The role of rice fields and constructed wetlands as a source and a sink of pesticides and contaminants of emerging concern: full-scale evaluation

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Abstract

Urban, industrial, and agricultural development in river basins has resulted in the pollution of estuarine and coastal ecosystems with a great amount of organic microcontaminants (OMCs) such as pesticides and contaminants of emerging concern (CECs). This study takes the Ebro Delta as a case study to assess the increase or reduction of 25 OMCs in rice fields and one 86 ha constructed wetland (CW). Bentazone and MCPA were the most abundant pesticides in the rice-field drainage water, with a peak concentration of 21,318 and 938 ng/L respectively, whereas the greatest CEC concentrations were found for caffeine, benzotriazoles, and bisphenol A (20-71 ng/L, on average) in the rice irrigation water. Pesticide concentration increased after the irrigation water passed through the rice fields (from 102 to 1,973 ng/L, on average), but CECs present in the irrigation water decreased by 37% (from 14 to 10 ng/L, on average). A mass balance study showed that the CW was capable of reducing OMCs by 67%. Risk assessment analysis showed that the cumulative hazard quotient for *Daphnia magna*, green algae, and fish was greater than 1 during several sampling campaigns for the rice-field drainage water, but the CW was capable of reducing it by 60-63%, resulting in values below 1, which indicates that the risk was not significant. The results thus indicate that rice fields reduce CECs, but increase pesticides, whereas the use of CWs seems to be a feasible nature-based solution to reduce the discharge of OMCs into estuarine and coastal areas.

Keywords: *rice field; constructed wetland; pesticides; emerging contaminants; risk assessment*

1. Introduction

Urban, industrial, and agricultural development in river basins has resulted in the pollution of estuarine and coastal ecosystems (Vikas and Dwarakish, 2015). Discharge from rivers and estuaries contributes to the presence of high amounts of organic microcontaminants (OMCs) in coastal areas, including pesticides from the agricultural runoff of both farmland located upstream and areas in the estuary itself (e.g., rice fields) (Bansal, 2011). Additionally, wastewater treatment plants (WWTPs) release contaminants of emerging concern (CECs) into rivers (Gogoi et al., 2018). The use of pesticides during the rice-growing season has been reported to be one of the most important sources of OMCs in estuarine areas (Añasco et al., 2010; Kuster et al., 2008), whereas CECs, mainly consisting of pharmaceuticals and household products, are released by WWTPs due to their inefficient treatment (Dulio et al., 2018). The presence of OMCs in coastal areas can have adverse effects for aquatic biota. For instance, the presence of certain pesticides has been shown to produce changes in the macroinvertebrate community structure and ecosystem functions (Schäfer et al., 2007), whereas certain CECs have been shown to reduce macroinvertebrate diversity in rivers (Ginebreda et al., 2010).

The Ebro River is 910 km long and has a drainage area spanning 85,362 km^2. It is the largest river in Spain and feeds the Ebro Delta, one of the largest wetland areas (320 km^2) in the western Mediterranean region (Ibáñez and Caiola, 2016). The lower Ebro River, including the delta, suffers from an historical pollution due to the presence of a chlor-alkali plant located about 115 km upstream from the mouth, as well as the use of chlorinated pesticides in agriculture (Alcaraz et al., 2011). This has resulted in a background contamination of PCBs and DDTs, among other persistent organic pollutants (Huertas et al., 2016; Quesada et al., 2014; Blanco et al., 2018). Nevertheless, in recent years different authors have reported the presence of other OMCs in the Ebro River, including pesticides such as azoles, organophosphorus, and triazine compounds (Ccanccapa et al., 2016) and CECs such as pharmaceuticals (carbamazepine or ibuprofen) or anticorrosive agents (benzotriazole) (Čelić et al., 2019; Matamoros et al., 2010). Rice cultivation in the Ebro Delta results in the runoff of a large amount of pesticides into the bays and open sea through drainage channels. The most abundant pesticides detected in these drainage channels are bentazone, MCPA, propanil, molinate, and atrazine (Kuster et al., 2008). Ochoa et al. (2012) reported the association of the presence of bentazone and propanil with oyster mortality episodes in the Ebro's bay. Similarly, the presence of pharmaceutical compounds in the Ebro's bay has been suggested to have potential adverse effects on marine organisms (Čelić et al., 2019).

