Effects of wetland construction on water quality in a semi-arid catchment degraded by intensive agricultural use

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\textbf{A B S T R A C T}

Many factors can influence the improvement of water quality in surface-flow constructed wetlands (SFW). To test if water quality was improved, especially in nutrient and salt content, after passage through SFW, 11 wetland plots of various sizes (50, 200, 800 and 5000 m\textsuperscript{2}) were established within constructed wetlands on agricultural soils in the Ebro River basin (NE Spain) that had been affected by salinization. A set of 15 water quality parameters (e.g., nutrients, salts, sediments, and alkalinity) was obtained from samples collected at the inflow and outflow of the wetlands during the first 4 years after the wetlands were constructed. NO\textsubscript{3}−N retention rates were as high as 99% in the largest (5000 m\textsuperscript{2}) wetlands. After 4 years, total phosphorus was still being released from the wetlands but not salts. Over the same period, in small wetlands (50, 200, and 800 m\textsuperscript{2}), retention rate relative to the input of NO\textsubscript{3}−N increased from 40% to almost 60%. Retention of NO\textsubscript{3}−N amounted to up to 500 g N m\textsuperscript{−2} per year, for an average load concentration at inflow of ∼20 mg l\textsuperscript{−1}. Release of Na\textsuperscript{+} declined from 16% to 0–2% by volume, for an average load concentration at inflow of ∼70 mg l\textsuperscript{−1}. At the current retention rate of NO\textsubscript{3}−N (76–227 g m\textsuperscript{−2} per year), 1.5–4% of the catchment should be converted into wetlands to optimize the elimination of NO\textsubscript{3}−N.

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1. Introduction

In agricultural landscapes, the control of non-point source pollution is a major concern and a significant challenge (Mitsch and Gosselink, 2000). Two of the most commonly advocated measures for reducing non-point source pollution are to restrict the upstream application of fertilizers (Arheimer et al., 2004; Causapé et al., 2004), or to construct ecosystems that remove pollutants from the agricultural runoff (Hammer, 1992; Raisen and Mitchell, 1995; Zedler, 2003). Surface-flow constructed wetlands (SFW) are an effective and economical tool to control non-point source pollution in large agricultural areas (Mitsch et al., 2001; Kovací et al., 2006).

The use of SFW to control non-point source pollution in agricultural catchments has been studied across a wide range of climatic conditions, including boreal (Brakerud, 2002; Arheimer et al., 2004; Koskiabo and Puustinen, 2005), temperate (Woltemade, 2000; Trepel and Palmeri, 2002; Jiang et al., 2007; Scholz et al., 2007), tropical (de Ceballos et al., 2001; Chimney and Goforth, 2006), and semi-arid zones (Comín et al., 2001; Howell et al., 2005). Under these conditions, many environmental variables (e.g., temperature, hydraulic load, pollutant concentrations, soil properties, plant cover, microbial activity) and features of wetland design (e.g., water-residence time, depth, shape, plant species composition) can sometimes promote the release of nutrients, particularly P. The construction of wetlands on agricultural soil can have a significant effect on the water quality of the wetlands. Of particular importance is the dynamics of the Ca–P system. This system allows the release of P from the soil into the water, as well as the precipitation of Ca and P processes which depend on factors such as water pH and Ca concentration (Van den Berg and Loch, 2000; Shenker et al., 2005).

After inundation, agricultural soils can release nutrients (nitrogen and phosphorus) into the water outflow, but nutrient concentrations decrease progressively during the first years after flooding (Bruland et al., 2003). In other circumstances, recently created wetlands can quickly develop the capacity to remove nitrogen from agricultural runoff (Romero et al., 1999; Fink and Mitsch, 2004; Borin and Tocchetto, 2007; Moreno et al., 2007).

In the field of wetlands restoration, the effect of soil salinity on water quality is not well studied. The effects of salt release caused by irrigation are well known because of the important drawbacks caused by agricultural runoff (Tedeschi et al., 2001; Causapé et al., 2004). In addition, salinity can affect plant growth (Lissner et al., 1999) and nitrogen mineralization (Irshad et al., 2005). Preliminary research in the study area indicated that SFW-rehabilitation of agricultural fields resulted in the removal of significant amounts...
of nitrogen, but less phosphorus, from agricultural runoff (Romero et al., 1999; Comín et al., 2001). During the early stages of wetland development after inundation (2 years), no significant exportation or retention of major salts from salinized soils took place (Moreno et al., 2007).

