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PRIMARY RESEARCH PAPER

Influence of operational parameters on nutrient removal from eutrophic water in a constructed wetland

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Abstract The present study offers several management strategies in order to improve the performance of a free water surface constructed wetland that treats mainly eutrophic water and which is also designed to improve and increase the biodiversity of habitat and wildlife. To attain these goals, it has been necessary to analyze the influence of certain operational parameters and environmental factors on the mass removal rates (MRRs) and the mass removal efficiencies (MREs), depending on if the objective is to maximize nutrient removal or to achieve low effluent concentrations. The system, referred to as FG, operated in a range of hydraulic loading rates (HLRs) from 7 to 58 m year^{-1} and removed phosphorus (P) and nitrogen (N) at an average rate of 7.15 g P m^{-2} year^{-1} and 60.07 g N m^{-2} year^{-1}. P and N removal varied seasonally, mainly due to input concentrations (C_{in}), but inlet mass loading and HLRs also strongly influenced MRRs. Based on these results, we propose to maintain a mean HLR of 58 m year^{-1} in winter and 25 m year^{-1} in summer to increase annual nutrient removal and thereby barely affecting pumping costs.

Keywords Free water surface constructed wetland · Eutrophication · Hydraulic and nutrient loading · Nutrient removal · Albufera de València Lake

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Abbreviations

FWSCWs	Free water surface constructed wetlands
FG	The FWSCW studied
MRRs	Mass removal rates
MREs	Mass removal efficiencies
HLRs	Hydraulic loading rates
P	Phosphorus
N	Nitrogen
C_{in}	Input concentrations
IML	Inlet mass loading
AV Lake	l'Albufera de València Lake
AVNP	l'Albufera de València Natural Park
CWs	Constructed wetlands
BP	Barranco del Poyo
DIN	Dissolved inorganic nitrogen
DIP	Orthophosphates
n-DIP	Non-orthophosphate phosphorus
DO	Dissolved oxygen

Introduction

Cultural eutrophication is the main problem facing most surface waters nowadays (Smith & Schindler, 2009). Successful eutrophication mitigation is based mainly on the restriction of nutrient inputs to the waterbody, and this can be achieved by a wide variety of external and internal controls (Cooke et al., 1993; Smith et al., 1999). Although external nutrient inputs tend to be the main cause of eutrophication in shallow lakes and other water bodies, internal nutrient loads, i.e., nutrients released into the water column from sediments and from phytoplankton biomass decomposition, could be a major nutrient source that delays their recovery (Søndergaard et al., 2003; Jeppesen et al., 2005). There are several methods to reduce internal loads, such as the use of phosphates inactivation agents (Cooke et al., 1993; Zamparas & Zacharias, 2014) or removal of sediment layers (Phillips et al., 1999). Recently, a new approach to reduce these loads, based on the use of FWSCWs (free water surface constructed wetlands), has been tested in *l'Albufera de València* Lake (AV Lake) (Martin et al., 2013; Rodrigo et al., 2013). The Lake is enclosed in the *l'Albufera de València Natural Park* (AVNP) (Fig. 1), which is a wetland of International Importance (Ramsar Convention, 1990) and a Zone of Special Protection for Birds. The main characteristics of AV Lake are that it is shallow (around 1 m deep), highly eutrophic, and it is surrounded by rice fields.

Constructed wetlands (CWs) are widely used for the removal of pollutants from wastewaters, for urban storm water treatment, for industrial wastewater treatment, for mine water treatment, and for field runoff treatment (Kadlec & Wallace, 2009). These systems present several advantages compared to conventional treatments (easy and low construction cost, relative lower-energy requirements, low operational and maintenance cost, and provide habitats for a wide diversity of plants and animals). These characteristics make them ideal candidates for the improvement of water quality in aquatic ecosystems (Pomogyi, 1993; Spieles & Mitsch, 2000; Kadlec et al., 2010), and as result of this, wildlife biodiversity is also enhanced. Comín et al. (2001) proved that the restoration of wetlands belts around lagoons increases spatial heterogeneity and diversity of the landscape, as well as improving their water quality. Fleming-Singer & Horne (2006) reported that it is possible to achieve a suitable habitat for birds as well as achieving high rates of nitrogen removal.

Recently, this technology has been tested in the treatment of eutrophic waters (Coveney et al., 2002; Li

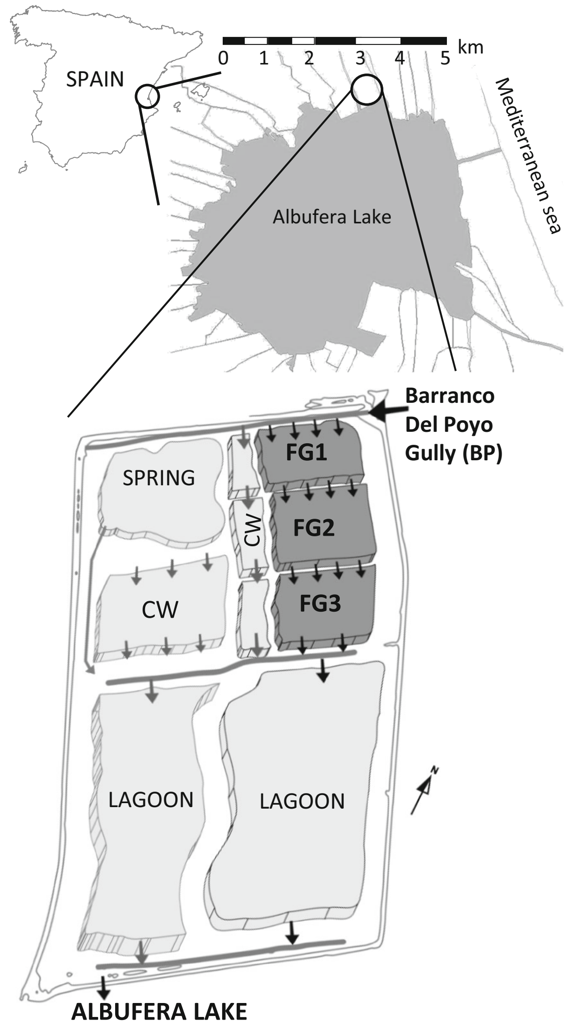

Fig. 1 Location of AV Lake and *Tancat de la Pipa* and map of FWSCWs showing FG cells

et al., 2008; Dunne et al., 2012, 2013*)*. However, there are scarce studies that report information concerning the management of these systems to enhance their performance, and in addition, these are, mostly, focused on the phosphorus removal. This is the case of the study carried out in Lake Apopka (Florida) by Dunne et al. (2012, 2015), the goal of which was to maximize P removal from the eutrophic lake water working at high HLR (30 m year^{-1}). Researchers found that P removal performance increased during cool periods and decreased during warm periods while operating cost remained constant. Drawing from these results, a seasonal operating regime with low warm-season flows to increase cost-effectiveness was adopted.

