Enhancement of total nitrogen removal through effluent recirculation in a hybrid constructed wetland system treating urban wastewater

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Abstract

The effect of effluent recirculation on the removal of total nitrogen (TN) and eight pharmaceuticals and personal care products (PPCPs) was evaluated during 9 months in an experimental hybrid constructed wetland (CW) system applied in the treatment of urban wastewater. An Imhoff tank was followed by three stages of CWs (two 1.5-m^2 vertical subsurface flow (VF) beds alternating feed-rest cycles, a 2-m^2 horizontal (HF) and a 2-m^2 free water surface (FWS) wetland in series). A fraction of the final effluent was recycled back to the Imhoff tank with a recirculation rate of 50% (hydraulic loading rate = 0.37 m d^{-1}). The system's performance varied throughout the study. In Period I (summer) consistently high load removal efficiencies of TN (89 ± 5%) and a removal rate of 6.6 ± 1.4 g TN m^{-2} d^{-1} were exhibited. In Period II (fall), the poor performance of the FWS during the senescence of macrophytes caused a large increase in organic matter, solids and nutrient concentrations, drastically deteriorating water quality. The determination of PPCPs was conducted during this period. Recalcitrant compounds, namely sulfamethoxazole, carbamazapine, TCEP and sucralose were negligibly removed in all CWs. However, noteworthy was the ≈30% removal of sucralose in the VF wetland. Caffeine (80%) and fluoxetine (27%) showed similar elimination rates in both VF and HF units, whereas trimethoprim and DEET were significantly better removed in the VF than in the HF. The concentration of the four latter compounds showed a severe increase in the FWS, indicating possible desorption from the sediment/biomass during adverse conditions. Harvesting of the aboveground biomass in this unit returned the system's performance back to normality (Period III), achieving 77 ± 7% TN removal despite the winter season, proving effluent recirculation as an effective strategy for TN removal in hybrid CW systems when stringent restrictions are in place.

Keywords

desorption; emerging organic contaminant; pharmaceuticals and personal care products; plant decay; recycling; treatment wetland.

1. Introduction

Constructed wetlands (CWs) are engineered systems that emphasize the physic-chemical and microbiological processes occurring in natural wetlands in a controlled manner to treat wastewater (García et al., 2010). They have proven to be a convenient solution for the decentralized treatment of wastewater of various origins worldwide due to their multiple advantages. Their operation and maintenance is very simple and they hold costs of O&M well below those produced in conventional wastewater treatment plants. They can be constructed out of local materials, and present great adaptability and resilience, providing multiple ecosystem services and even acting as revenue generators (Hansson et al., 2012; Ni et al., 2016; Wang et al., 2015). In recent decades the CW technology has rapidly evolved through the use of various designs and operational modes or other intensifications so as to improve effluent water quality with respect to various pollutants (i.e. organic matter, nitrogen and phosphorus, trace elements, pathogens, emerging organic contaminants) from wastewater (Fonder and Headley, 2013; Nivala et al., 2013).

In light of the increasingly stringent nitrogen discharge standards in many parts of the world due to the environmental (e.g. eutrophication) and health hazards (to infants and pregnant women and to livestock) originated from the contamination of surface and groundwater with nitrified effluents (Ward et al., 2005), the enhancement of nitrogen removal from wastewater has become one of the main issues in the development of the CW technology (Pelissari et al., 2017; Wu et al., 2014; Zhai et al., 2016). The complete elimination of the nitrogen content of wastewater (usually relying on the process of nitrification of ammonia nitrogen followed by denitrification of nitrate) remains largely unsatisfactory in passive single-stage CW systems due to their inability to provide both aerobic and anaerobic conditions at the same time. The use of hybrid systems combining different wetland types has become a very common strategy to improve total nitrogen removal (Vymazal, 2013). While vertical subsurface flow (VF) wetlands are especially suitable to provide an efficient nitrification due to their great oxygen transport ability facilitated by the intermittent feeding regime and unsaturation of the bed between pulses, denitrification is the prevailing nitrogen transforming process in horizontal subsurface flow (HF) wetlands under the anaerobic conditions provided by a regime of permanent saturation when sufficient carbon is available (Liu et al., 2016; Vymazal, 2007). Average nitrogen removal rates in hybrid CW systems have been significantly higher than those of single-stage CW systems, especially when a free water surface (FWS) wetland is included in the treatment line (Vymazal, 2013).

However, one of the main limiting factors for the broader implementation of CWs is their relatively large footprint, especially in regions where land resources are scarce and with high population density, which ranges 5-6 m^2/PE for HF beds, 2-3 m^2/PE for VF and slightly lower for hybrid systems (Kadlec and Wallace, 2009), exceeding by far the area required by conventional wastewater treatment plants (<1 m^2/PE) (Veenstra et al., 1997). Other strategies to improve total nitrogen removal unfold several intensifications which use mechanical power inputs, such as tidal-flow systems, the use of intermittent aeration, step-feeding, or the use of various substrates. The implementation of these intensifications is, for each case scenario, a trade-off between the footprint and the energy required, which will increase the lifecycle cost of the system (Austin and Nivala, 2009; Boog et al., 2014; Nivala et al., 2013; Wu et al., 2014).

Recycling of the final effluent back to the influent has recently been reported by a small number of studies including a single CW stage as a good alternative to improve the elimination of nitrogen while reducing investment costs and footprint. Both nitrification and total nitrogen removal have been shown to be enhanced in VF wetlands (Prost-Boucle and Molle, 2012; Arias et al., 2005), especially when operating under high hydraulic loading rates (HLRs), decreasing the required area to 1.4-1.8 m^2/PE (Foladori et al., 2013). In HF wetlands the effect of recirculation has shown variable results, exhibiting an improvement of total nitrogen removal in a two-stage HF system (White, 1995), but a negative effect on general wetland performance including nitrogen in a HF mesocosm fed with synthetic wastewater (Stefanakis and Tsihrintzis, 2009). The recirculation strategy was also recently tested in hybrid CWs system at pilot-scale consisting of an anaerobic reactor followed by a HF and VF wetlands and average of 66% of TN removal was observed when applying 100% recirculation, as opposed to 29% without recirculation (Ayaz et al., 2012). Moreover, various lab-scale hybrid constructed wetland configurations containing HF and VF wetlands showed stable average of 80% TN removal under a load of 2-8 g TN m^{-2} d^{-1} (Torrijos et al., 2016).

An experimental three-stage hybrid constructed wetland system -consisting of two alternating VF beds, a HF and a FWS wetlands in series- treating urban wastewater started operation in 2010 and was gradually submitted to increasing HLRs (nominal of 0.06 m d^{-1}, punctual HLRs of 0.13 and 0.18 m d^{-1}) to test its treatment capacity under large organic and hydraulic loads (Ávila et al., 2014, 2013). Since the system seemed to be oversized, it was subsequently submitted to a HLR of 0.27 m d^{-1} for a year, accomplishing removal efficiencies as high as those achieved in previous studies. Although the specific area required was as low as 2 m^2/PE, still limited nitrogen removal was achieved, due to poor denitrification with the HF and FWS wetlands (Ávila et al., 2016). Therefore, with the aim of enhancing the elimination of nitrogen, in the current study a recirculation loop was applied from the final effluent up to the primary settler and the performance of the system was evaluated for a period of 9 months.

Moreover, a sampling campaign for the determination of various pharmaceuticals and personal care products (PPCPs) was also accomplished during two months with the purpose of assessing their behavior under this operational strategy. The occurrence and fate of PPCPs and other emerging organic contaminants in CWs systems have only recently come under scrutiny, and these low-cost natural systems have proven a great potential for the removal of multiple PPCPs showing oftentimes superior performances than conventional wastewater treatment plants (WWTPs) due to their physic-chemical and microbiological complexity (Ávila and Garcia, 2015; Verlicchi and Zambello, 2014; Zhang et al., 2014). However, more studies are needed for a complete and thorough understanding of the behavior of emerging organic contaminants in CWs and for a more extended set of compounds. The current study investigated eight substances, including four pharmaceuticals (i.e. carbamazepine, fluoxetine, sulfamethoxazole and trimethoprim), and four personal care products (i.e. N,N-diethyl-meta-toluamide –DEET-, tris (2-chloroethyl) phosphate –TCEP-, caffeine and sucralose). To the best of our knowledge, the present study is the first to investigate the fate of sucralose in CW systems.

2. Materials and methods

2.1. Treatment plant design and operation

The hybrid CW system was located outdoors at the experimental facility of the GEMMA research group (Department of Civil and Environmental Engineering of the Universitat Politècnica de Catalunya-BarcelonaTech) in Barcelona (Spain), where a Mediterranean climate predominates. It consisted of a stirred wastewater tank, followed by an Imhoff tank, two VF wetlands alternating operation, a HF wetland and a FWS wetland in series (Fig. 1). Commissioning of the system took place in May 2010 and since then it has been object of extensive investigation under different operational criteria. The current study involved the application of recirculation and took place from June 2015 to January 2016. The treatment plant operated under a flow of about of 750 L d^{-1} of urban wastewater, and 375 L d^{-1} from recirculation (HLR= 0.37 m d^{-1}). The recirculation flow rate (RFR) was of 50% (RFR = daily recirculated effluent volume/daily raw wastewater volume x 100).