The major aim of this study was to estimate the changes in various agricultural runoff parameters, especially nutrients and salts, that affect the quality of water passing through SFW on old irrigated agricultural fields under semi-arid conditions. A secondary aim was to study the potential effect of wetland size on these agricultural runoff parameters. Our hypothesis proposed that nutrient and salt concentrations decreased after passing through constructed wetlands. Retention/release rates of nutrients (nitrogen and phosphorus), salts, and sediments were estimated for 16 variables recorded at inflow and outflow channels. Interactions between these variables will allow greater understanding of the patterns of retention/release.

2. Materials and methods

2.1. Study area

Monegros is a 270,000-ha region in the center of the Ebro River basin, NE Spain (Fig. 1). The climate is semi-arid and Mediterranean-continental. The average annual temperature is 14.5°C, and the average annual precipitation is 400 mm (Pedrocchi, 1998), but interannual variability is high (Comín and Williams, 1993). The soils are dominated mainly by a tertiary structure that consists of clays, with variable levels of salinity (conductivity = 1–10 mS cm⁻¹) and inserted sandstone strata. Locally, the structure is covered by a layer of gravel that is 2–4 m deep. Most of the land was converted into irrigated agricultural fields during the second half of the 20th century. Soil salinization is now widespread throughout the region and agriculture has largely been abandoned. The original pseudo-steppe vegetation, predominantly rosemary (Rosmarinus officinalis), thyme (Thymus sp.), and halophytes (Salicornia sp.), as well as perennial grasses (Lygeum spartium, Brachypodium retusum) in abandoned, dry zones and by halophytes (Phragmites australis, Typha latifolia, Scirpus holoschoenus, S. maritimus, Carex divisa) in the abandoned wetter zones of the valleys. Most of the wetlands have been colonized by P. australis, which is spreading and increasingly dominating the plant community, due to its tolerance of fluctuating water levels and salinity (Lissner et al., 1999). In the study area, the Phragmites-dominated wetlands are at the base of non-irrigated valleys, which suggests that these wetlands develop naturally within the hydrological discharge zones of the valleys.

2.2. Constructed wetlands

In 2004, 11 experimental plots of various sizes [5 m × 10 m (S = small), 10 m × 20 m (M = medium-sized), 20 m × 40 m (L = large), and ~5000 m² (XL = extra-large); Fig. 1] were established in abandoned agricultural fields and were operative during the growing seasons between 2004 and 2007. The fields were within a 22-ha subcatchment that consisted entirely of irrigated farmland. The plots were in fields that were essentially covered by P. australis (with scattered stands of T. latifolia, S. lacustris, and C. divisa), which had grown naturally after the fields were abandoned 4 years earlier. Wetland vegetation persisted due to the presence of sufficient water, leaked continuously from a ditch nearby. These leaking points were sealed before wetland management for nutrient removal began in 2004. Between 2004 and 2006, the mean (S.D.) density, height, and biomass of P. australis increased from 213.5 (64.4) stems/m², 88.3 (24.0) cm, and 0.84 (0.39) kg/m², to 599.8 (205.6) stems/m², 193.2 (50.5) cm, and 3.00 (1.02) kg/m², respectively (Moreno et al., unpublished data). All of the plots were flooded each year for as long as possible during the irrigation campaign (from April to October). The agricultural runoff collected in a ditch that had a dike 100 m away and was conveyed to each plot separately by way of distribution pipes (Fig. 1). The hydrological regime of the ditch was strictly dependent on the watering regime of the agricultural fields located upstream. During the irrigation campaign, three events produced relevant alterations in the water quality of the streams: first, the initial tillage, sowing and fertilization in mid-April; second, the second fertilization and application of pesticides and herbicides...
in May; third, cropping and final tillage in October. In between these events, water characteristics were considered as constant (Forés and Comin, 1987) under the experimental conditions in this study. Outside of the irrigation campaign (October–April), the water flow from the ditch allowed maintenance of continuous flow in only one medium-sized wetland (800 m²). Due to the limited data provided by only one wetland plot, this continuous-flow situation was not considered in this study. The other wetlands were maintained as flooded and stagnant for most of the winter to avoid salt from deeper layers to flow upward to the wetland surface (Rodríguez-Ochoa et al., 1998).