The role of the FWSCWs built in AVNP is multiple: to treat the lake water, to improve and increase the biodiversity of habitat and wildlife (from the bottom to the top of the food web), while ensuring its public use compatible with the above. These desired outcomes imply that some operational or design parameters, such as water depth, vegetation cover, or the lining of the substratum, besides enhancing nutrient removal, should also provide a suitable habitat for wildlife, specially when the surrounding rice fields are dry, given that there are times when FWSCWs play an important role as a food source and refuge for birds.

Following on from this, the hypothesis of this study is that it is possible to enhance the system's performance, based on knowledge and management of the main factors that influence it. In addition, our premise is that if the abovementioned analysis is found to be feasible, we propose the establishment of a range of optimum values for these factors depending on the goal, namely to maximize nutrient and phytoplankton removal from eutrophic water and point sources or to achieve the lowest possible effluent concentrations.

The efficiency obtained during the first 2 years of operation (April 2009–March 2011) by these FWSCWs has already been reported (Martín et al., 2013). The objectives of this study are (1) to determine the feasibility and the efficiency of a given FWSCWs to remove and retain P and N from eutrophic lake water operating over a longer period, (2) to analyze the influence of different operational parameters and environmental factors on nutrient removal, and (3) to establish optimum operating conditions and propose recommendations for the management and design of artificial wetlands to treat eutrophic waters.

The operational parameters studied are IML, HLR, water column depth, and vegetation cover. Otherwise, the environmental factors are C_{in}, temperature, pH, dissolved oxygen concentration (DO), and presence of birds into the FWSCW.

Materials and methods

Site description and operation

The research described in this paper was conducted at *Tancat de la Pipa,* an area of approximately 40 ha, located on the north of AVNP (Valencia, Spain), and that was formerly a rice field. Site details are described in Martin et al. (2013). Briefly, three FWSCWs (named FG, fp, and F4) were built for treating eutrophic water from the AV Lake. This paper focuses on the operation of one of them, the system called FG, which is divided into three cells arranged in series and named FG1, FG2, FG3, respectively (Fig. 1). This design allows the independent operation and management of each cell.

Lake water enters to FG from a gully named *Barranco del Poyo* (BP) (Fig. 1). This flow is continuous, by gravity and it is measured daily through a V notch weir. The inlets to each cell are four small sluices (Fig. 1), 0.3 m wide, spaced every 30 m, with wooden or riser boards that can be raised or lowered to manipulate the water column depth and, therefore, the hydrological gradient between inlets and outlets. The outlets from FG are two sluice gates (Fig. 1) of 0.5 m width. The flows in each of these sluices are regularly measured with a properly calibrated mini current meter (specifically with SEBA F1). The treated water is pumped back into the AV Lake. Environmental restrictions prevent the cells from being artificially waterproofed; nevertheless, substantial percolation was not obtained from the water balance (only about 5% with respect to inflow). This low percolation is related to the low hydraulic conductivity of the soil, since its texture is silty-clay/silty-clay-loam.

The initial planting period was January–February 2009. The kind of plants and the initial plant density are shown in Martin et al. (2013). The vegetation cover in each treatment cell is displayed in Fig. 2. In early summer of 2009, FG1 and FG2 had already reached complete vegetation cover, but in October 2009, FG1 was harvested and after that, a suitable plant cover was never recovered. This was mainly due to strong herbivore predation of soft shoots. FG operation was interrupted again in March 2011, for planting *Phragmites* spp. in FG1, and in August 2011, to allow the spread of these macrophytes. Nevertheless, the reed that had been planted did not grow properly. The gradual disappearance of vegetation cover in FG2 was also caused by herbivore predation. Unlike previous cells, in FG3 the vegetation cover increased, though slightly, over time. This was mainly due to the invasion of *Phragmites* spp. and the low-density planting of *Iris pseudacorus* in FG3 in March 2011. However, FG3

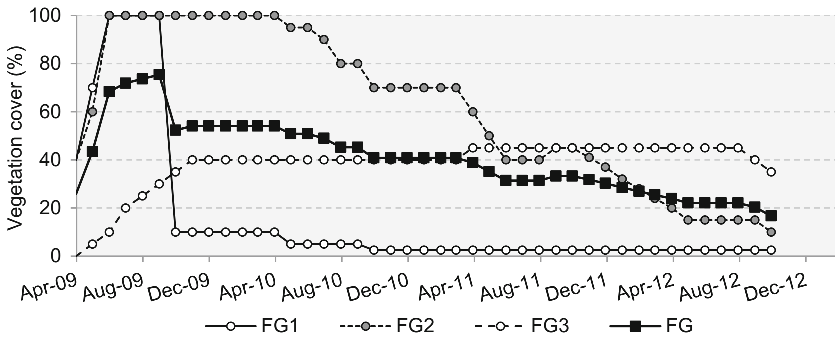

Fig. 2 Vegetation cover in FG1, FG2, FG3, and FG. Plant cover was estimated as the area occupied by vegetation considering the projection of the aboveground biomass on the ground. FG is the weighted average, where the weight assigned is the cell area

never reached a high cover probably due to the low initial plant density (Fig. 2).

Sample collection and analysis

In this paper, wetland operation data from April 6, 2009 to October 29, 2012, are reported. A total of 304 water samples were collected in 76 samplings carried out at the inflow and outflow of each cell, between 9 a.m. and 14 p.m. From April 2009 to October 2011, the samplings were carried out once a fortnight and from November 2011, on a monthly basis.

Water temperature, pH, conductivity and DO were measured in situ using portable field measurement equipment (WTW® probes) and water samples were taken with 2 L bottles placed to mid-water depth and preserved in cold storage until arrival at the laboratory. DO continuous measurements were recorded every 15 min for 24 h at each sampling point. The measurements were carried out on consecutive days for each point and in the following seasons: early autumn 2011, early winter 2012, early spring 2012, and early summer 2012. The days were randomly selected.

Water samples were filtered according to Standard Method (APHA, 1991) and analyzed for total nitrogen (TN), ammonium (NH_4^+–N), nitrite (NO_2^-–N), nitrate (NO_3^-–N), total phosphorus (TP), and orthophosphates (DIP-P), using the Spectroquant® Analysis System by Merck. The difference between TP and DIP measured is called non-orthophosphate phosphorus (n-DIP). The organic nitrogen (ON) was estimated as difference between TN and dissolved inorganic nitrogen (DIN, the sum of NH_4^+–N, NO_3^-–N, NO_2^-–N). Nutrient loads from dry and wet atmospheric deposition were estimated from samples obtained with a total atmospheric deposition sampler. This consists of a 35-cm-diameter funnel and a 5-L container to collect such deposition. After each rainfall event, the sample collected is analyzed.