Urban wastewater from a nearby municipal sewer was pumped daily into a raw wastewater tank before it flowed into an Imhoff tank (0.2 m^3) with a nominal HRT of 24 h (for a nominal HLR of 0.06 m d^{-1}), but a HRT during the time of this study of 4.2 h. Effluent of the Imhoff tank flowed by gravity to a storage tank (0.2 m^3) and from this point water was conducted into two parallel 1.5 m^2 VF beds alternating their operation in cycles of feed and rest (3.5 d each). These were intermittently fed by means of hydraulic pulses with a flow of about 55 L per pulse, resulting in about 20 pulses per day. The effluent of the VF wetlands was pumped to a 2 m^2 HF wetland, and finally to a 2 m^2 FWS unit. The recirculation took place on a continuous basis by pumping a fraction of the final effluent (FWS effluent) up to the Imhoff tank where it mixed with the raw wastewater. All wetland units were constructed in polyethylene and were planted with *Phragmites australis* since the commissioning period, thus the vegetation was very well established during the time of the study. Further design and operational details of the system are shown in Table 1.

Several electromagnetic flow meters (SITRANS F M MAGFLO®) were installed along the treatment system to follow up flow values entering the different units of the treatment system during the experimental period, which allowed expressing the results on a mass balance basis. Further specific design and operational parameters and previous performance of the system can be found in Ávila et al. (2016, 2014, 2013).

2.2. Sampling and analysis of conventional water quality parameters

Effluent samples from each treatment unit were grabbed twice a week (Tu and Th, 10am) by taking about 1.5 L of sample (Fig. 1). Measurement of onsite water quality parameters (i.e. temperature, pH, electrical conductivity –EC- and redox potential –E_H-) was done at the time of sample collection. Samples were taken to the adjacent laboratory for the immediate analysis of the following parameters: total suspended solids (TSS), biochemical oxygen demand (BOD_5), total organic carbon (TOC), total nitrogen (TN), ammonium nitrogen (NH_4-N), nitrate and nitrite nitrogen (NO_x-N), and sulfate (SO_4^{2-}).

Onsite measurements of water temperature, pH and EC were taken by using a Checktemp-1 Hanna thermometer, a Crison pH-meter and an EH CLM 381 conductivity meter. E_H was also measured onsite by using a Thermo Orion 3 Star redox meter and values were corrected for the potential of the hydrogen electrode. The determination of conventional wastewater quality parameters, including TSS and NH_4-N was done by following the Standard Methods (APHA, 2012). TN and TOC were measured using a Multi N/C (2100 S) analyzer (APHA, 2012). BOD_5 was determined by using a WTW® OxiTop® BOD Measuring System. NO_x-N and SO_4^{2-} were analyzed using a DIONEX ICS-1000 chromatography system.

2.3. Sampling and analysis of PPCPs

The determination of PPCPs took place during the fall season (Sep to Nov 2015). 8-h composites samples were collected twice per week (n=10) by grabbing a volume of about 100 mL 3 times per day (at 9, 13 and 17h), in order to buffer diurnal and weekly variations. Samples were immediately taken to the laboratory and a solid phase extraction (SPE) was carried out within 24h. Analysis of the target compounds was performed by an Agilent 6410 Triple Quadrupole LC/MS-MS at the University of Catania (Catania, Italy) according to the procedure reported by Sgroi et al. (2016) and here described in Supplementary material (Text S2, Table S1, Table S2, Table S3).

2.4. Chemicals and reagents

All purchased solvents, standards, and reagents were of high purity. The details concerning these materials are reported in the Supplementary material section (Text S1). The selection of PPCPs analyzed in this study was based on data presented in previous literature that rely on chemical-physical properties, occurrence data, detection frequency, availability of robust analytical methods and removal during wastewater treatments (Heidler et al., 2008; Luo et al., 2014; Sgroi et al., 2016). Detailed information about all target analytes used in this study is shown in Table 2.

3. Results and discussion

Since the performance of the hybrid system treatment varied substantially during the current study, results were divided in three periods and data was treated and discussed separately for each period accordingly. During Period I (Jun to Aug 2015) the CW system presented an excellent performance, provided by the applied recirculation loop. However, during Period II (Sep to Nov 2015) the overall treatment performance of the system extensively declined due to the recontamination of the water during its passage through the FWS unit, which showed a very poor performance. This was attributed to the senescence of the macrophytes in this wetland unit during the fall season, which resulted in the release of carbon, nitrogen and solids into the water table, consequently causing a drastic decrease on the overall efficiency of the system. In order to reverse this tendency, a bioremediation measure, consisting of the pruning of the plants of the FWS unit, was adopted in early November (Fig 2). As a result of the clearance of dead plant material (Period III: Nov to Jan 2016) the performance improved significantly, displaying removal efficiencies similar to those of Period I, thus demonstrating the recirculation as a successful strategy for the enhancement of total nitrogen removal in CW systems.

3.1. General performance of the treatment system

Concentration values of conventional water quality parameters obtained during the three consecutive periods of operation are shown in Table 3. The mean redox potential (E_H) in the raw wastewater for the three periods was -78 ± 88 mV, and it remained constant after the Imhoff tank. Inside the VF beds mean E_H values increased to +142 ± 84 mV, indicating oxidative conditions within these units, which are crucial to ensure efficient nitrification rates (Kayser and Kunst, 2005). In the HF unit E_H values decreased down to a mean value of +66 ± 130 mV (for all periods), and in the FWS wetland effluent E_H values showed a large variability across the whole study interval (average of +61 ± 143 mV) owing to the poor performance of this unit during Period II, which caused a reducing environment in the water table (-6 ± 87 mV). The retention of TSS at the Imhoff tank was generally good at all periods (mean concentration removal efficiency of 79 ± 18%) despite the high concentrations in the raw wastewater (877 ± 170 mg L^{-1} for Period I, 221 ± 45 mg L^{-1} for Period II, and 295 ± 97 mg L^{-1} for Period III) and short hydraulic retention time (HRT) (85% lower than nominal value). The average load of solids applied to the CW system during the whole study interval was 33 g TSS m^{-2} d^{-1} (taking into account the area of VF beds). During Periods I and III, the overall TSS load removal efficiency for the CW system was very high (mean removal efficiencies of 93 ± 3% and of 96 ± 6%, respectively), observing mean concentration values below 10 mg L^{-1} in the final effluent (Fig. 3), which is in agreement with previous results in the same plant that show the quality of the final effluent suitable to be reused in various applications (Ávila et al., 2016, 2013). However, in Period II the concentration of solids highly increased in water by its passage through the FWS unit, due to the large release of particulate matter into the water column during plant decay (25 ± 45% overall TSS load removal), releasing a mean TSS concentration at the final effluent as high as 114 ± 63 mg L^{-1}. Despite the recirculation loop, no signs of clogging were detected in any of the subsurface flow CWs during this period, presumably due to the compensating relatively lower solids amount in the raw wastewater during this time span.

The hybrid CW system exhibited an excellent removal of organic matter in spite of the high hydraulic and organic loading rates (OLR). During Period I (mean OLR = 107 g BOD_5 m^{-2} d^{-1}), the elimination of BOD_5 was consistent overtime, showing an overall load removal efficiency of 97 ± 2% (final effluent concentration of 20 mg/L), which agrees with results previously observed at this treatment plant without recirculation and identical OLR (Ávila et al., 2016). Removal rates correlated very well with the influent loading rates (Fig. 3), as observed by other studies in CWs (Calheiros et al., 2007; Saeed and Sun, 2012). Per contra, during Period II (Sep to Nov) the overall performance of the CW system exhibited a drastic decline, presenting a mean load removal efficiency of 77 ± 13% of BOD_5 (Fig. 3), which was associated with the die-back and decomposition of plant biomass in the FWS wetland coinciding with the fall season. Organic matter concentrations (as well as other contaminants) steeply increased in this wetland unit, being especially remarkable for TOC (mean concentration of 18 and 115 mg/L in influent and effluent of the FWS unit, respectively), indicating that the major part of the increase was mainly caused by plant matter of non-easy biodegradability (lignine and cellulose). *P. australis,* as well as other aquatic macrophytes, has been repeatedly observed to leach nutrients rapidly upon death and decomposition into the water column, thus affecting treatment performance (Kouki et al., 2009; Kröger et al., 2007). In this way, the contribution of macrophytes to nutrient removal is often only temporary because of the nutrient loss at senescence. *P. australis* is one of the wetland species with the highest biomass generation (approximately 5.27 kg m^{-2} $year^{-1}$ in a Mediterranean climate) and it holds the major part of the biomass in the belowground organs (roots and rhizosphere) (Ennabili et al., 1998). The high belowground biomass production of this species is attributed to the fact that it is a perennial species that allocates nutrients to belowground organs at the onset of senescence, and when high nitrogen loads are applied higher rhizome production is observed (Maucieri et al., 2014; Ravit et al., 2007). During its decomposition, vegetation debris releases nutrients (e.g. nitrogen, phosphorus, potassium, calcium, etc.) and dissolved organic carbon, which are leached into the water body (Wetzel, 2001). Moreover, it has been widely reported that *P. australis* and other aquatic macrophytes exhibit 'luxury' uptake of both N and P when high nutrient loads are applied, subsequently releasing sequestered nutrients back into the receiving water upon the conclusion of the growing season (Farahbakshazad and Morrison, 1997; Hill, 1979; Kröger et al., 2007), and progressively accumulating in the underlying sediments since the saturated conditions retard decomposition (Passoni et al., 2009). Luxury uptake has also been observed by sediment bacteria by

Khoshmanesh et al. (2002), which hypothesized that some phosphorus was accumulated during the aerobic stage, being released during the subsequent anaerobic step. This could indicate that the biomass associated to the rhizosphere and the sediment in the FWS wetland might contribute to the release of accumulated nutrients to the water column during adverse conditions, together with the influence of other physic-chemical factors such as E_H, pH, and a complexity of multiple bonding forces occurring within the rhizosphere.