Due to the high rates of evapotranspiration (ET) occurring in the study area, the monthly averages of ET from a 20-year series performed by two meteorological stations (Diputación-General-de-Aragón, 1991) were used to correct retention rates \( R_e \). These meteorological stations were located less than 10 km from the study area, the monthly averages of ET from a 20-year series were maintained as flooded and stagnant for most of the winter.

Table 1: Water-residence time (WRT) (mean ± S.E.) in constructed wetlands in Monegros, Ebro River basin, NE Spain.

<table>
<thead>
<tr>
<th>Size (m²)</th>
<th>Year</th>
<th>WRT (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2004</td>
<td>0.70 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td>2.24 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>3.48 ± 0.88</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>2.12 ± 0.40</td>
</tr>
<tr>
<td>200</td>
<td>2005</td>
<td>4.18 ± 1.34</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>4.43 ± 1.94</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>2.31 ± 0.28</td>
</tr>
<tr>
<td>800</td>
<td>2004</td>
<td>10.59 ± 3.21</td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td>5.64 ± 0.86</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>3.06 ± 0.74</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>2.31 ± 0.50</td>
</tr>
<tr>
<td>5000</td>
<td>2004</td>
<td>31.16 ± 9.62</td>
</tr>
<tr>
<td></td>
<td>2006</td>
<td>8.69 ± 0.86</td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>8.84 ± 3.17</td>
</tr>
<tr>
<td>Overall</td>
<td>–</td>
<td>5.02 ± 1.64</td>
</tr>
</tbody>
</table>

Water stored in the plot (in m³) was then calculated as the water depth (measured with a 20-cm calibrated pole), multiplied by the plot area (50, 200, 800, or 5000 m²).

2.3. Water sampling

To quantify the characteristics of the agricultural runoff of the subcatchment, samples were collected before the water entered the experimental plots (Table 2). During the irrigation campaign, we attempted five sampling campaigns to collect inflow and outflow water from each flooded wetland plot. The number of plots sampled during each sampling campaign varied from 3 to 11. Three sampling campaigns coincided with those moments where agricultural practices produced the most important alterations in water quality (initial tillage, sowing and fertilization in mid-April; second fertilization and application of pesticides and herbicides ending in May; and cropping and final tillage ending in October). Two more sampling campaigns were carried out between fertilization in May and cropping in October. Due to unforeseen circumstances, in 2004 only the two last sampling campaigns could be completed because the wetlands were flooded in August; in 2005, the first sampling could not be conducted due to drought; in 2006, all five campaigns were completed; in 2007 the last campaign was not carried out because of ownership issues. Calibrated electronic devices were used to record in situ measurements of water temperature, pH, dissolved oxygen (DO), and electrical conductivity (EC). Water samples were filtered (0.8 μm mesh pre-combusted filters) on the day they were collected. Total dissolved solids (TDS), total suspended solids (TSS), turbidity, alkalinity, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, and K⁺ concentrations were measured using standard laboratory methods (APHA, 1998). One month after the samples were collected, standard procedures (APHA, 1998) were used to quantify micronutrients in frozen \( T = -30 \) °C aliquots. Soil salinity was estimated based on the EC of a saturated paste derived from a 1:5 ratio of soil and distilled water. To estimate the total contribution of pollutants from the catchment on the hydric habitat between 2004 and 2006, water was collected prior to the entering the wetlands at every sampling. The flow of the catchment was measured using the principle of salt conservation (Comín et al., 2001) at each sampling time.

Retention rate \( R_e \) was estimated relatively to the inflow for each paired sample (inflow and outflow) of a wetland plot as follows:

\[
R_e = \frac{C_i \times Q - C_o \times (Q - ET)}{C_o \times Q} \times 100,
\]

where \( C_i \) was the concentration of one element at inflow, \( Q \) was the flow, \( C_o \) was the concentration at outflow and \( ET \) was the average
evapotranspiration for the month when samples were collected. To estimate \( R_e \) for a sampling campaign, all \( R_e \) values for each wetland plot sampled in that sampling campaign were averaged. To estimate annual \( R_e \) relative to the input, all \( R_e \) values from samples throughout the year for each wetland plot were averaged.