Wetland treatment systems are effective in treating organic matter, nitrogen, and phosphorus, as well as for decreasing the concentrations of heavy metals, organic chemicals, and pathogens (Haberl et al., 2003). In this regard, various studies have demonstrated the effectiveness of wetlands for reducing the discharge of OMCs from agricultural runoff water (Matamoros and Bayona, 2013; O'Geen et al., 2010; Vymazal and Březinová, 2015). Wetlands are widely recognized as critical components of our planet providing a wide variety of ecosystem services: regulation of the hydrologic cycle and flood protection, groundwater recharge zones, pollutant and nutrient removal, carbon sinks, biodiversity hot spots, habitats of rare and endangered species, and aesthetic values (McLaughlin and Cohen, 2013). Restored and constructed wetlands (CWs) have been created to enhance and protect wetland biodiversity and improve the quality of surrounding surface waters (O'Geen et al., 2010). Restoring and creating wetlands at the watershed scale has been suggested as a general strategy to promote sustainable agricultural development by buffering the impacts of non-point-source pollutants on aquatic ecosystems (Comín et al., 2014). They are capable of attenuating OMCs through different naturally occurring processes (photodegradation, sorption, hydrolysis, and biodegradation) (García et al., 2010). Nevertheless, to the authors' knowledge this is the first time they have been assessed with regard to the attenuation of pesticides and CECs from rice-field drainage waters, taking into account the role of the rice fields in OMC dynamics.

The present study aims to assess the effect of a system of rice fields and a CW as a sink and source of OMCs (12 pesticides and 13 CECs) as an integrated solution for reducing pollutant discharge to the coastal area. It also assesses the ecotoxicological risk of the presence of these OMCs in water.

2. Material and methods

2.1. Sampling site description

The Ebro Delta is located in the Western Mediterranean (Catalonia, NE Spain). The delta plain has a surface area of 320 km^2 (Fig. 1). Although at the beginning almost all Deltaic area was covered by wetland systems, up to 80% of the delta area has been reclaimed (250 km^2), mostly for rice agriculture (210 km^2), and currently only 56 km^2 of wetlands remain (Ibáñez and Caiola, 2016). Rice agriculture is the main activity, but tourism, fisheries, and aquaculture are also important industries, which benefit from the ecosystem services provided by marshes, coastal lagoons, bays, and the continental shelf influenced by the Ebro River discharge. The Ebro Delta is the second largest wetland area in Spain and is protected as a Natural Park and an EU Natura 2000 site (Day et al., 2019).

To sustain rice farming, two main canals, regulated at their source (40 km upstream from the river mouth), are split into numerous secondary canals and ditches to bring fresh water to the Ebro Delta rice fields. The freshwater supply is interrupted between October and April to prepare the fields for the next growing season. During the cultivation period, drainage water from the rice fields is drained to the bays (Alfacs and Fangar) and, to a lesser extent, to the outer sea (Fig. 1). Although rice farming has many positive environmental aspects such as providing feeding areas for certain birds species (Ibáñez et al., 2011), the intensive use of pesticides, fertilizers, and artificial drainage systems has some negative consequences, such as the impacts on coastal bivalve aquaculture carried out in the Ebro Delta bays (Faria et al., 2018) and on wetland conservation (Ibáñez et al., 2011; Prado et al., 2014).

In 2015, two CWs started to operate, one in the north (Illa de Mar CW) and the other in the south (Embut CW) of the Ebro Delta, with the aim of reducing the pollution caused by nutrients and pesticides used in rice production. The present study examines the Embut CW. This CW has a total surface area of 86 ha with ca. 60% of helophytic vegetation coverage. It is divided into three consecutive sections that are hydrologically connected, allowing the drainage water from the rice fields to flow throughout the whole CW. The depurated water flow from the last CW section is evacuated by pump to a coastal lagoon (El Clot) connected to the Encanyissada lagoon and Alfacs Bay (Fig. 1). Total water runoff is, on average, 1 m^3/s with the water level inside the wetland varying between 20 and 100 cm. Although this CW has the capacity to depurate drainage water from rice fields from the southern hemi-delta, it only receives a small amount of the total drainage (1-5%) due to limited pumping capacity and energy cost constraints.