Although the current event had not been previously recorded in this wetland unit since its commissioning, it has been reported that resource translocation patterns between rhizomes and the aboveground organs depends not only on the season but also on rhizome age. Environmental conditions, in particular temperature and solar radiation, among other factors also affect translocation rates (Asaeda et al., 2006). Nevertheless, after harvesting of the aboveground biomass in the FWS (end of Period II), the performance of the hybrid CW system improved significantly returning back to normality despite the winter season (Fig. 3), achieving a high overall BOD_5 load removal efficiency during Period III (96 ± 3%), under an OLR of about 48 g BOD_5 m^{-2} d^{-1}.

3.2. Total nitrogen removal

Nitrogen transformations within the hybrid system occurred also in different magnitudes during each of the three periods owing to the varying conditions in the performance of the FWS unit (Fig. 4 and 5). The average NH_4-N load applied in the VF was of 6 ± 2 g m^{-2} d^{-1} for the three periods, and the overall removal of NH_4-N varied throughout the study (96 ± 5% for Period I, 38 ± 15% for Period II, and 89 ± 5% for Period III). The main mechanism associated with ammonia nitrogen removal in CWs is nitrification, which occurs especially well in VF wetlands due to their high oxygen availability (Kadlec and Wallace, 2009). In this study the nitrification remained stable in the VF beds in the three periods (mean VF effluent of 14 mg NO_x-N L^{-1} at all periods). However, the overall NH_4-N efficiency drop during Period II was associated with the FWS conditions in this period, where a steep increase of NH_4-N occurred in final effluent of the FWS unit (Fig. 5) after its almost complete removal in the HF unit (3 ± 1 mg L^{-1}), exhibiting an average value even higher than the raw wastewater (24 ± 12 mg NH_4-N L^{-1}).

Bonanomi et al. (2014) evaluated the decay of submerged plant litter in a microcosm simulating a reservoir under Mediterranean climate and observed how the N concentration in the sediment of the reservoir increased significantly over the 100 days of decomposition. These results are in accordance with this study, showing how the increase of NH_4-N in the final effluent in Period II may be the result of organic nitrogen release due to the decomposition of vegetable tissues of the macrophytes, followed by the process of ammonification (promoted by low redox conditions in the FWS).

Overall NH_4-N removal rates were of 3, 1 and 5 g m^{-2} d^{-1} in Periods I, II and III, respectively. Except for the failure of the performance during Period II, in Periods I and III the hybrid system showed a very robust behavior (Fig. 4), achieving removal rates significantly higher than those reported at a review of 60 hybrid systems of different configurations (2.1 ± 1.7 at hybrid systems consisting of HF - FWS, 2.5 ± 2.8 at VF - HF, and 2.3 ± 2.6 g NH_4-N m^{-2} d^{-1} at hybrid systems with FWS in line). The authors indicate that if NH_4-N is the target parameter for the removal, the combination of various types of CW which include a VF stage does not provide enhanced NH_4-N removal as compared to a single VF (Vymazal, 2013). In fact, in the current study about 70% of the removal of ammonium nitrogen took place in the VF beds.

The dynamics of denitrification and TN removal showed great variability between the three periods and within different treatment units. In Period I where a mean TN concentration of 68 ± 12 mg L^{-1} was applied, the CW system presented an overall total nitrogen load removal efficiency as high as 89 ± 5%, releasing final effluent concentrations of 12 ± 5 mg TN L^{-1}. This excellent removal of nitrogen was consistent during the whole duration of Period I as can be seen in Fig. 5. Previous studies performed in the same plant treatment (without recirculation, and ORL of 8.9 g BOD_5 m^{-2} d^{-1}) showed overall TN removal of 46 ± 22% (Ávila et al., 2013), therefore proving the implementation of effluent recirculation as an effective measure for the enhancement of nitrogen removal. In the current study the HF wetland was the main unit responsible for denitrification, removing about 50% of TN in this unit in Periods I and III. The enhanced denitrification capacity of the HF in respect to previous operational periods (Ávila et al., 2016, 2013) seem to be related to the higher HLRs applied in this study, which would presumably provide higher carbon substrate and/or create the required anaerobic conditions to promote the denitrification activity.

Conversely, the overall removal efficiency of TN in the CW system in Period II was of only 46 ± 9%, owing to the release of nitrogen from the plant tissue decomposition in the FWS wetland (Vymazal, 2007; Wetzel, 2001). Final average effluent concentrations were of 58 mg TN L^{-1}, similar to the influent concentrations (68 ± 12 mg L^{-1}). However, during this period a high denitrification activity took place within the FWS wetland, achieving almost a complete NO_x-N removal. This is in agreement with the relatively low redox conditions in the FWS during this period.

In Period III the overall removal efficiency of TN increased significantly (77 ± 7%) despite the colder temperatures, discharging a final effluent with ca. 25 ± 5 mg L^{-1} of TN, and 9 ± 5 mg L^{-1} of NO_x-N. This was possible thanks to the bioremediation measure implemented to reverse the poor FWS performance (harvesting of aboveground biomass), thus returning the recirculation strategy viable again. This measure can also be implemented at full-scale if this tendency wanted to be reverted. Harvesting in July or August has been recommended to achieve optimal shoot-bound nutrient stock while preserving a healthy stand for the subsequent years (Karunaratne et al., 2004; Meuleman et al., 2002). These results are in accordance with those observed at a hybrid CW system (HF + VF), whose TN removal ranged 19-55% when no recirculation was applied, and it increased to 66% when VF effluent was recycled to the HF in a ratio of 1:1 - 2:1 (Ayaz et al., 2012). The lower TN removal performance during this period in comparison to Period I can be associated with the lower water temperature in the winter season (12ºC). Akratos and Tsihrintzis (2007) evaluated the effects of temperature over three years in five HF (2.25 m^2 each) with synthetic wastewater, and reported that the removal of TKN and NH_4-N were dependent on temperature (74% and 69% when above 15ºC, and 58% and 38% when below 15 ºC for TKN and NH_4-N, respectively).

The TN load applied to the CW system along the whole study period showed little variability (18 ± 4 g TN m^{-2} d^{-1}). In Periods I and III wetlands units exhibited an outstanding TN reduction, with removal rates of 6.6 ± 1.4 and 6.2 ± 1.8 g TN m^{-2} d^{-1}, respectively. These values agree with those reported by Torrijos et al. (2016)

evaluating the effect of effluent recirculation in a hybrid CW system (HF-VF) treating synthetic domestic wastewater, where a TN removal efficiency of about 80% at loading rates ranging from 2 to 8 g TN m^{-2} was observed. High TN removal rates (8.4 g TN m^{-2} d^{-1}) were also performed by a recirculated hybrid CW system (VF-HF) treating high strength industrial wastewater. In a review of hybrid CW systems by Vymazal (2013) removal rates were best for systems having a FWS unit in series, and averaged 4.2 ± 5.1 g TN m^{-2} d^{-1}. The sustainable high TN load removal during Periods I and III has proven effluent recirculation to be a convenient strategy for enhanced nitrogen elimination in hybrid CW systems, especially when restoration projects to prevent eutrophication of water courses or stringent guidelines regarding urban effluent discharge are in place.

3.3. Behavior of PPCPs

The sampling period where the determination of PPCPs was carried out coincided with almost the totality of Period II (except for 6 out of 16 sampling days). As it has been observed in the previous sections, during this period the FWS showed a very poor performance, increasing solids, organic matter and nutrient (mainly organically bound nitrogen and ammonium) concentrations in water. Fig. 6 shows the concentration profile of target PPCPs along the different treatment units in each of the sampling days (n=10). The concentration of the compounds in the Imhoff tank varied as a function of the recycled effluent concentrations. Four of the investigated compounds, i.e. caffeine, trimethoprim, DEET and fluoxetine, were progressively removed through the different CW units before a severe increase in the effluent of the FWS occurred, being consistent for every sampling day. These results are in accordance with the general deterioration of water quality exhibited by the conventional water quality parameters during Period II, and suggest that desorption of PPCPs and other contaminants could also be taking place from the sediment and rhizosphere to the water column during adverse conditions at plant senescence stage.

For caffeine and trimethoprim, which are hydrophilic compounds with log $K_{ow} < 1$ (Table 2), the main removal mechanisms in CW systems have been reported to be biodegradation and plant uptake, whereas fluoxetine and DEET, which are hydrophobic compounds, should be preferably removed by sorption and biodegradation (Verlicchi and Zambello, 2014; Zhang et al., 2014). However, strong evidence demonstrates that the binding mechanisms of a contaminant onto a solid matrix are much more complicated than what can be described by log K_{ow}, and instead depend on other interactions specific to the functional groups involved on sorbates and sorbents, which in turn depend on many factors such as pH, temperature, ionic strength or the presence of cations in the medium (Anumol et al., 2015b; Hörsing et al., 2011; Svahn et al., 2015; Wu et al., 2015). It has been observed that positively-charged pharmaceutical compounds show a high degree of sorption onto negatively-charged sediment particles, showing a relatively easy desorption capacity. While negatively charged pharmaceutical compounds exhibit a lower desorption capacity, neutral compounds are negligibly adsorbed (Martínez et al., 2014; Stevens-Garmon et al., 2011). The results obtained in the current study suggest that mechanisms other than hydrophobic interactions played a significant role in the sorption process of some PPCPs. In agreement, caffeine has been detected in gravel samples of CWs (Matamoros and Bayona, 2006), in sludge from WWTPs (Martín et al., 2012) and in river sediments at greater concentration than values predicted with traditional log K_{ow} based methods (Fairbairn et al., 2015). For the abovementioned PPCPs, it is plausible to expect an accumulation in sediments and plant tissues and a possible release in water under specific conditions as observed in the FWS unit during Period II. The remaining four compounds, i.e. sulfamethoxazole, sucralose, carbamazepine and TCEP, were negligibly removed in all the CW units (Fig. 6). Only sucralose presented a consistent removal of around 30% in the VF wetland. Due to their recalcitrance, these compounds passed through the plant with a substantially unchanged concentration. They can be assumed to be scarcely accumulated or adsorbed in sediments and plants, and their possible desorption was not observed in the FWS effluent.