Estimations of \( R_e \) in absolute terms for each sampled wetland plot were calculated as \( C_i - Q - C_o \times (Q - ET) \) (following the same nomenclature as in the previous formula) per square meter, per day, multiplied by the number of days between sampling campaigns. \( R_e \) in one sampling campaign was extrapolated to the period between that sampling campaign, assuming \( R_e \) was constant. The annual absolute \( R_e \) per area was then estimated per square meter by adding all \( R_e \) values obtained for each sampled wetland plot throughout the year. \( R_e \) values for all wetland plots were then averaged. As the number of sampling campaigns varied between years, the total number of days in a year for which we could estimate retention or export of nutrients, salts, or sediments also varied: 92 in 2004, 152 in 2005, 183 in 2006, and 154 in 2007. Loading rates were calculated as the concentration of nutrients, salts, and sediments at inflow. The annual export of nutrients from the subcatchment was estimated (in kg) as the concentration of the nutrients multiplied by the flow, averaged for all water samples collected on each sampling campaign.

2.4. Statistical analysis

Spearman’s Rank Correlation coefficients were used to evaluate the relationships among water quality parameters and WRT. Variables that were strongly correlated (\( p < 0.01 \)) with two or more variables were excluded from further analyses. As the data were non-normally distributed, non-parametric tests were used. The Kruskal–Wallis test was used to test for statistical differences in the characteristics of inflow and outflow and nutrient \( R_e \) among plots of different sizes. To determine which plot sizes exhibited the most variance, orthogonal contrasts were performed. For all of the tests, the \( p \)-value for statistical significance was set at \( p < 0.05 \). All of the statistical analyses were performed with SPSS for Windows 13.0 (SPSS Inc.).

3. Results

3.1. Nutrients

In the study area at Monegros, in the Ebro River basin, NE Spain, the concentrations of nitrate and phosphate in inflow runoff were higher than the standards adopted in the EU (\( \text{NO}_3^-\text{N}: 11.3 \text{mg l}^{-1} \)) (European-Communities, 2000). In most quality parameters, the water in the inflow and outflow differed significantly (Table 3; Fig. 2). The \( R_e \) by volume differed significantly between wetland plot sizes S–M–L and wetland plot size XL for some of the water parameters (Fig. 3). Co-linearity was significantly (\( p < 0.01 \)) high (1) between \( \text{Cl}^- \), \( \text{SRP-P} \), alkalinity, and DO, (2) between TDS, alkalinity, and EC, and (3) between SRP-P, TP, and \( \text{NO}_3^-\text{N} \). Therefore, \( \text{Cl}^- \), TDS, and SRP-P were excluded from the analysis.

In the S, M, and L-wetland plots the \( R_e \) of \( \text{NO}_3^-\text{N} \) relative to the input was very similar for all 4 years (Fig. 3). In 2007, the average concentration of \( \text{NO}_3^-\text{N} \) for all wetland plots ranged from 18–19 mg l\(^{-1} \) in the inflow to 8–10 mg l\(^{-1} \) in the outflow (Fig. 2). The S and M wetland plots showed substantial \( \text{NO}_3^-\text{N} \) retention relative to the input, during all periods of each year for which we were able to give estimates (92 days between August and October in 2004, 152 days between June and October in 2005, 183 days between April and October in 2006, and 154 days between June and October in 2007; Table 4). L and XL wetland plots showed the lowest \( \text{NO}_3^-\text{N} \) retention per area per time during most of the study periods, with the exception of the L wetland plot in 2007. These data highlight the extremely high \( \text{NO}_3^-\text{N} \) retention per area per time (>500 g N m\(^{-2} \)) of the M wetlands during the study period of 2007. Relative to the input, M-wetlands in 2007 displayed a \( \text{NO}_3^-\text{N} \) retention of 42 ± 7%.

In the largest wetlands, \( \text{NO}_3^-\text{N} \) retention reached 99 ± 0.3% during the study period of 2007. In that period, the water leaving the XL wetlands had ∼1 mg l\(^{-1} \) of \( \text{NO}_3^-\text{N} \) (Fig. 2). Other nitrogen compounds, such as NH\(_4^+ \) and NO\(_2^-\), were only detected occasionally in the samples and, therefore, excluded from further analysis. The average release of \( \text{NO}_3^-\text{N} \) from the subcatchment was 731 kg per year.