Calculations

Data of rainfall and evapotranspiration were obtained from a regional agricultural research center (IVIA, http://riegos.ivia.es), for proximity at study area. The inlet mass loading (IML), mass removal rates (MRRs), and annual mass removal efficiencies (MREs) were calculated as follows:

$$\text{IML}\ \left(\text{g m}^{-2}\ \text{year}^{-1}\right) = \left(\frac{(Q_{\text{in}}C_{\text{in}}) + (Q_{\text{P}}C_{\text{P}})}{A}\right) \times 365,$$

$$\text{MRR}\ \left(\text{g m}^{-2}\ \text{year}^{-1}\right) = \left(\text{IML} - \frac{((Q_{\text{in}} + Q_{\text{P}} - \text{ET})C_{\text{out}})}{A}\right) \times 365,$$

$$\text{MRE}\ \ (\%\ ) = \left(\frac{\text{MRR}}{\text{IML}}\right) \times 100,$$

where Q_{in} is the inflow from BP (m^3 days^{-1}), C_{in} is the input concentration (g m^{-3}), Q_P is the precipitation flow (m^3 d^{-1}), C_P is the atmospheric deposition concentration (g m^{-3}), ET is the evapotranspiration (m^3 days^{-1}), C_{out} is the output concentration (g m^{-3}), and A is the wetland area (m^2). These variables were considered constant between measurements, except for precipitation, since it is highly variable in this area. The overall MRE were calculated as accumulated mass removed during the period of the study and divided by accumulated mass input during the same period.

We used the results obtained by Hernández-Crespo et al. (2016), in relation to aboveground biomass and the amount of nutrient storage in plant tissue (NPT) at the end of each growing season, to calculate the nutrient mass removed by plants uptake in FG system.

$$\text{Annual plant storage } (\%) = \left(\frac{\text{NPT}}{\text{Mass nutrient removed April}_i - \text{March}_{i+1}}\right) \times 100,$$

$$\text{Nutrient removal by plants } (\%) = \left(\frac{\text{NPT in FG1in October 2009} + \text{NPT in FG in October 2012}}{\text{Mass nutrient removed Abril 2009} - \text{October 2012}}\right) \times 100.$$

Statistics

We report descriptive statistics such as mean, maximum, minimum, and standard deviations. The normal distribution of each variable studied in this paper was ascertained using the Kolmogorov–Smirnov test ($N > 30$) or Shapiro–Wilk test ($N < 30$), and the Levene test was used for ascertaining homoscedasticity of data. After confirming normality and homoscedasticity, one-way ANOVA test was applied; otherwise, the Kruskal–Wallis non-parametric test was used to compare seasonal variations. When the ANOVA was significant, the post hoc Bonferroni test was used to identify different groups and for non-parametric samples Mann–Whitney U test. Student's *t* test and Wilcoxon test for non-parametric variables were used to compare the influent and effluent pollutant concentrations. Spearman's correlation coefficients were computed to study the relationship between variables. Multiple linear regression models were performed to predict nutrient mass removal rate as function of inflow concentration and hydraulic loading rate. In the present study, the forward stepwise method was used to build the linear regression models. Other non-linear models were performed (logarithmic). A level of $P < 0.05$ was considered statistically significant in all comparisons. Analyses were performed in SPSS 15.0 for Windows (SPSS Inc. Chicago, USA), except linear regression models that were carried out with Statgraphics Plus 5.1.

Results

Hydraulics, temperature, dissolved oxygen, and pH

During the study period, FG treated 5.4×10^6 m^3 of water from BP (that is approximately 20% of the lake's water volume) and a water volume from the rainfall lower than 0.1 Hm^3. The evapotranspiration represented about 4% of the treated water, justifying its inclusion in the mass balance. The HLR (Fig. 3) was increased in several steps with mean values of 7, 25, 32, and 58 m year^{-1} from April 2009 to March 2011. However, from April 2011 the HLR had to be decreased to 27 m year^{-1} in order to minimize the pumping costs. The HLR tested were always within a suitable range value for wildlife habitat. The water depth oscillated between 0.08 and 0.25 m (Table 1), because of concern for the health of the newly emerging vegetation and the bird habitat. Nonetheless, the design limit is 0.35 m. The mean theoretical hydraulic residence time (HRT) was 3 days, but the values were variable (Table 1).

Temperature and DO measured at the outflow were significantly lower than inflow ones ($P < 0.01$). Effluent temperatures ranged among 3.7 and 30.7°C, with a mean value of 17.5°C, which is lower than mean inflow value (19.7°C). DO outflow concentrations ranged between 0.14 and 15.43 mg L^{-1}, with a mean value of 3.71 mg L^{-1}. Nevertheless, in the case of DO, its behavior in each FG cell was different. FG1 was oxygen producer, especially in autumn and winter, which is depleted into the following cells (FG2 and FG3). As expected, temperature and DO at the all points showed seasonal variation and inverse patterns. The lowest DO values in FG3 effluent were recorded in summer and the highest values were

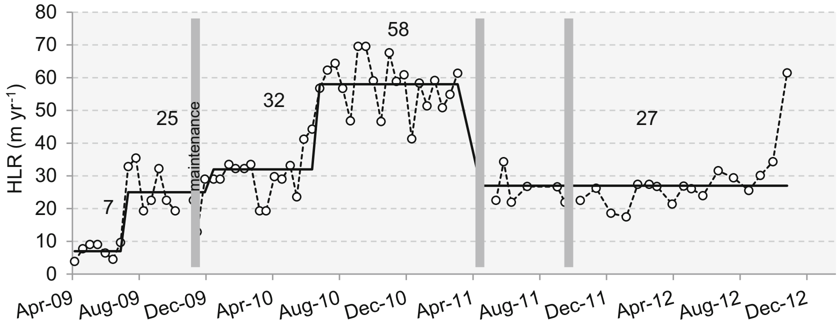

Fig. 3 Time series (April 2009 through October 2012) of hydraulic loading rates measured. The *solid line* represents the mean value tested in FG

Table 1 Characteristics of FG

Features	FG1	FG2	FG3
Water depth (m)	0.2 (0.15–0.25)	0.18 (0.15–0.20)	0.17 (0.08–0.20)
HRT (days)	1.0 (0.35–5.4)	1.2 (0.3–8.0)	0.9 (0.3–3.8)

Both water column depth and hydraulic residence time (HRT) are mean (minimum–maximum) values for all the study period

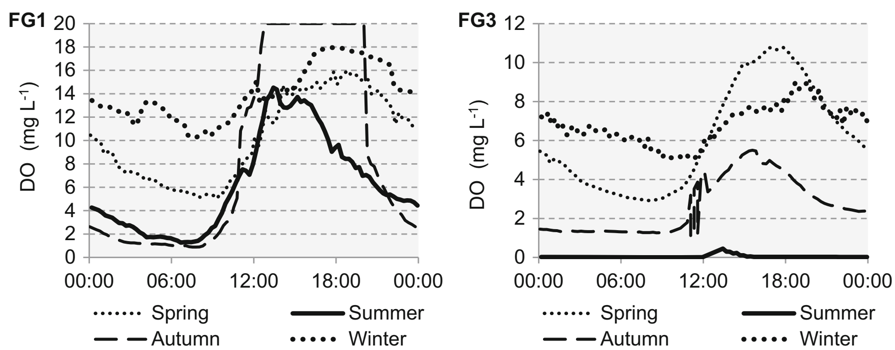

Fig. 4 Daily cycles of dissolved oxygen observed in each season for FG1 and FG3 effluents

registered in winter and early spring (in accordance with the lowest temperatures and the largest DO production in FG1). Figure 4 shows daily oxygen oscillations registered in FG1 and FG3 effluents in each season. It shows higher DO concentrations in FG1 and FG3 effluents during the day in winter than in summer. The higher values were usually measured after midday (coinciding with a higher photosynthetic activity) and the lowest values just before sunrise. Note the low DO concentrations, almost zero, measured in FG3 in summer. Over the study period, DO concentrations showed a continuous decrease in FG3 effluent and an increasing trend in BP and FG1 and FG2 effluents.