The box plots of the observed PPCPs removal efficiencies in VF and HF wetlands are shown in Fig. 7. The VF unit showed a better biodegradation potential for trimethoprim, DEET and sucralose, likely due to a better oxygenation which can enhance microbial biodegradation. For several compounds, including trimethoprim and DEET, previous studies have also reported higher removal efficiencies in VF wetlands than in anaerobic HF units (Verlicchi and Zambello, 2014; Zhang et al., 2014). Caffeine showed a very high removal in both VF and HF wetlands (80% average), whereas fluoxetine had around 30% average removal in these two CWs. Sulfamethoxazole, carbamazepine and TCPE were scarcely removed and often negative removals were observed. This is in accordance with the literature regarding PPCP removal in CWs (Verlicchi and Zambello, 2014) and with the poor removal of sulfamethoxazole previously observed in this treatment plant (Ávila et al., 2014). In a few cases, negative removal was also observed for sucralose, DEET, fluoxetine and trimethoprim. For some compounds this phenomenon is clearly ascribable either to the presence of conjugated forms of these substances (e.g., carbamazepine glucoronide conjugates or N_4-acetylsulfamethoxazole) in the influent that can subsequently break down to release their respective parent compounds during biological treatment or to the release of PPCPs sorbed onto the particulate dissolving after the biological treatment (Blair et al., 2015; Verlicchi and Zambello, 2014). Generally, all the removal efficiencies observed for the investigated PPCPs were similar to what has been reported previously in CW systems and conventional WWTPs (Anumol et al., 2016; Ávila et al., 2015; Luo et al., 2014; Sgroi et al., 2016; Verlicchi and Zambello, 2014; Zhang et al., 2014). It is noteworthy to highlight the 30% average removal observed for sucralose in VF wetland. Sucralose is a recalcitrant compound and very low elimination rates have been reported in conventional WWTPs for this contaminant. Similar removals (around 30%) for the investigated sweetener have been observed in WWTPs operating with high sludge retention time (Anumol et al., 2016; Sgroi et al., 2016).

4. Conclusions

The removal efficiency of total nitrogen, as well as pharmaceuticals and personal care products (PPCP) of a hybrid constructed wetland (CW) system treating domestic wastewater operated with a recirculation of rate of 50% (HLR= 0.37 m d^{-1}) was evaluated during 9 months, and based on the variable performance of the system results were divided into 3 evaluation periods, coinciding with three different seasons.

In Period I (summer), the CW system showed an excellent performance, achieving overall removal efficiencies above 90 for TSS, BOD_5 and NH_4-N, and a consistent removal of total nitrogen (89 ± 5%), discharging a final effluent with an average concentration of 12 mg TN L^{-1}. In Period II the efficiency of the hybrid system significantly dropped, due to the release of solids, organic matter and nutrients from the decomposition of macrophytes in the free water surface (FWS) wetland which severely affected water quality, exhibiting overall load removal efficiencies of 25, 77 and 38% for TSS, BOD_5 and NH_4-N, and of 46% of TN. After harvesting the aboveground biomass in the FWS the hybrid system showed a substantial improvement in treatment performance, achieving mean efficiencies of 96, 96, 89% for BOD_5, TSS and NH_4-N, respectively, and 77 ± 7% total nitrogen removal despite the winter season (Period III).

The determination of various PPCPs was also carried out during Period II. The more recalcitrant compounds sulfamethoxazole, carbamazepine, TCEP and sucralose were scarcely removed. However, sucralose showed a consistent removal of around 30% in the vertical subsurface flow (VF) wetland. On the other hand, caffeine, thrimethoprim, DEET and fluoxetine presented high or moderate removals in all treatment units before increasing in concentration in the final effluent of the FWS wetland, as similarly observed for conventional water quality parameters. This indicates that desorption from the sediment/biomass could be occurring upon adverse conditions generated by plant decay in the fall season. Overall, the VF wetlands showed a better biodegradation potential than the horizontal subsurface flow (HF) wetland.

In general, the recirculation loop has proven to be an appropriate strategy to enhance the removal of total nitrogen in CW systems, achieving an excellent mean removal rate of about 6 g TN m^{-2} d^{-1} in summer and winter seasons. It is also worth emphasizing the importance of remediation measures being feasible at full-scale (harvesting of the biomass) in order to maximize the sequestration of nutrients from macrophytes before the senescence stage and to avoid the decline in treatment performance.

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FIGURES

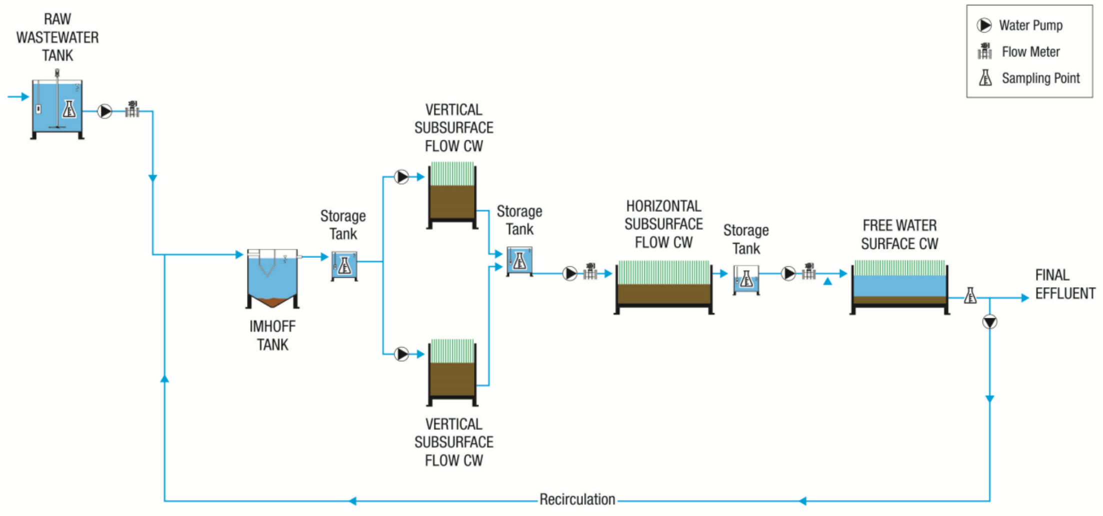

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Figure 1. Diagram of the experimental hybrid constructed wetland system.

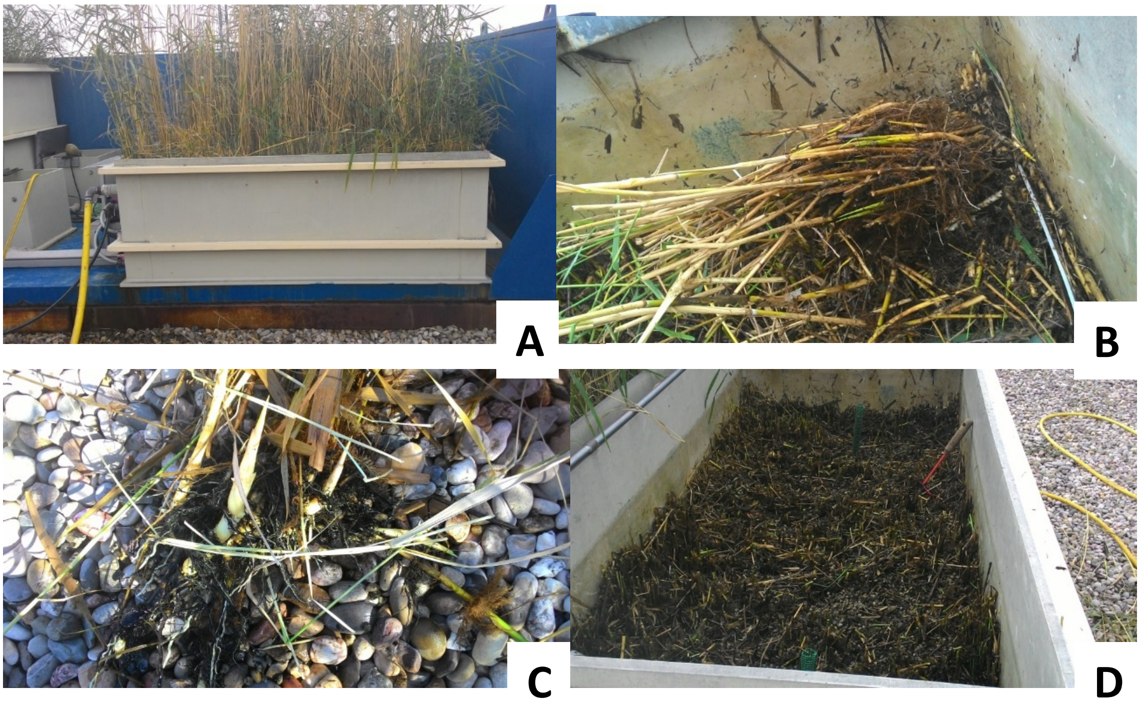


Figure 2. Harvesting of the aboveground biomass in the free water surface wetland at the end of Period II (11/11/2015). (A) macrophytes in senescence; (B,C) decomposing biomass; (D) wetland after harvesting.