TP was only significantly released from the wetlands in 2007 (Fig. 2; Table 3), when the average concentration varied from 2.7 ± 0.3 \( \mu \text{g l}^{-1} \) at the inflow to 6.7 ± 1.8 \( \mu \text{g l}^{-1} \) at the outflow. This reflected a high variability in annual release during the study period of 2007 which ranged from no export in the small (S) wetlands to a release of 53 ± 28 mg P m\(^{-2} \) in the medium-sized (M) wetlands. Release of TP expressed relative to the input tended to be higher in the larger wetland plots (Fig. 3), but the relationship was not statistically significant.

3.2. Salts

The concentrations of salinity-related parameters were higher in the outflow than they were in the inflow (Fig. 2). The values for these parameters in the XL wetlands, where flooding was very irregular, were highly variable; therefore, the data from the XL wetlands were analyzed separately. In the S, M, and L wetlands considered together, based on a constant concentration of Na\(^+ \) at inflow throughout all study periods, the release of Na\(^+ \) expressed relative to the inflow decreased drastically from 36% to almost zero in 2005 (Fig. 4). The annual average release of Na\(^+ \) expressed relative to the inflow for the three smaller wetland plots did not show a significant decrease throughout the study periods of 4 years (Table 4). Considering all years together, the release of Na\(^+ \) by mass tended to be higher in the larger wetlands (Fig. 3), but the relationship was not statistically significant.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Results of the Kruskal–Wallis test for differences in the runoff parameters in the inflow and outflow of constructed wetlands at Monegros, Ebro River basin, NE Spain.</th>
<th>All</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>Outflow/inflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{pH} )</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>EC</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>DO</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>TSS</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>Sulphate</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>( \text{K}^+ )</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>( \text{NO}_3^-\text{N} )</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>TP</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

ns = not significant. Outflow/inflow represents the increase (↑) or decrease (↓) in the values of parameters in the outflow relative to those in the inflow. In that column, only those parameters that were significantly different for all years combined or in more than 1 year are included.

\( \bullet \ p < 0.05 \)
\( \bullet \ p < 0.01 \)
\( \bullet \ p < 0.001 \)
Fig. 2. Concentrations of water quality parameters in the inflow and outflow of constructed wetlands in the Ebro River basin, Spain that were statistically significant (p < 0.05). Samples were collected on the same day for both inflow and outflow (S—50 m², M—200 m², L—800 m², and XL—5000 m²).

3.3. Other parameters

Alkalinity and pH were significantly higher in the outflow than they were in the inflow, considering all wetland sizes and sampling campaigns together (Table 3; Fig. 2). The highly variable values obtained for alkalinity and pH in the XL wetlands were analyzed separately. Alkalinity and pH in the outflow of S, M, and L wetlands were only 0.3% and 5.4% higher, respectively, than they were in the inflow (pH = 7.84; CO$_3^{2-}$ concentration = 248 mg l$^{-1}$). In 2007, the amount of CO$_3^{2-}$ released by the XL wetlands was 53% higher at the outflow than it was in the inflow. Significant differences in the levels of SO$_4^{2-}$ between the inflow and outflow were apparent in 2006, but these differences were only an average of 10 mg l$^{-1}$ out of 130 mg l$^{-1}$ for inflow measured during the same year.

3.4. Water-residence time

$R_t$ of NO$_3$-N and WRT were significantly positively correlated. Throughout the high retention ($\sim 99\%$) period in the XL wetlands in 2007, the average WRT was 9 days (range = 4–14 days). In addition, the Ca$^{2+}$ retention rate was positively correlated with WRT, par-
Retention rates are corrected for ET. Particularly in the XL wetlands throughout all study periods, which exhibited long WRT (11 days), TP and SO\textsubscript{4}\textsuperscript{2}\textsuperscript{-} release were positively correlated with WRT.