The pH values at the outflow oscillated between 6.91 and 8.20, but in FG1 and FG2 cells it reached values of 9.

Input–output concentrations and seasonal variations

The main component of TP in the inflow was the n-DIP (average of 77%), which responds to a high eutrophication level (Fig. 5). In contrast, TN in the inflow was mostly DIN (61% of TN) and NO_3^- (76% of DIN) in particular (Fig. 5). Nevertheless, in samples taken after rainfall events the DIP was the main TP component (reaching up to 76%) and the ammonium for TN. In these cases, the TP and the ammonium reach values higher than 1 mg L^{-1}.

For all the studied parameters, C_{in} were significantly greater than outflow concentrations ($P < 0.01$), being the differences greater in n-DIP and NO_3^-. In addition, seasonal differences were observed in both inflow and outflow concentrations (Fig. 5). At the

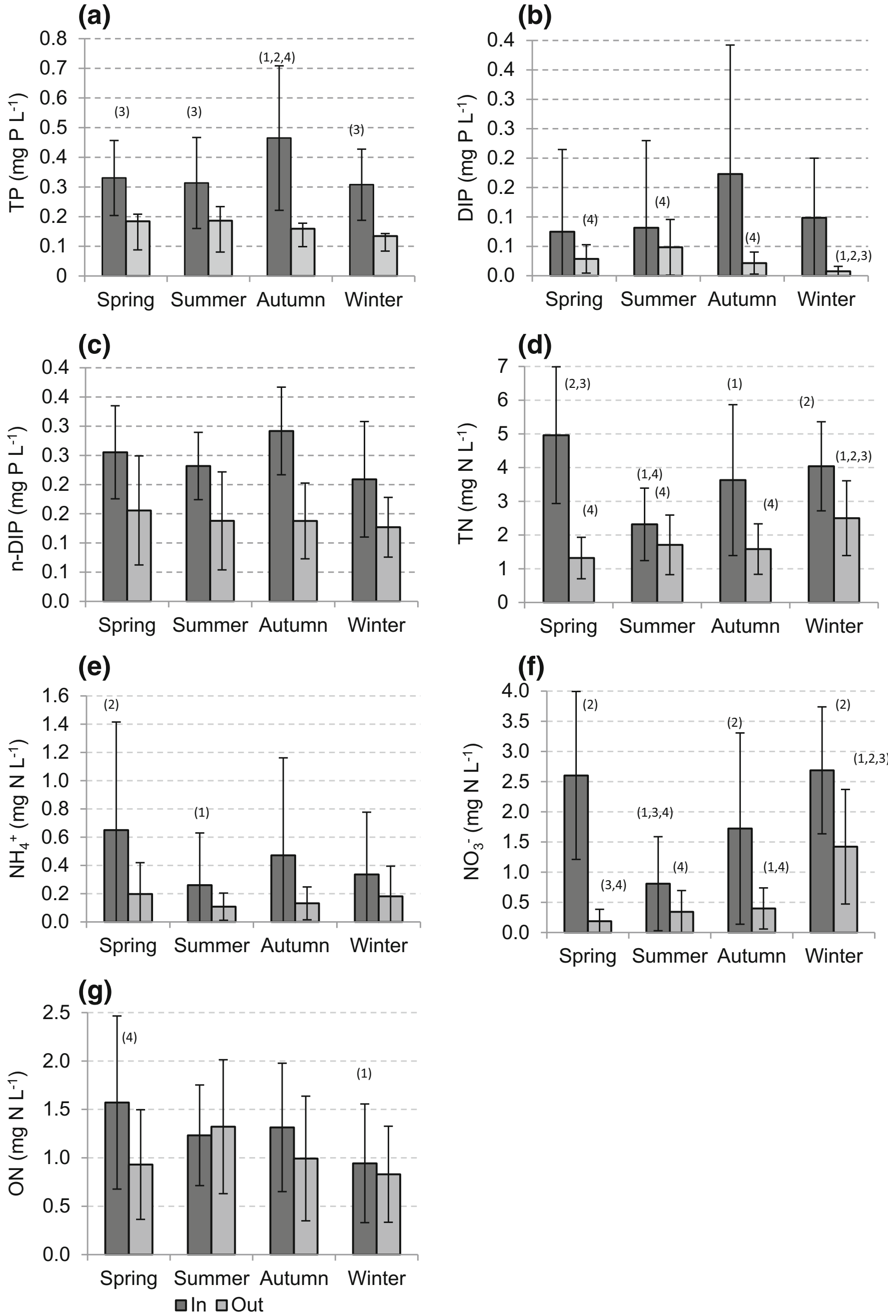

Fig. 5 Mean and standard deviation observed in each seasons for **a** TP, **b** DIP, **c** n-DIP, **d** TN, **e** NH_4^+, **f** NO_3^-, and **g** ON. For significant differences: *1* spring, *2* summer, *3* autumn, *4* winter

inflow, the highest mean values were registered in autumn and winter for P and in spring and winter for N. The low levels of DIN recorded in summer are noteworthy. At the outflow, the minimum values for P were observed in winter and for N in spring, while the highest values were measured in summer for P and in winter for N (mainly due to high levels of nitrates). The ON outflow concentrations were higher than the inflow ones in summer.

A relevant result was that DIP outflow concentrations were significantly correlated with DO concentrations ($r = -0.747$, $P < 0.01$).

Table 2 Inlet mass loading measured during 43 months of operation

g m^{-2} $year^{-1}$	TP	n-DIP-P	DIP-P	TN	NH_4^+–N	NO_3^-–N
Mean	12.48	8.82	3.87	120.05	14.31	61.20
Minimum	1.62	1.11	0.04	15.33	0.66	2.19
Maximum	61.21	23.14	44.32	433.01	117.27	245.75

Nutrient removal

Inlet mass loadings were highly variable (Table 2) and significant correlation between these and the outflow concentrations were not found [except weakly for NO_3^- ($r = 0.237$, $P < 0.05$)]. Atmospheric loads accounted around 2% with respect to the input from the BP. P and N mass removal rates (Table 3) and mass removal efficiencies (Table 4) ranged also widely over time, decreasing in the case of efficiencies, except for NO_3^-. For P, the highest removal rates were obtained for n-DIP and the highest MREs for DIP. For N, both were achieved for NO_3^-.