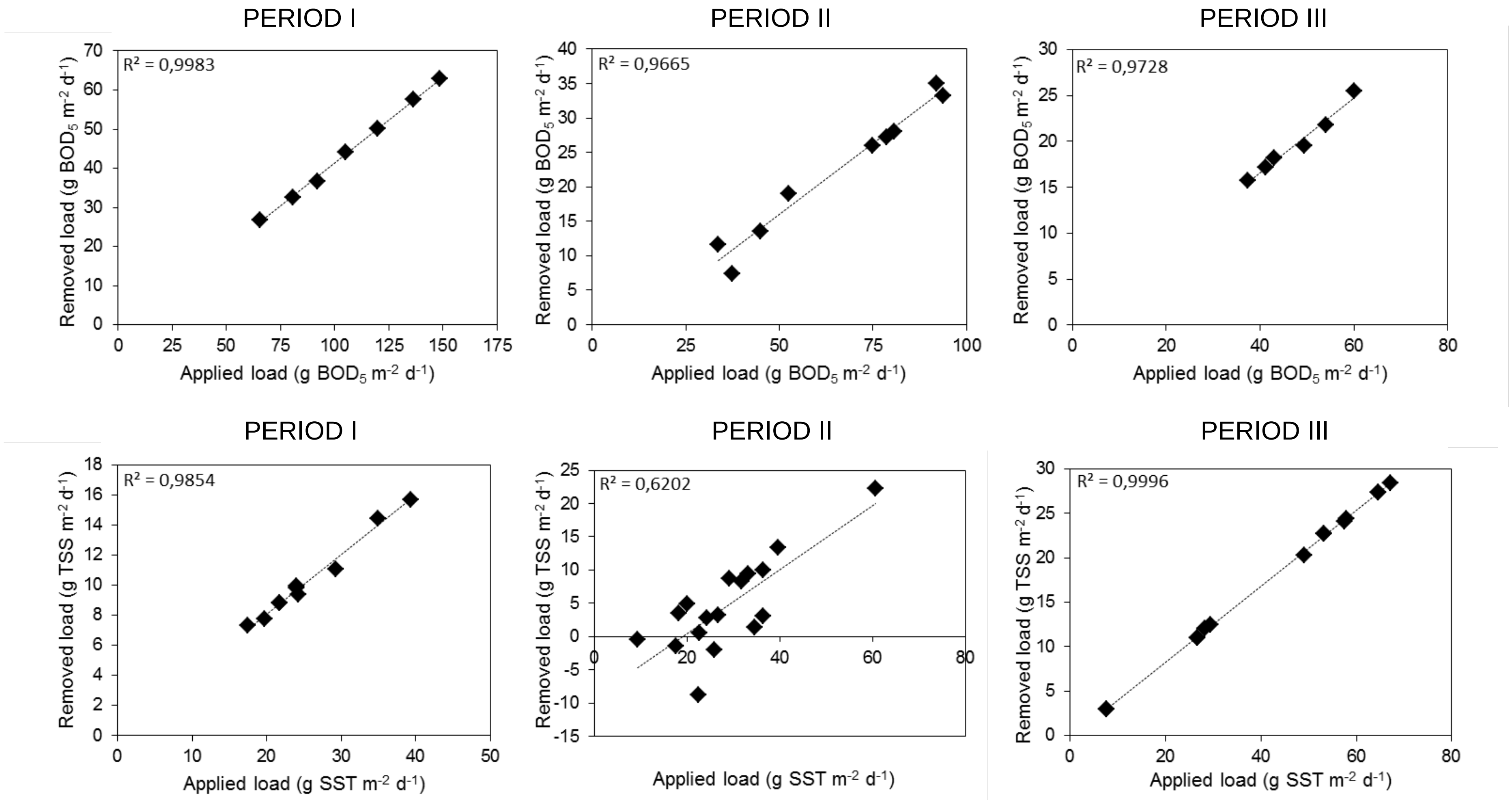


Figure 3. BOD_5 and TSS applied and removed loads in the hybrid constructed wetland system.

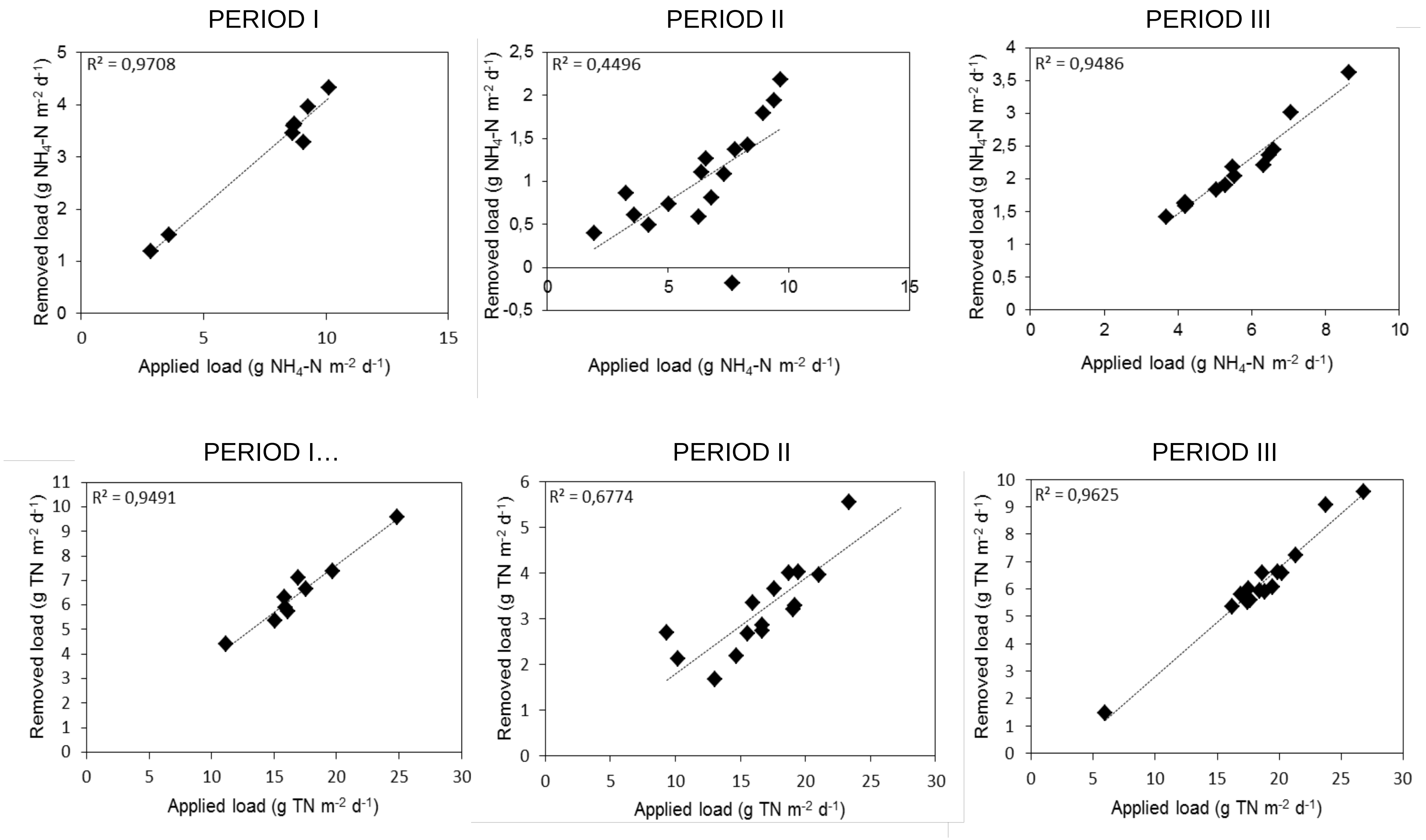


Figure 4. NH_4-N applied and removed loading rates in the hybrid constructed wetland system.