### 3.5. Temporal patterns

The NO\textsubscript{3}-N concentration in the inflow of all wetland plots averaged 20 mg\textsuperscript{-1}, ranging from 10 to 150 mg\textsuperscript{-1} (Fig. 5). In this analysis, the data from the XL wetlands were separated because of high variability and the smaller sample size that resulted from the extreme hydrological conditions. In 2006, the average NO\textsubscript{3}-N concentration in the inflow rose to 23 mg\textsuperscript{-1}. Overall, the R\textsubscript{s} of NO\textsubscript{3}-N among all of the wetland plots increased from 44% in 2004 to 52% in 2005, declined to 34% in 2006 and rose again to 44% in 2007. In 2004, the retention rates of Na\textsuperscript{+} were highly variable. From 2005 to 2007, the Na\textsuperscript{+} concentration in the inflow varied little (62 mg\textsuperscript{-1}; Fig. 5). In the S, M, and L wetlands, the release of Na\textsuperscript{+} to outflow water decreased progressively from 2004 to 2007 (Fig. 5).

### 4. Discussion

#### 4.1. Nutrients

Our hypothesis that nutrient and salt concentrations decreased after passing through constructed wetlands was only fulfilled for N, but not for P. Surface-flow constructed wetlands (SFW) in old agricultural fields showed significant differences between inflow and outflow water for most of the measured parameters after spontaneous revegetation. All of the wetlands in the study appeared to be very efficient in the retention of NO\textsubscript{3}-N. In the small (50 m\textsuperscript{2}), medium-sized (200 m\textsuperscript{2}), and large (800 m\textsuperscript{2}) wetlands, the global retention rate of NO\textsubscript{3}-N since the first year of wetland functioning reached 45% and remained at similar levels throughout the rest of the study. NO\textsubscript{3}-N retention was significantly higher in the extra-large wetlands (5000 m\textsuperscript{2}) than it was in the smaller wetlands. Throughout 2007, those large wetlands eliminated almost all of the NO\textsubscript{3}-N in the runoff (∼99%). However, retention of NO\textsubscript{3}-N calculated in absolute terms per area in these wetlands (XL wetlands; max. 75 g N m\textsuperscript{-2} in 2007) was lower than that measured in small wetlands (S and M wetlands) during all of the study periods (average >100 g N m\textsuperscript{-2} max. >500 g N m\textsuperscript{-2} in 2007; Table 4). WRT and wetland size were correlated positively (Table 1); however, conclusions cannot arise based on strict definitions of size and WRT. The high retention per area found in S and M wetlands could be due to the more stable flow (measured as shorter periods with dry soil) as compared to L and XL wetlands, which likely facilitated the development of aquatic vegetation. A more constant flooding regime could also facilitate development of the microbial community, leading to denitrification and a higher utilization of NO\textsubscript{3}-N by plants. The NO\textsubscript{3}-N retention rates observed in our XL wetlands are similar to levels recorded for wetlands of similar size in semi-arid regions, e.g. wetlands in the Ebro River

### Table 4

Annual retention rates by mass of the wetland plots grouped by sizes. Positive signs indicate release and negative ones indicate retention.

<table>
<thead>
<tr>
<th>Year</th>
<th>Size (m\textsuperscript{2})</th>
<th>NO\textsubscript{3}-N (g N m\textsuperscript{-2})</th>
<th>Na\textsuperscript{+} (g m\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>50</td>
<td>−291 ± 115</td>
<td>260 ± 48</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>−37 ± 41</td>
<td>298 ± 100</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4.9 ± 77</td>
<td>3.6 ± 13.4</td>
</tr>
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<td>43 ± 9</td>
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<td>−63 ± 25</td>
<td>58 ± 10</td>
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<td>−161 ± 112</td>
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<td>−111 ± 61</td>
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<td>−75 ± 52</td>
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Fig. 5. Temporal evolution of the retention and load concentration of Na⁺ and NO₃-N in the inflow in wetlands in the Ebro River basin, NE Spain. Dots represent mean ± S.E. of all samples collected during each sampling period in all wetland plots. Retention rates are corrected for ET.

delta (~1 ha, NE Spain; Comín et al., 2001) and wetlands in NE Italy (0.32 ha, Borin and Tocchetto, 2007). NO₃-N retention in the S, M, and L wetlands (45%) were similar to those observed in wetlands on forest soils in the midwestern USA (30–40%; Kovacic et al., 2006) and in integrated constructed wetlands in Ireland (58%; Harrington et al., 2007). Fink and Mitsch (2004) observed a retention of about 40 g N m⁻² per year in a 1.2-ha SFW in Ohio, USA, during storm events. In cold climates, retention values of 50–285 g N m⁻² per year were recorded in small (<1000 m²) wetlands in Norway (Braskerud, 2002). In similarly sized wetlands in Finland, rates were 6–45 g N m⁻² per year (Koskiaho et al., 2003).