Regarding to seasonal variation, for P the highest MRRs and MREs were achieved in autumn and winter ($P < 0.05$). For N, the highest removal rates were reached in winter and spring, and the lowest in summer ($P < 0.01$). The lowest N efficiencies were obtained in winter and summer ($P < 0.05$). Therefore, the nutrient removal rates in FG are lower in summer and higher in winter.

The average annual mass removed for FG from the AV Lake was 306 kg $year^{-1}$ of TP and 2558 kg $year^{-1}$ of TN (2111 kg as DIN) from April 2009 to October 2012, representing between 0.1 and 0.9% and between 0.1 and 0.2% of input annual P and N loads to the lake (data not shown here).

Influence factors on nutrient removal

For almost all parameters, C_{in} and IMLs were positive and significantly correlated with both MRRs and MREs (Table 5). In the case of MRRs, the relationships followed a linear trend, so the highest ones were obtained with the highest C_{in} and IMLs, although for TN and NO_3^- a logarithmic trend also fitted well to data with IMLs (Fig. 6). For MREs, the relationship was logarithmic approaching the asymptote at 100%.

In addition, TP, n-DIP, and TN mass removal rates were positive, significant, and linearly correlated with HLRs, while DIP and DIN mass removal rates were not (Table 5). From the results shown in Table 5, it might be suspected that the HLR did not influence on P removal efficiency. However, it increased slightly with HLR up to 32 m $year^{-1}$, although there were no significant differences working among 7–58 m $year^{-1}$ ($P > 0.05$) (Fig. 7). Conversely, the MREs obtained operating at 27 m $year^{-1}$, and coinciding with lower plants presence (Fig.2), were significantly lower than the MREs achieved with the previous HLRs ($P < 0.05$) (Fig. 7). As will be discussed later, the tested HLRs did not influence TN removal efficiencies (Fig. 7).

With respect to temperature, only TN, NO_3^-, and DIP mass removal rates and DIP mass removal efficiencies were significant and negatively correlated with it (Table 5). These relations were linear, although really weak, so that the highest removal coincided with the lower effluent temperatures. The lack of relation may indicate that the temperature does not significantly influence in removal or that other factors are interfering with this influence.

Other factors studied were DO and pH of water and the vegetation cover (not shown in Table 5). TP, DIP, and NH_4^+ removal efficiencies were positive and

Table 3 Mass removal rates obtained during 43 months of wetland operation

(g m^{-2} $year^{-1}$)	TP	n-DIP-P	DIP-P	TN	NH_4^+–N	NO_3^-–N
Mean	7.15	4.37	2.89	60.07	8.85	38.69
Minimum	−4.7	−3.43	−3.35	−90.65	−22.22	−60.21
Maximum	49.30	19.00	42.03	273.30	101.29	180.55

Table 4 Overall mass removal efficiencies and mass removal efficiencies obtained with an annual balance

	TP (%)	n-DIP (%)	DIP (%)	NH_4^+ (%)	TN (%)	NO_3^- (%)	DIN (%)
April 2009–March 2010	64	56	83	77	58	68	72
April 2010–March 2011	65	57	82	71	48	51	55
April 2011–March 2012	39	40	30	−9	42	66	59
April 2012–October 2012	26	20	39	−7	39	79	68
Overall MRE	55	48	71	58	48	63	62

Data for the first two years have already been reported in Martin et al. (2013)

significantly correlated with vegetation cover within the CW ($r = 0.347$, $P < 0.01$, $r = 0.307$, $P < 0.01$, $r = 0.413$, $P < 0.01$, respectively). DIP removal efficiencies were correlated non-linearly with DO concentrations and with pH values ($r = 0.506$, $P < 0.01$, $r = 0.477$, $P < 0.01$, respectively).

Two models for P and N retention were developed with the main factors analyzed: C_{in} and HLR (Model 1 and Model 2). The multiple linear regression models were significant ($P < 0.0001$) and for TP it explains about 83% of the variable-dependent variance and for TN the 58%. The C_{in} was the most important independent variable in both models.

Model 1

$$\text{TP MRR}\,(\text{g m}^{-2}\ \text{year}^{-1}) : 35.105 \cdot C_{in} + 0.272 \cdot \text{HLR} - 14.369$$

Model 2

$$\text{TN MRR}\,(\text{g m}^{-2}\text{year}^{-1}) : 21.82 \cdot C_{in} + 1.631 \cdot \text{HLR} - 75.45.$$

The main factor that influenced nutrient removal efficiencies was clearly the C_{in} (Table 5). "Threshold C_{in}," below which is unlikely to achieve positive efficiencies, was estimation by fitting the data to a logarithmic curve (Table 6).

Plant biomass and nutrient storage

The estimated values of aboveground biomass in FG varied between 0.61 and 0.73 kg d m m^{-2} (Table 7). Nonetheless, these values increase appreciably if the vegetated area alone is considered (Table 7). Furthermore, these values were not homogeneous between cells and over time.

N and P accumulation in aboveground standing crop varied between 0.1 and 16 gN m^{-2}, and 0.01 and 2.3 gP m^{-2}. Annual mass balance calculations showed that plant storage represented between 7 and 31% of the N and 9 and 41% of the P removed by FG. However, these nutrients were not definitively removed from the FG, as only aboveground biomass of FG1 was harvested at the end of the first growing season, representing the 9% of N and 14% of P removed that year for this cell. In the whole of the study period, nutrient removal by plants only accounted 5% of N and P removed in total by FG.

Discussion

The FWSCWs located in *Tancat de la Pipa* (Valencia, Spain) are efficient in removing nutrients and phytoplankton biomass from AV Lake (Martin et al., 2013). This study has focused on the operation of one of them, FG system, and analyzes the main factors that influence nutrient removal from eutrophic water.

The main aim is to establish optimum operating conditions and propose recommendations for the management and design of FWSCWs to treat eutrophic waters. These have to guarantee the removal of high amount of nutrients, obtaining low outflow concentrations and creating suitable habitat for the wildlife, conditions that are usually difficult to achieve simultaneously. As removing high quantities of nutrients implies working at high HLRs and the efficiency in nutrient removal is inversely related to the loading (Nichols, 1983), it should be prioritized getting maximized removal or alternatively low concentrations in the outlet, depending on the objective pursued in each case. In this work, the main parameters that influence in both performance indicators (removal rates and efficiencies) are analyzed.