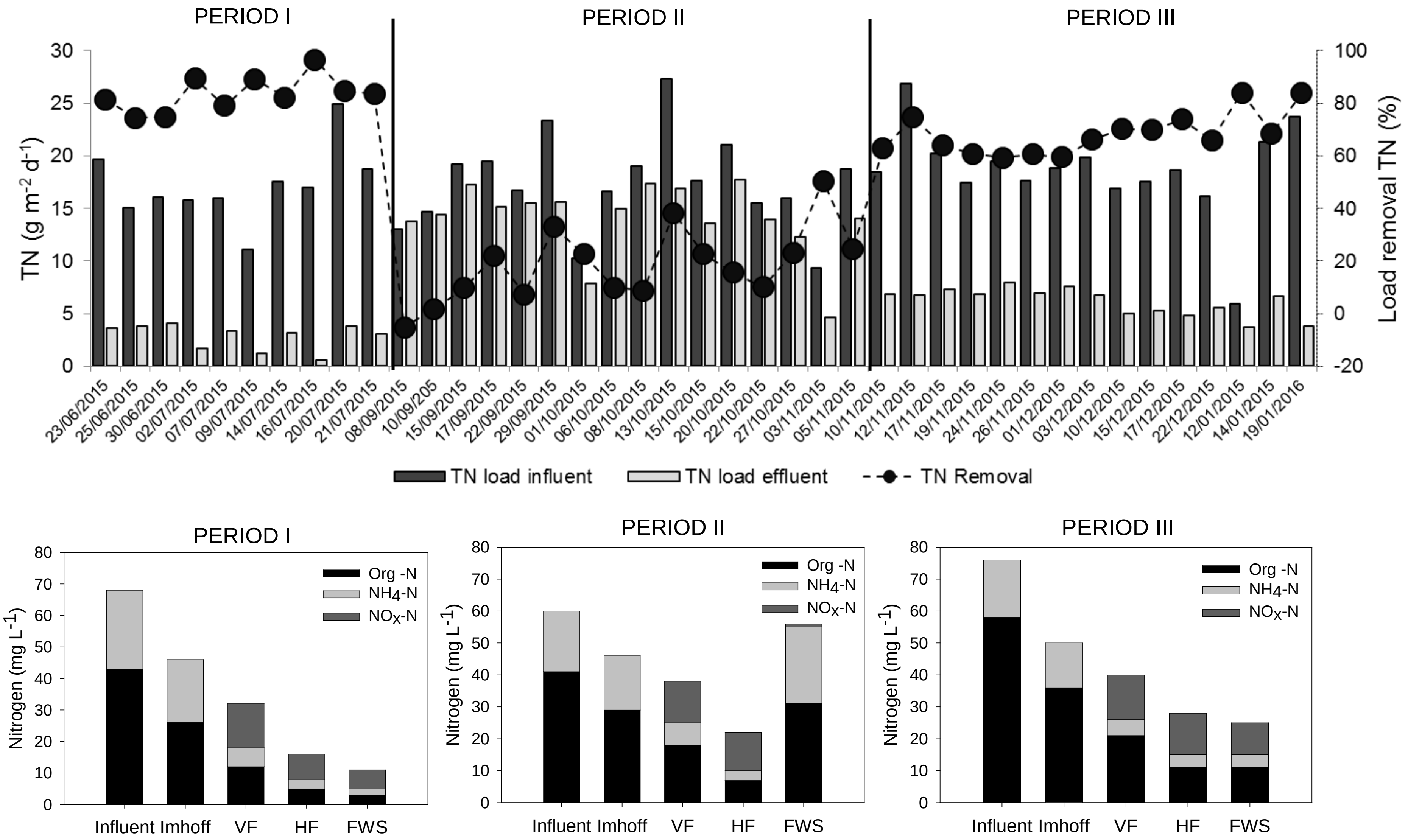
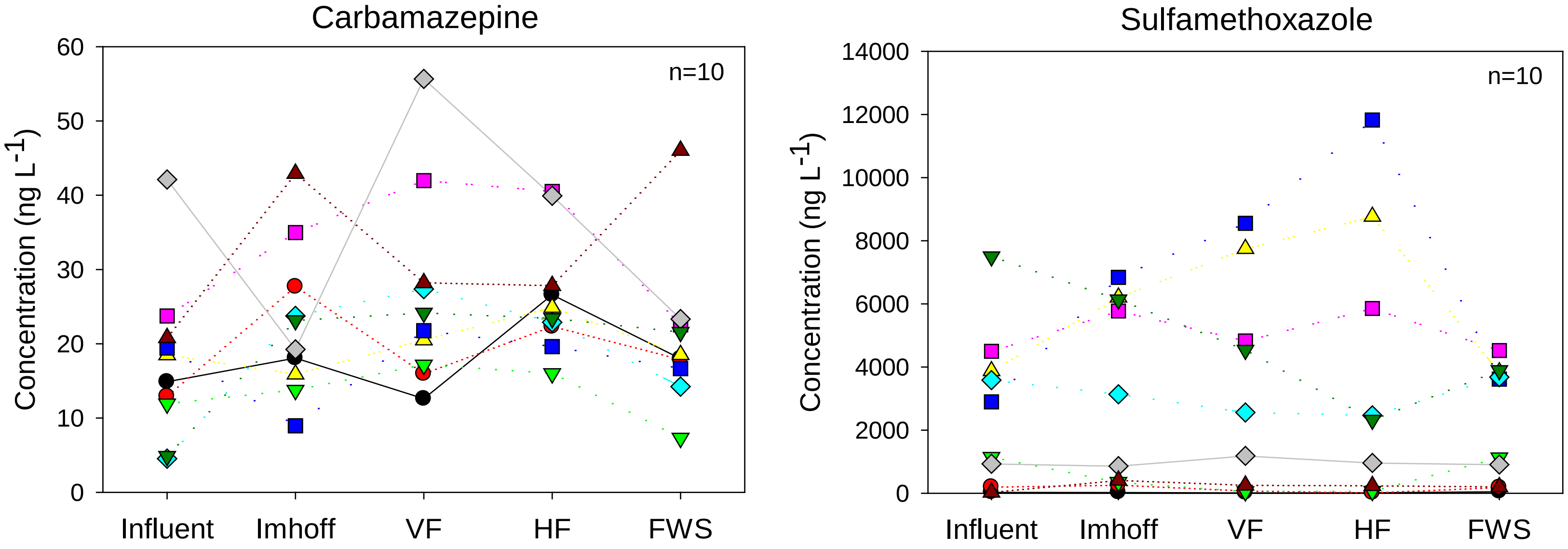
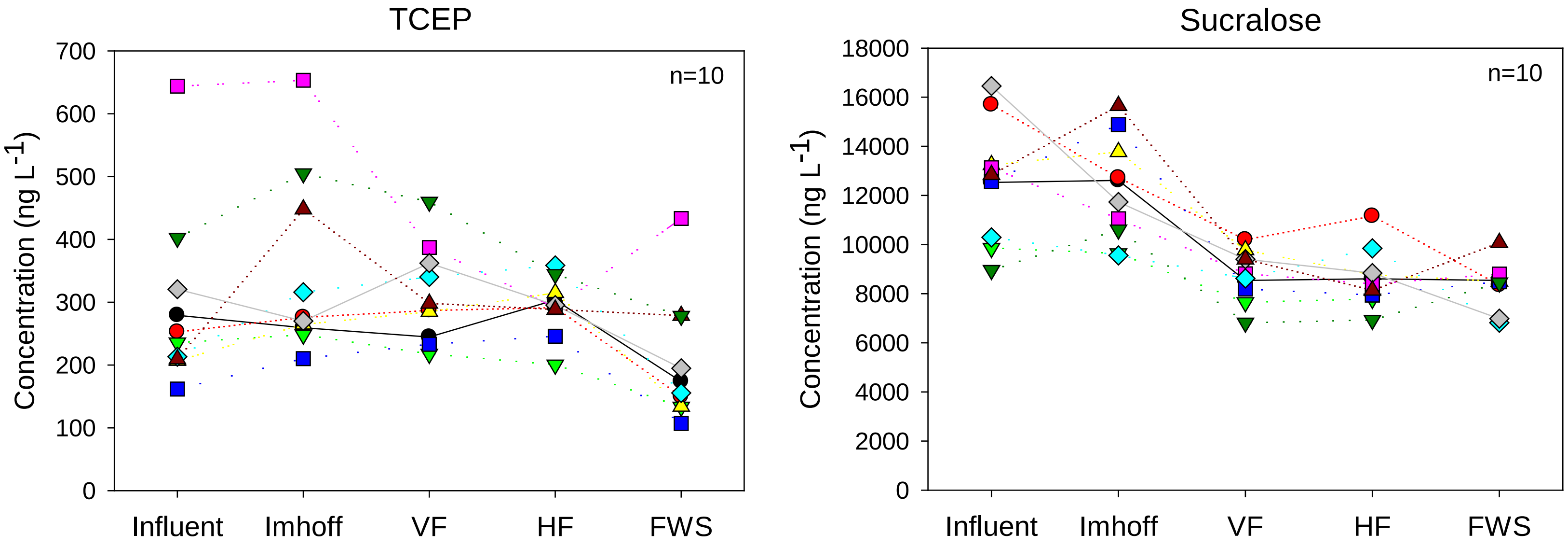
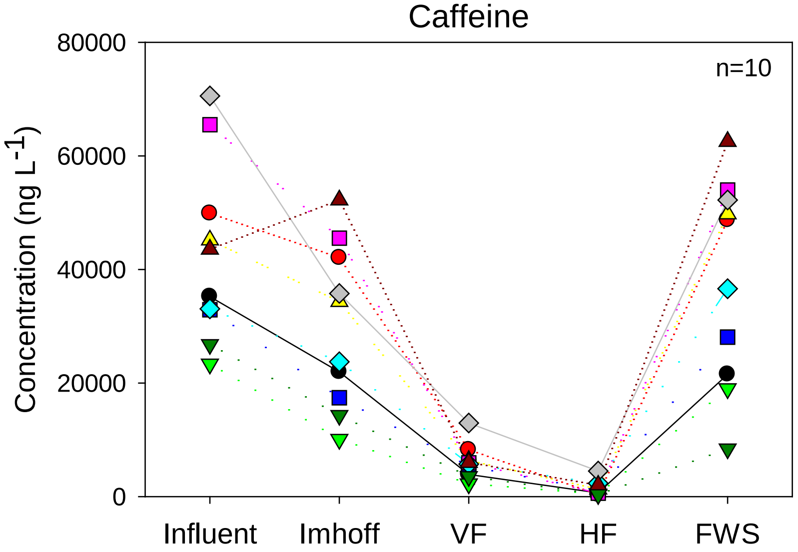
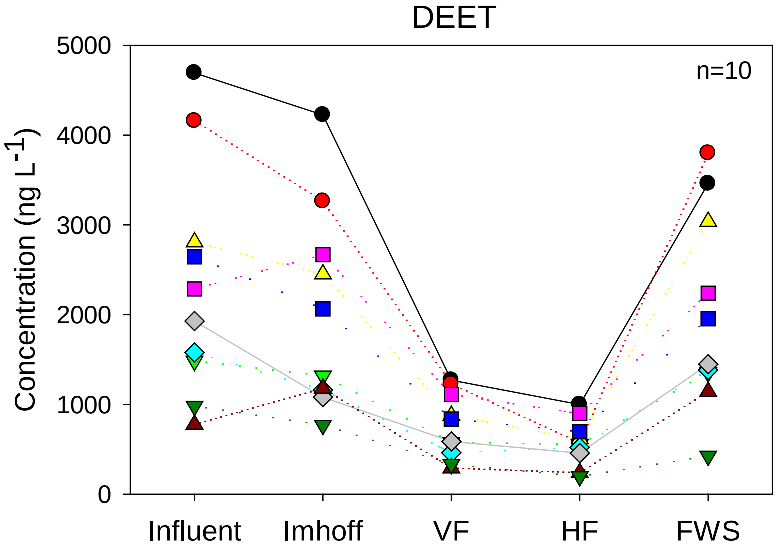