In our study, 4 years after the wetlands had been constructed, retention of TP had not been achieved. The high accumulation of TP within the soil matrix throughout the period during which the land was used for agriculture (20 μg g⁻¹ of available P, Moreno-Mateos et al., 2008) meant that most of the soil particles that were capable of retaining P were already saturated when the abandoned croplands were flooded. After the soils were flooded, some of the available P was released into the water column and exported. That process was enhanced by the drying and rewetting conditions that occur during the driest periods (Venterink et al., 2002). During the 4 years of our study, TP release did not decrease significantly. The largest (XL) wetlands tended to export relatively more TP than did the smaller S, M, and L wetlands (Fig. 3). XL wetlands retained Ca significantly, probably because of the capacity of Ca to interact with the large amount of available P that was released by the soil into the water column under alkaline conditions (pH ~ 8). Consequently, the Ca–P system controlled the Ca and P concentrations in the outflow water, which indicated that some of the released P and dissolved Ca were fixed by the precipitation of Ca–P minerals under high pH (Shenker et al., 2005). In North Carolina, release of P to the outflowing water occurred 6 years after the construction of wetlands on abandoned agricultural fields (Bruland et al., 2003).

4.2. Salts

Our hypothesis of lower concentrations after passage through the wetlands was not correct with regard to salts. Release of Na decreased drastically after the first year following construction of the wetlands (Fig. 4). This could mean that significant amounts of salts will not be released if the current flooding conditions are maintained. If drying–rewetting periods occurred, then salts in lower soil layers could be dissolved during rewetting and enter the water column (Rodríguez-Ochoa et al., 1998). The high release of Na in the first year was due to the high salinity of the soil matrix (226.41 ± 232.90 μg g⁻¹) (Moreno-Mateos et al., 2008). Despite a general annual decrease in outflow salt concentration and, therefore, in salt export, there was not a significant annual decrease in Na export as measured on an areal basis. This could be due to an unforeseen water flow variability not perceived by our design of low-frequency water sampling (2–5 sampling campaigns per
year). Probably, a more frequent sampling design and longer study period would have revealed a general decrease in salt exportation as revealed by mass. In 2005, a substantial amount of most cations (Ca²⁺, Na⁺, and K⁺) was released into the water outflow. In that year, a severe drought necessitated leaving the wetlands without water up to 2 months, but they were later rewetted. Drying and rewetting of the saline mudstones can promote the capillary ascent of additional salts from the deeper layers of the soil (Rodríguez-Ochoa et al., 1998). The high EC recorded in the outflow of the XL wetlands might have been due to the longer time that the water was in contact with the soil (high WRT) and the larger surface of contact between the soil and the water column, which provided larger amounts of soluble salts to the water column.

4.3. Other parameters

The increase in alkalinity (i.e., the concentration of CaCO₃) in the outflow from XL wetlands is probably caused by two processes: the release of CaCO₃ from the soil matrix and the release of products by microbial respiration (McCartney et al., 2003). The increase in carbonates in the water was probably the cause of the small increase in the water pH. Intermittent flooding and the rewetting of soils could cause the decalcification of soils because of the increase in CO₃²⁻ pressure and the drainage of pore-water solutes (Van den Berg and Loch, 2000); these processes will be greater in XL wetlands where water–soil contact is greater, and might explain the release of CaCO₃ in outflow studied during 2007 (219 mg l⁻¹ at inflow and 336 mg l⁻¹ at outflow). Small amounts of lime can enhance the retention of P in the soil matrix (Zarayk et al., 1997). We suspect that the system soil matrix–water column was entirely saturated with CaCO₃ and P, and retention of P by carbonated soils was not a factor at this stage in the XL wetlands.