Table 5 Spearman's correlation coefficients (S) and Person's correlation coefficients (P)

	C_{in} (mg L^{-1})			IML (g m^{-2} $year^{-1}$)			HLR (m $year^{-1}$)			T (°C)		
	MRR		MRE	MRR		MRE	MRR		MRE	MRR		MRE
	S	P	S	S	P	S	S	P	S	S	P	S
TP	0.727**	0.509**	0.588**	0.943**	0.896**	0.429**	0.540**	0.626**	0.095	0.122	−0.201	−0.139
DIP	0.864**	0.831**	0.814**	0.986**	0.783**	0.709**	0.091	0.066	−0.050	−0.221	−0.450**	−0.431**
n-DIP	0.392**	0.416**	0.453**	0.842**	0.821**	0.276*	0.606**	0.570**	0.015	0.118	0.092	0.201
TN	0.593**	0.580**	0.496**	0.723**	0.767**	0.118	0.242*	0.311**	−0.276*	−0.297*	−0.314**	−0.113
NH_4^+	0.814**	0.770**	0.752**	0.954**	0.713**	0.571**	0.169	0.012	−0.158	−0.156	−0.067	−0.036
NO_3^-	0.753**	0.750**	0.481**	0.713**	0.841**	0.254	0.095	0.067	−0.371**	−0.383**	−0.394**	−0.018

MRR mass removal rates (g m^{-2} $year^{-1}$), *MRE* efficiencies (%), C_{in} input concentration, *IML* inlet mass loading, *HLR* hydraulic loading rate, *T* temperature at outflow (°C)

* Significant at the 0.05 probability level

** Significant at the 0.01 probability level

Dissolved oxygen and temperature

DO and temperature are among the main factors that can influence on wetland efficiency, since they affect several biogeochemical processes. In FG, both variables show a decrease from inflow to outflow; in the case of DO this was mainly related with organic matter degradation and nitrification. Temperature decreases an average of 2.2°C, affecting microbiological process rates. This is an important issue to consider in the design of new CWs with similar characteristics.

On the other hand, seasonal variations at inflow and outflow were observed for both variables, and this could imply differences in nutrient removal depending on the season. In FG, there was a difference of almost 30°C between the maximum temperature in summer and the minimum temperature in winter (4°C). In fact, the low temperatures reached in winter could have affected processes sensitive to temperature, e.g, nitrification (Jing & Lin, 2004). DO oscillated inversely with temperature, due to the lower solubility and the greater biochemical oxygen demand (carbonaceous and nitrogenous) when the temperature increases (Kadlec & Reddy, 2001).

Since FG1 was harvested, this cell operated as an oxygen producer because of algal growth. This same trend was also observed in FG2. In fact, the algal photosynthesis in FG1 provoked wide oscillations of DO and high concentrations of this as shown in Fig. 4. In seasons with high phytoplankton biomass, as in the autumn, the concentrations oscillated from oversaturation to values close to zero. These daily fluctuations can affect biological and physical–chemical processes during the day, e.g., nitrification–denitrification, adsorption/desorption (Picot et al., 1993; Garcia et al., 2006). In FG3, daily DO oscillations were also observed, but not as pronounced as FG1, mainly due to the lower phytoplankton biomass.

Input–output concentrations and seasonal variations

Compared to FWSCWs that treat industrial or urban wastewater (Kadlec & Wallace, 2009), FG operated at low input nutrient concentrations and the main TP component was n-DIP instead of DIP (Fig. 5). Otherwise, in contrast with systems that treat eutrophic water (Dunne et al., 2013), in this study most of TN was DIN, and more concretely NO_3^- (Fig. 5),

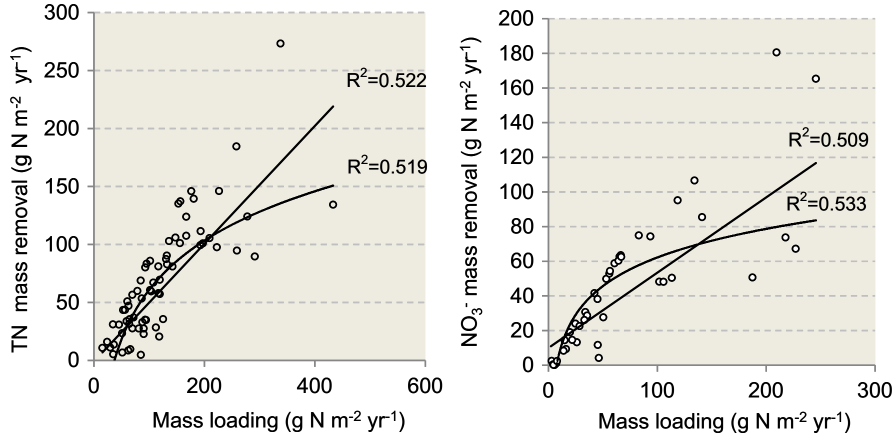

Fig. 6 TN and NO_3^- mass loading versus TN and NO_3^- mass removal rates. The *solid line* represents the linear fit and the *dotted line* the logarithmic

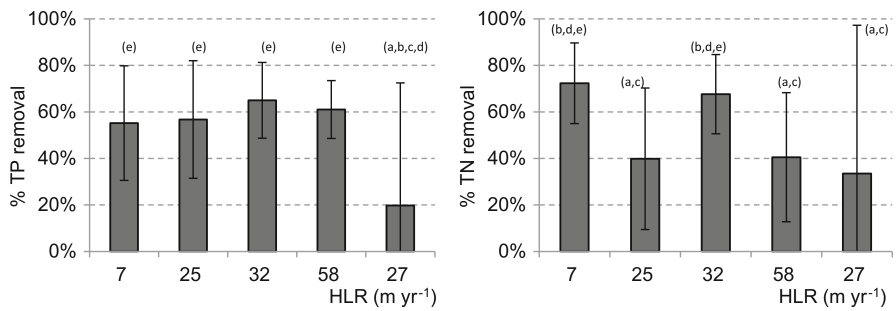

Fig. 7 Mean and standard deviation of mass removal efficiencies (%) obtained in each HLR tested (m $year^{-1}$). For significant differences: *a* 7, *b* 25, *c* 32, *d* 58, *e* 27

Table 6 Threshold C_{in} estimated

Variable	Threshold C_{in} (mg L^{-1})
TP	0.107
DIP-P	0.076
n-DIP-P	0.147
TN	1.15
NH_4^+-N	0.179
NO_3^--N	0.25

showing a great influence of the rice fields drainage on BP, mainly from January to March. (Fig. 5f). Nevertheless, this water composition changed after intense Mediterranean rainfall events (normally in winter and autumn), when DIP and NH_4^+ concentrations strongly increased as a consequence of the arrival of urban runoff and the flushing effect on phytoplankton (Fig. 5b). During spring and autumn the particulate forms (n-DIP and ON) were high (Fig. 5c, g), related with the phytoplankton blooms (data not shown) in the AV Lake. Thus, this study demonstrates the versatility of the CW in the treatment of highly variable influents, both in terms of composition and pollution level.

FG successfully laminated the peaks of DIP, NH_4^+, and NO_3^-, being the mean reductions in autumn and winter of 88–92% for DIP and 72–47% for NH_4^+ (Fig. 5b, e) and in spring and winter of 93–47% for NO_3^- (Fig. 5f). Therefore, building CWs around AV

Table 7 Aboveground biomass estimated in FG. Values obtained in October

	Vegetated area (Kg m^{-2})				Cell (Kg m^{-2})			
	2009	2010	2011	2012	2009	2010	2011	2012
FG1	0.80	0.10	0.63	3.48	0.80	0.005	0.016	0.087
FG2	1.28	1.85	1.85	1.85	1.28	1.48	0.83	0.19
FG3	0.10	1.69	3.04	5.89	0.02	0.51	1.06	1.47
FG	0.98	1.75	2.31	4.62	0.71	0.73	0.69	0.61

Lake would help reduce the impact of storm water and agricultural pollution on the water body, as it has been observed in other shallow eutrophic lakes (Jiang et al., 2007; Sollie et al., 2008). This role is especially important in sensitive aquatic systems, since the excess of these nutrients can lead to its eutrophication and, in the case of NH_4^+, also because of its toxic form at high pH levels and its oxygen demand (Kadlec & Wallace, 2009).

