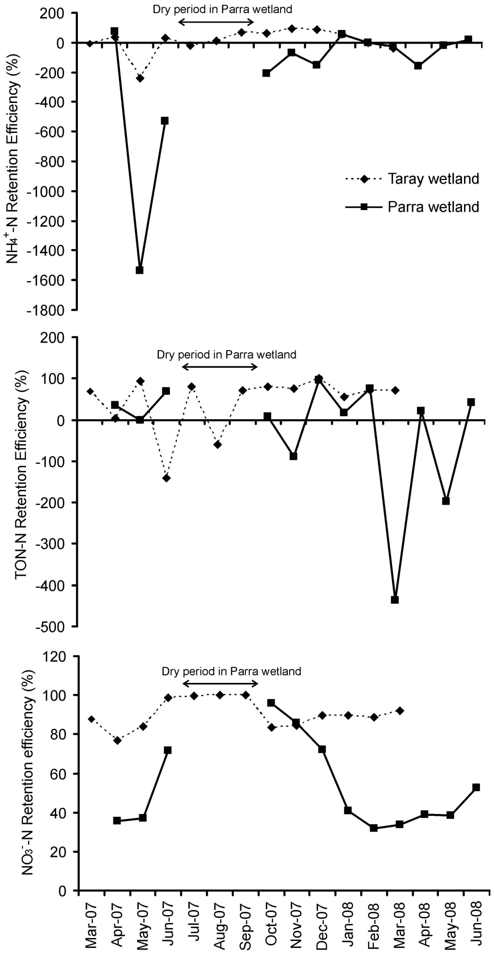

Fig. 5. Temporal variation of NH_4^+-N, TON-N and NO_3^--N retention efficiencies in the Taray and Parra wetlands.

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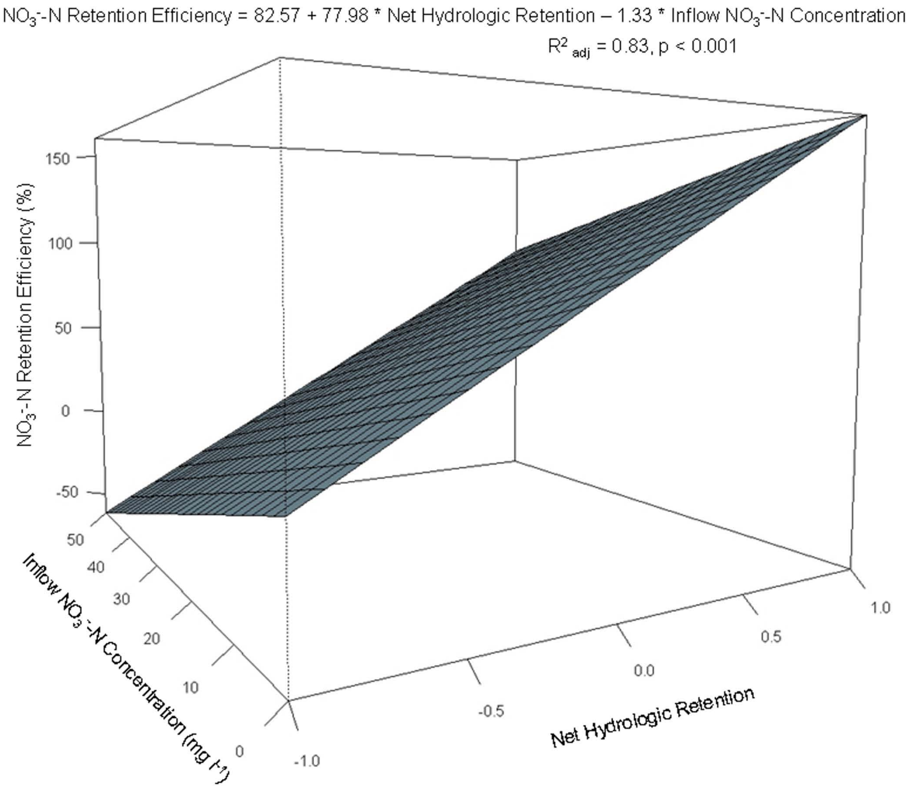

Fig. 6. Simulation model of NO_3^--N retention efficiency of Mediterranean wetlands under different net hydrologic retentions and inflow NO_3^--N concentrations.