4.4. Water-residence time

In the XL wetlands, at the time of maximum NO₃-N retention (≈99% in 2007), WRT varied from 4 to 14 days (average 9 days in 2006 and 2007). In similar constructed wetlands, retention rates of 99% and WRT of 5 days have been reported (Comín et al., 2001). In boreal regions, Koskiaho et al. (2003) found that the highest retention rates of TP and TN occurred in the wetlands that had the longest WRT (1.63 days). Mitsch and Gosselink (2000) reported an optimum range of 5–14 days of WRT for nutrient retention. In XL wetlands, we considered that a WRT less than 9 days could satisfy the conditions for retention of NO₃-N. The WRT was 3–6 days longer in the XL wetlands than it was in the S, M, and L wetlands (Table 1), where it was insufficient for complete retention of NO₃-N. It is important to highlight that longer WRT is correlated with higher concentrations of TP, salts, and sulphates in the outflow.

4.5. Temporal patterns

After the NO₃-N retention percentage increased from 2004 to 2005, it dropped by half in 2006. In this year, the NO₃-N load in the inflow increased because of an increase in the amount of fertilizer applied to irrigated fields upstream (personal communication). In 2006, the absolute retention per area was almost the same as in 2005; consequently, the relative retention decreased, which meant that, in those years, the size of the wetlands was insufficient to retain high proportions of through-flowing NO₃-N. In 2007, the relative retention increased to the 2005 level because of lower nitrate concentrations in the inflow as a result of reduced fertilizer use. This shows that the capacity of this system of constructed wetlands is suitable for effective nitrate removal, provided that the level of fertilizer use is moderate. Throughout the study, TP levels were highly variable, and no temporal trends were apparent. Despite a constant load of Na⁺ in the inflow after 2004, the release of Na⁺ was remarkably reduced the next year and remained relatively constant until the end of the study. That situation would suggest that wetlands under permanent flooding would exhibit negligible release of salts to the streams.

4.6. Catchment considerations

Considering the nitrogen retention rates shown here (76–227 g N m⁻² per year (minimum–maximum annual averages for 2004 and 2007), as well as the study catchment’s annual export of NO₃-N (730 kg N), 1.5–4% of the catchment will need to function as wetlands to ensure an optimal removal of NO₃-N from the water flowing into the hydric network. In an earlier study of those wetlands, we suggested that 3–6% of the catchment should be in use as wetlands (Moreno et al., 2007). Hammer (1992) recommended devoting 2% of the catchment area to the establishment of wetlands, which is similar to the lowest percentage obtained in this study. Larson et al. (2000) suggest using a 22:1 ratio for wetlands in small agricultural catchments in Illinois, which is equivalent to 4.7% of the catchment; Kovacic et al. (2006) suggested 5% for small agricultural catchments in the Midwestern USA. In the Mississippi River Basin, Mitsch et al. (2001) advised reserving 3–5% of the catchment for wetland restoration. The wetlands used in our study currently make up 5.8% of the catchment area ~ greater than the necessary ratio, but they did not work optimally. Thus, to ensure water quality improvement, having a wetland/catchment ratio within the prescribed range is not adequate. Other requirements (e.g., biological structure, morphological design, soil characteristics) must be considered in order to effectively improve the agricultural runoff discharged into the hydric network by using constructed wetlands.

5. Conclusions and recommendations

In Monegros, the wetlands had not stabilized 4 years after they were constructed. Phosphorus and salts and, to a lesser extent, carbonates were still being exported. After a large loss of salts during the first year of wetland functioning, the release of salts was close to zero (only 2% in 2007). Intermittent flooding appeared to have an important influence on the amount of salts released; permanent flooding can minimize that risk.

In all of the wetlands, significant retention rates of NO₃-N were achieved (76–227 g N m⁻² per year). The largest wetlands (5000 m²) with longer WRT (9 days) achieved optimal retention of NO₃-N relative to the input (99%), but the absolute retention rate per area was highest in medium-sized wetlands (200–500 g N m⁻² per year). However, large wetlands had longer WRT and exported more TP, salts, and carbonates than the small wetlands. The incorporation of the use of constructed wetlands into new or existing agricultural policies, will allow land planners to improve the water quality in irrigated agricultural catchments in the semi-arid region of the Ebro River basin and other semi-arid regions. Land planners must recognize that the agricultural soils of Monegros and the Ebro River basin have problems with overfertilization and salinization, which can delay the development of optimal water quality. With that in mind, we strongly recommend the use of wetlands to improve water quality; such practices can also provide ancillary benefits (landscape heterogeneity, biodiversity reinforcement or soil improvement) in areas heavily degraded by intensive agriculture.
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References