The highest TP outflow concentrations were observed in summer due to a slight increase of the levels of DIP into the water column, which is inversely related with DO. When soils are under anaerobic conditions, iron is reduced from ferric to the ferrous state, releasing phosphorus that was previously held as insoluble ferric phosphate compounds (Mitsch & Gosselink, 2000). Moreover, the higher temperatures observed in this season could have favored the mineralization of organic matter, thus increasing the release of P from sediments to the water column.

For TN, the outflow concentrations were higher in winter and its reduction moderate (34%, Fig. 5d); this is probably due to the limitation of the nitrification (low temperatures), denitrification (high DO), and low macrophyte uptake (spring–summer phenomenon (Vymazal, 2007)). Nevertheless, the N reduction in summer was also low mainly due to high levels of ON, related with an increase of the plant litter decomposition and a rise of phytoplankton biomass in warmer months.

Nutrient removal and factors that affected them

Mass removal rates

The mean TN removal rate obtained (Table 3) is almost twice the value obtained by Dunne et al. (2013), with similar TN load, likely because of nitrates are the main inflow component in FG and these are more easily removed than organic forms in CWs (Phipps & Crumpton, 1994).

The main factors that affected TN mass removal rates were C_{in} and IML (Table 5). MRRs appeared to increase linearly up to the highest loads (Fig. 6), in line with other authors (Tanner et al., 1995; Kadlec & Knight, 1996; Spieles & Mitsch, 2000). Nevertheless, some data may be indicating a logarithmic trend, and therefore a likely upper limit for TN loading (Fig. 6), but more data at high loading would be necessary to define a maximum MRR. HLR seems to weakly affect the TN removal rates, but not DIN (Table 5). For TN and NO_3^-, the negative rates were obtained mainly in summer, being MRRs in this season significantly lower than that of the remaining seasons ($P < 0.05$). Owing to TN input concentrations and temperature data presented an inverse relationship, removal rates were higher in winter than summer, and it is reflected in the negative correlation found between temperature and MRRs (Table 5). It follows then, that the influence of temperature is obscured by the strong influence of C_{in} in TN removal rates. For NH_4^+, seasonality was not found.

The mean TP mass removal rate obtained (Table 3) in this study was higher than the values obtained for other CWs treating natural waters (Nairn & Mitsch, 2000; Dunne et al., 2012) likely because of the higher C_{in} and IMLs in FG. In this survey, TP mass removal rates appeared to increase linearly up to the highest C_{in}, IMLs, and HLRs (Table 5), according with other authors (Reddy et al., 1999; Nairn & Mitsch, 2000; Dunne et al., 2012). So, the results obtained suggest that the maximum removal rate has not been reached, and FG could work at higher loadings. This maximum is reached when soil exchange sites are filled, biological uptake is inhibited, or water velocities limit physical and chemical retention processes (Nairn & Mitsch, 2000). However, it is likely that the limit for HLR is not far in FG since the maximum limit in the water column depth for this CW is 0.35 m, and HLR much higher than 58 m year^{-1}, without increasing the water column depth, would imply very low hydraulic residence time, which could limit the effective sedimentation and denitrification processes within CW. In addition, greater depth of water column than 0.3-0.35 m could affect the communities of emergent vegetation and the birds' habitat. Kadlec (1999) suggested that the upper HLR limit is 100 m year^{-1}.

Seasonality was found for TP and DIP. MRRs obtained in winter and autumn were significantly higher than those obtained in summer and spring ($P < 0.05$). This was associated with a higher C_{in} of DIP in the coldest months, a higher DO concentration into the wetland (greater retention of PID in the sediment), a lower organic matter decomposition rate (the temperature values are at their lowest), and a DIP uptake by phytoplankton present. For n-DIP, seasonality was not found.

The C_{in} was the most important independent variable in the multiple linear regression models developed. These models are really useful as management tools, for example, to establish the HLR that permits achieving an optimal MRR when the C_{in} decreases or in the estimation of the removals achieved without measuring the effluent concentration, hence enabling significant cost savings.

Mass removal efficiencies

Overall nutrient mass removal efficiencies achieved in FG (Table 4) are close to the highest values found in CWs treating surface waters (Pomogyi, 1993; Moustafa et al., 1998; Hey et al., 1994; Coveney et al., 2002; Li et al., 2008; Kadlec et al., 2011).

C_{in} was the main factor that influenced nutrient removal efficiencies (Table 5). HLRs did not influence in these, at least in the range tested in this study. The decrease in TP removal efficiencies observed at 27 m year^{-1} (Fig. 7) was related with a worsening of the sedimentation process owing to loss of vegetation (Fig. 2), since it led to the appearance of hydraulic short-circuiting and the exposure of the sediments to the re-suspension (Brix, 1997). In fact, the TP removal efficiencies were correlated with the percentage of vegetation cover in the wetland. In relation to TN removal efficiencies, the negative correlation found with HLRs (Table 5) corresponds to the fact that the highest C_{in} were measured when the system worked at 7 m year^{-1}, and it was shown that HLR did not really influence N mass removal efficiencies, as can be observed in Fig. 7. Nevertheless, it is likely that higher HLRs could negatively affect DIN removal because of the decrease in the contact time between the pollutants and microorganisms, as long as the depth is not increased.

Apart from the factors analyzed previously, there were other ones that had a negative influence, though to a lesser extent, on MREs obtained. One of them was the presence of birds within FG. Particularly in the period from late March to early May, a high density of birds use the CW for feeding, nesting, and roosting, and they provoke a decrease in MREs, specially for TP. This has been related with the re-suspension of material previously settled and with the input loads of nutrients through bird's excrements. Fortunately, these loads only represent in average (annual basin) 0.5% of TN loading and 2.2% of TP load from the lake (CHJ, 2012), although they are greater between March and May, and thus, they were not considered for performances. Finally, the influence of DO concentrations and pH on DIP efficiencies is noteworthy. Although phosphorus inorganic precipitation has not been directly measured in this study, it probably occurred thanks to the CW's high planktonic primary production and the alkalinity and calcium concentration of the water.