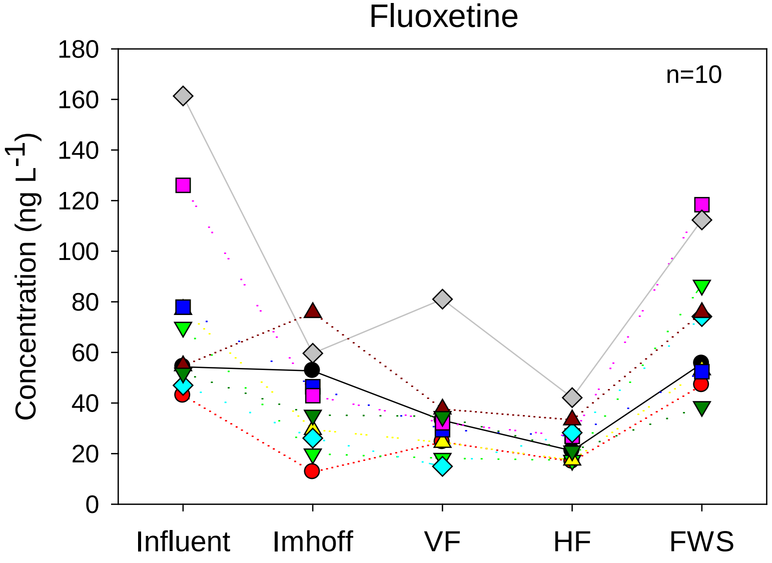
Figure 5. a) Total Nitrogen loading rates at influent and effluent of hybrid constructed wetland system and overall load removal efficiency; b) Average concentration of the different nitrogen species along the treatment train during the three periods of the study.

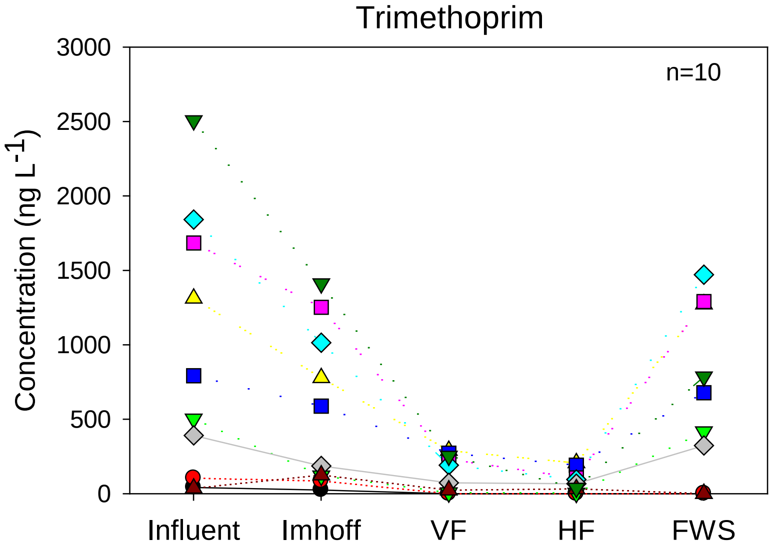

Carbamazepine
n=10
Concentration (ng L-1)
0
10
20
30
40
50
60
Influent
Imhoff
VF
HF
FWS
Sulfamethoxazole
n=10
Concentration (ng L-1)
0
2000
4000
6000
8000
10000
12000
14000
Influent
Imhoff
VF
HF
FWS


TCEP
n=10
Concentration (ng L-1)
0
100
200
300
400
500
600
700
Influent
Imhoff
VF
HF
FWS
Sucralose
n=10
Concentration (ng L-1)
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
Influent
Imhoff
VF
HF
FWS


Caffeine
n=10
Concentration (ng L-1)
80000
60000
40000
20000
0
Influent
Imhoff
VF
HF
FWS

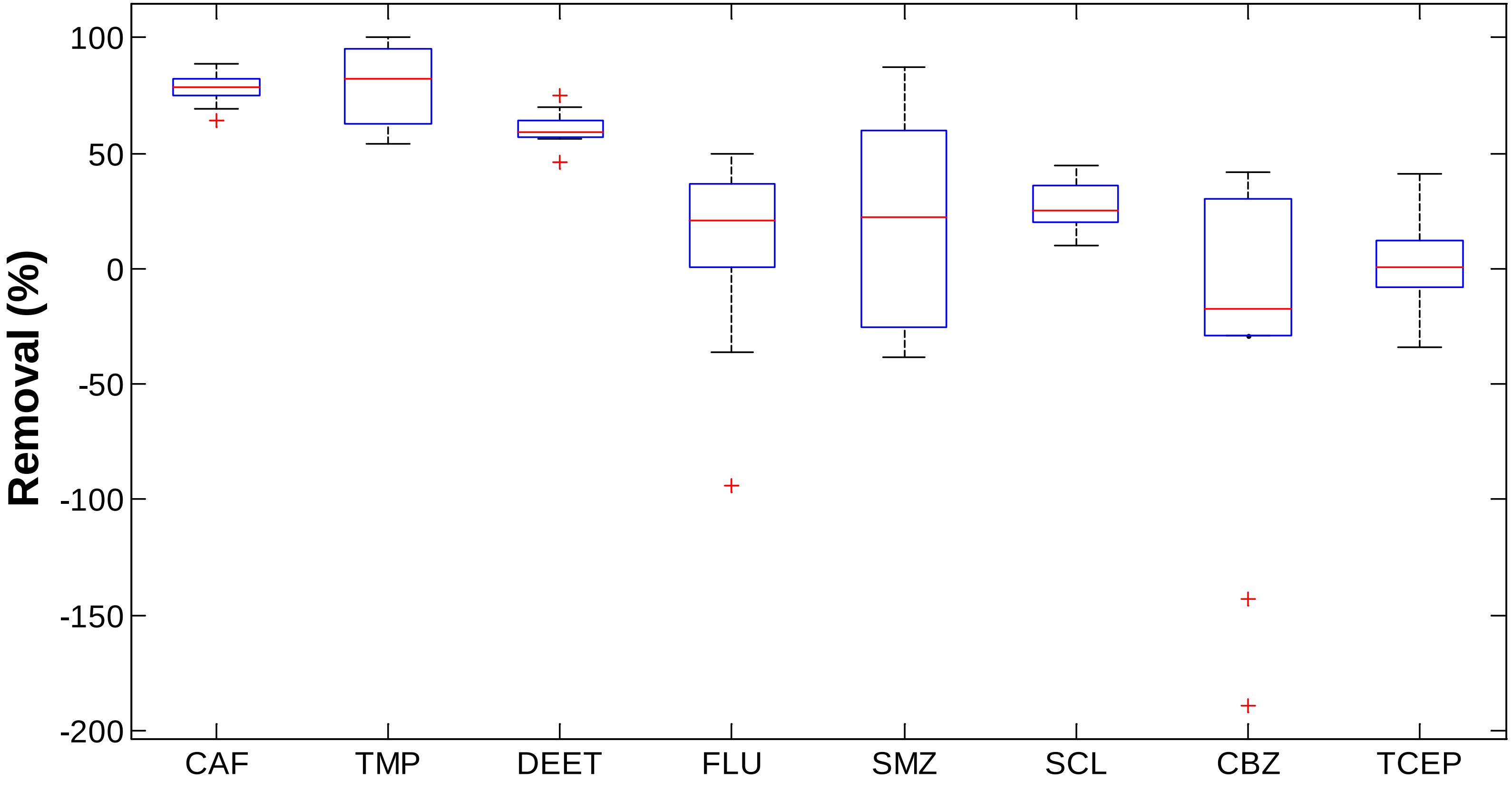

DEET
n=10
Concentration (ng L-1)
5000
4000
3000
2000
1000
0
Influent
Imhoff
VF
HF
FWS


Fluoxetine
n=10
Concentration (ng L-1)
180
160
140
120
100
80
60
40
20
0
Influent
Imhoff
VF
HF
FWS

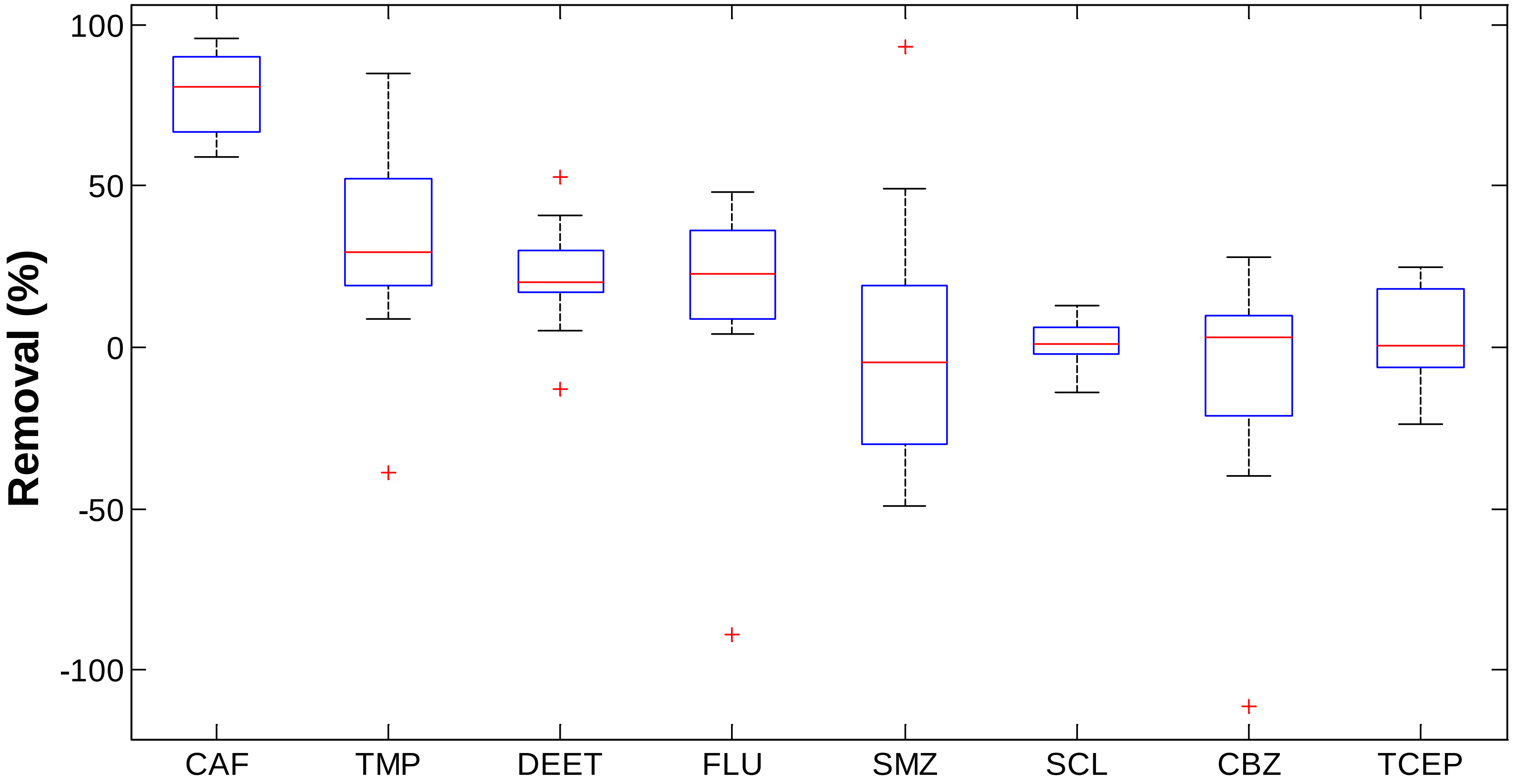

Trimethoprim
n=10
Concentration (ng L-1)
3000
2500
2000
1500
1000
500
0
Influent
Imhoff
VF
HF
FWS

806 Figure 6. Concentration profile of target pharmaceuticals and personal care products along the treatment train at every sampling event (Period II).

807



a)



b)

808 Figure 7. Box plot of target PPCPs removal after a) VF wetland, b) HF wetland (Period II; n=10).

809

Table 1. Main characteristics of the treatment system.

Parameter	Unit	Value and unit
Average Inflow	$m^3 d^{-1}$	1.125 (0.75 raw wastewater + 0.375 recirculation)
Recirculation flow rate	%	50
Average hydraulic loading rate*	$m d^{-1}$	0.37
Nominal hydraulic retention time	h	21
Volume Imhoff tank	m^3	0.2
Dimensions VF wetlands (each)	m (W x L x D)	1.0 x 1.5 x 1.3
VF filter media	Depth of layers: m	Upper layer: 0.1 m sand (1-2 mm)
	Grain size ø: mm	Bottom layer: 0.7 m fine gravel (3-8 mm)
Dimensions HF wetland	m (W x L x D)	1.0 x 2.0 x 0.3
HF water level	m	0.25
HF filter media	Main media ø: mm	Main media: 0.3 m gravel (4-12 mm)
	Inlet and outlet: cm	Inlet and outlet: stone (3-5 cm)
Dimensions FWS wetland	m (W x L x D)	1.0 x 2.0 x 0.5
FWS free water column	m	0.3

*These value was calculated taking into consideration only the area of the VF units (i.e. 3 m^2).

Table 2. Classification, typical use and properties of target PPCPs selected in this study.

Compound	Use	Category	MW	Log Kow	pKa	Reference
Caffeine	Stimulant	Personal care product	194.2	-0.07	10.4	Trenholm et al. (2006)
Carbamazepine	Anti-seizure	Pharmaceutical	236.3	2.45	13.9	Petrie et al. (2015)
N,N-diethyl-meta-toluamide (DEET)	Insect repellant	Personal care product	191.3	2.18	na	Trenholm et al. (2006)
Fluoxetine	Antidepressant	Pharmaceutical	309.3	4.2	9.5	Anumol et al. (2015a)
Sucralose	Sweetener	Personal care product	397.64	-0.4	na	Anumol et al. (2015a)
Sulfamethoxazole	Antibiotic	Pharmaceutical	253.3	0.89	6.0	Trenholm et al. (2006)
Trimethoprim	Antibiotic	Pharmaceutical	290.3	0.91	7.12	Trenholm et al. (2006)
Tris (2-chloroethyl) phosphate (TCEP)	Flame retardant, plasticizer	Personal care product	285.5	-1.2	na	Anumol et al. (2015a)

MW = molecular weight; na = not available

Table 3. Water quality parameters (mean concentration ± SD) at the influent and effluent of the different treatment units of the hybrid system during each of the three periods of operation.

	PERIOD I (Jun-Set 2015) n=10					PERIOD II (Set-Nov 2015) n=16					PERIOD III (Nov 2015-Jan 2016) n=15				
Parameters	Influent	Imhoff tank	VF	HF	FWS	Influent	Imhoff tank	VF	HF	FWS	Influent	Imhoff tank	VF	HF	FWS
T (ºC)	28 ± 1	28 ± 1	27 ± 1	27 ± 1	28 ± 1	21 ± 4	21 ± 4	21 ± 4	22 ± 5	22 ± 4	12 ± 2	12 ± 3	12 ± 3	12 ± 3	13 ± 4
EC (mS cm^{-1})	2.6 ± 0.8	2.4 ± 0.4	2.3 ± 0.3	2.3 ± 0.4	2.7 ± 0.4	1.9 ± 0.5	1.8 ± 0.3	1.9 ± 0.3	1.9 ± 0.3	1.9 ± 0.5	2.2 ± 0.7	1.9 ± 0.4	1.9 ± 0.4	1.9 ± 0.4	1.8 ± 0.4
E_H (mV)	-20 ± 61	-98 ± 22	+208 ± 44	+216 ± 78	+254 ± 20	-99 ± 119	-80 ± 100	+146 ± 92	+55 ± 133	-6 ± 87	-85± 24	-74 ± 21	+95 ± 64	-17 ± 9	+29 ± 15
pH	7.4 ± 0.3	7.3 ± 0.4	7.6 ± 0.4	7.6 ± 0.4	7.5 ± 0.4	7.9 ± 0.2	7.6 ± 0.3	7.4 ± 0.3	7.3 ± 0.2	7.9 ± 0.2	7.8 ± 0.3	7.7 ± 0.3	7.6 ± 0.3	7.5 ± 0.2	7.6 ± 0.2
TSS (mg L^{-1})	877 ± 170	68 ± 19	34 ± 4	6 ± 2	10 ± 2	221 ± 45	75 ± 31	67 ± 53	6 ± 4	114 ± 63	295 ± 97	121 ± 47	41 ± 30	15 ± 12	8 ± 13
BOD_5 (mg L^{-1})	411 ± 37	292 ± 81	135 ± 66	41 ± 12	20 ± 6	392 ± 101	181 ± 63	67 ± 24	26 ± 9	82 ± 29	388 ± 56	126 ± 23	72 ± 25	27 ± 90	19 ± 8
TOC (mg L^{-1})	356 ± 191	112 ± 31	32 ± 2	22 ± 5	23 ± 5	135 ± 69	78 ± 22	51 ± 23	18 ± 4	115 ± 37	268 ± 139	100 ± 42	57 ± 38	29 ± 17	28 ± 16
TN (mg L^{-1})	68 ± 12	46 ± 9	32 ± 11	16 ± 7	12 ± 5	60 ± 15	46 ± 12	38 ± 8	22 ± 5	56 ± 16	76 ± 9	50 ± 12	40 ± 10	28 ± 6	25 ± 6
NH_4-N (mg L^{-1})	25 ± 8	20 ± 7.5	6 ± 2	3.0 ± 2	2 ± 3	19 ± 7	17 ± 6	7 ± 2	3 ± 1	24 ± 11	18 ± 3	14 ± 4	5 ± 2	4 ± 2	4 ± 2
NO_x-N (mg L^{-1})	<LOD	<LOD	14 ± 6	8 ± 5	6 ± 5	<LOD	<LOD	13 ± 7	12 ± 7	0.4 ± 0.3	<LOD	<LOD	14± 3	12± 3	9± 5
SO_4-$^{2-}$	82 ± 13	63 ± 19	74 ± 14	78 ± 19	79 ± 18	66 ± 23	63 ± 19	83 ± 22	84 ± 19	67 ± 27	114 ± 19	106 ± 30	128 ± 19	133 ± 16	133 ± 19

<LOD: below limit of detection