Plant role

The values obtained regarding nutrient storage in plants are in the range of values found in the literature for slightly loaded CWs (Coveney et al., 2002; Kadlec, 2006). Nevertheless, if the biomass is not harvested prior to fall senescence, most of the nutrients storage could return to the water column in the decomposition process (Brix, 1997). In general, it has been reported that removal of nutrients via plant harvesting is low, but it could be substantial for lightly loaded systems such as FG (Vymazal, 2007), and so there is much controversy in the literature about the fact of recommending the harvest or not. In this case, the annual storage of nutrients in aboveground biomass represents a substantial percentage of the nutrients removed from the inflow, particularly when input loadings are lower than 90 g m^{-2} year^{-1} of TN and 8 g m^{-2} year^{-1} of TP, thus being the plant harvesting an important via for permanent nutrient removal in FG, according to other studies treating eutrophic water (Tang et al., 2009).

In addition to the aforementioned, plant cover is also important in FG because it promotes the sedimentation and decreases the re-suspension (P removal), provides DO to the sediment (nitrification) and attachment sites for microorganisms, it is an organic matter source (denitrification), attenuates solar radiation (reduces algal growth), increases wildlife diversity (specially, it is a food source and refuge for birds), and offers aesthetic appearance to the system. Moreover, vegetated wetlands can act as a carbon sink (Mander et al., 2008; Mitsch et al., 2013), playing hence an important role in climate change.

Nevertheless, the main mechanism identified in FG for nutrient removal was sedimentation for TP and nitrification–denitrification process for TN (Martin et al., 2013). Sedimentation is usually the dominant TP removal mechanism FWSCWs (Coveney et al., 2002; Dunne et al., 2012) and the denitrification process is frequently considered as the major mechanism for removing N in most types of CWs (Vymazal, 2007), including some that treat river/lake water (Pomogyi, 1993; Reilly et al., 2000); notwithstanding this, other mechanisms, such as N uptake by macrophytes, algae and microorganism, or N sedimentation, have also been identified as main mechanisms in CWs treating eutrophic water (Dunne et al., 2013).

Efficiencies trend over time

MRE decreased over time, with the exception of nitrates (Table 4). Probable causes include the decrease in input concentrations (except for NO_3^-), the accumulation of organic matter in sediments (which is mineralized releasing nutrients to the water column), the strong reduction of vegetation cover, and the global DO reduction. In the case of P, another cause could be that the load was continually greater than 1 g m^{-2} year^{-1}, so P adsorption capacity of the soil could become saturated and then lose the capacity of retain P (Nichols, 1983; Richardson & Quian, 1999).

Conversely, the loss of vegetation could have improved the NO_3^- removal because of the decrease of the oxygen production and the increase of phytoplankton biomass. The latter provoke daily DO cycles within FG, reaching anoxic conditions at night (Fig. 4). Moreover, the DO measured at FG3 effluent decreased over time, which responds to wetland maturation. However, it has been established that plants play an important role in the nitrogen removal via sequential nitrification–denitrification (Gersberg et al., 1986) since they supply organic carbon and act as a support to surface area for microbial growth.

Management strategies

In the present study, HLR and IML have been identified as the main operational parameters and C_{in} as the main environmental factor that influence nutrient removal rates. Thus, increasing the flow when inflow concentrations are higher, in autumn and winter for P and in spring and winter for N in this case, presents an excellent opportunity for increasing the nutrients removed from BP (inlet), which leads to further eutrophication in AV Lake. In both cases, mass removal rates are higher in winter due to mainly random pollution events from storm water and agricultural runoff.

So, it could be interesting to raise the flow during winter and decrease it during summer (the season with the lowest nutrient mass removal rates). This change increases annual nutrients removal, scarcely affecting pumping costs. In summer, a mean HLR of 25 m year^{-1} could be maintained and 58 m year-1 in winter. In this case, approximately 3 g m^{-2} year^{-1} of TP and 16 g m^{-2} year^{-1} of TN would be removed in summer and 12 g m^{-2} year^{-1} of TP and 106 g m^{-2} year^{-1} of TN in winter. Moreover, with a mean water depth of 0.2 m, the mean hydraulic residence time would be about 3 days in summer, avoiding an excessive HRT, which would favor, together with warm temperatures, algal blooms into the CW. Nevertheless, taking into account that the limiting nutrient in AV Lake is the P, it could also be interesting to increase the HLR in autumn. For example, if a HLR of 58 m year^{-1} was applied in this season, the mass removal rate would be approximately of 18 g m^{-2} year^{-1} of TP and 98 g m^{-2} year^{-1} of TN.

Another strategy could be to stop flow during the summer months and increase it in the other seasons. In summer, draw down water cells stimulate the growth and spread of vegetation and the mineralization of organic matter in sediments. Nonetheless, it can be expected that if suitable recovery of vegetation cover takes place in the wetland in forthcoming years, the support of oxygen to the wetland and N and P plant uptake will increase in this season, thereby achieving better nutrient removal.

In regard to removal efficiencies, the main parameter that influences these is C_{in}, which cannot be managed in our case. Moreover, HLRs in the range of 7–58 m year^{-1} do not affect them. Therefore, MRRs can be maximized at 58 m year^{-1} without affecting to MRE, as long as the vegetation cover remains high.

Conclusions

FWSCWs are efficient at removing nutrients from eutrophic lake water and they are presented as a feasible alternative for the recovery of highly degraded surface waters. This study demonstrates that FG is efficient at removing NO_3^-, DIP, and NH_4^+ from agricultural and urban runoff. In these cases, it operates as nutrient trap that protect the AV Lake.

The main factors that affected the TN and TP MRRs were the C_{in}, the IMLs, and the HLRs. MRRs increased linearly with these factors suggesting that the maximum mass removal rates were not achieved in FG. On the other hand, the MREs mainly depended on C_{in}, whereas HLRs between 7 and 58 m year^{-1} did not influence on nutrient MREs.

From the results obtained, to reach the desired balance between mass removal rates and efficiency, it is recommended working with HLR at a rate between 32 and 58 m year^{-1}, depending on monetary constraints of pumping water into the lake. This study provides recommendations of operation, based on seasonal variation of C_{in}. In CWs, that treats highly variable nutrient input concentrations (for example, due to point inputs from storm water or agricultural runoff), is interesting to manage the flow in order to increase the removal of nutrients and optimize the pumping cost. For that, we propose to increase the flow when the C_{in} are high and reduce it when C_{in} are low.

In the first year of operation, the cattail grew rapidly, attaining complete cover in the middle of the first growing season, and high nutrient removals. So, the monoculture of cattails is recommended when the herbivorous depredation is not a relevant problem. Otherwise, we recommend mixed systems with reeds and yellow iris since they are less attractive for depredation. The drawback is that reed would need approximately two growing seasons with a minimum water depth (lower than 0.1 m) for reaching a proper standing stock. Once the minimum cover required for system start-up (normally 60–80%, Kadlec & Wallace, 2009) is reached, the water flow can be gradually increased. In both cases, the harvest should be done by cells, thereby ensuring the presence of vegetated zones for water treatment and for bird habitat. As a general rule, each cell should be harvested every three years. The importance of having a high vegetation cover to achieve good results at removing nutrients has been demonstrated.

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Compliance with ethical standards

Ethical approval This manuscript has been prepared according to the ethical rules of Hydrobiologia and it has not been submitted to other journals.

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