2.2. Sampling procedure

The water sampling was carried out between June and October 2018 during the rice-growing season. Figure 1 shows the different sampling points: river irrigation water (RIW), originating from the Ebro River 30 km upstream from the delta through an irrigation canal; rice-field drainage water (RFDW), receiving water from rice fields; CW section 1; CW section 2; and the CW effluent. Grab samples were collected every week, resulting in a total of 21 sampling campaigns (n=105). Water samples for the analyses of the water quality parameters were collected in plastic bottles, whereas pre-cleaned 2.5 L amber glass bottles were used for the determination of OMCs. All samples were kept refrigerated during transport to the laboratory, where they were stored at 4 °C until they were analyzed (less than 24 hours).

2.3. Analytical methodology

In this study, the prioritization of OMCs was based on their use, occurrence in the Ebro Delta, and persistence (Čelić et al., 2019; Kuster et al., 2008).The determination of OMCs was performed as described by Matamoros and Bayona (2006). Briefly, 250 mL of filtered water samples were spiked with 100 ng of a surrogate standard mixture (atrazine D_5, bisphenol A-D_{10}, caffeine-$^{13}C_3$, carbamazepine-$^{13}C_6$, ibuprofen-D_3). The samples were then percolated through a conditioned 200 mg polymeric solid-phase extraction cartridge (STRATA X, Phenomenex, Torrance, USA). The cartridges were eluted with 15 mL of hexane/ethyl acetate (1/1, v/v). The eluted extract was evaporated under a gentle nitrogen stream until ca. 100 µL remained, at which point 100 ng of triphenylamine was added as an internal standard. After that, the vial was reconstituted to 250 µL with ethyl acetate. Derivatized and non-derivatized aliquots of the sample extracts were analyzed with an EI-GC–MS/MS Bruker 450-GC gas chromatograph coupled to a Bruker 320-MS triple-stage quadrupole mass spectrometer (Bruker Daltonics Inc., Billerica, MA, USA). The derivatization of samples was carried out in a programmed temperature vaporizing (PTV) injector of the GC by adding 10 µL TMSH to a 50 µL sample aliquot before injection. A volume of 5 µL was injected into a Bruker 450-GC gas chromatograph coupled to a Bruker 320-MS triple quadrupole mass spectrometer (Bruker Daltonics, Billerica, MA, USA) fitted with a 20 m × 0.18 mm ID, 0.18 μm film thickness Sapiens X5-MS capillary column coated with 5% diphenyl 95% dimethyl polysiloxane provided by Teknokroma (Sant Cugat del Vallès, Spain). The PTV injector was set at 60 °C for 0.5 min and then rapidly heated up to 300 °C at 200 °C/min and held for 10 min. It was then cooled to the initial 60 °C at 200 °C/min. The ion source temperature and transfer line were both held at 250 °C. Limit of detection and quantification ranged from 0.1 to 2 and from 1 to 10 ng/L, respectively, with recoveries greater than 80% and relative standard deviation lower than 20%.

In addition, other water quality parameters were analyzed within the CW monitoring program that was underway since 2016. The total chlorophyll and pheophytin concentrations were determined using the colorimetric method (Jeffrey and Humphrey, 1975). The analyses of dissolved and total nutrient concentration (P-PO_4, TP, N-NH_4, N-NO_2, N-NO_3, and TN) were carried out following Koroleff (1977). The total suspended solid concentration (TSS) was determined in compliance with the UNE-EN 872 standard (AENOR, 1996). A YSI 556 multi-parameter probe was used to measure water temperature, dissolved oxygen concentration and saturation, pH, conductivity, and redox potential.

2.4. Ecotoxicological risk assessment

An aquatic risk assessment was performed at the RIW, RFDW (CW influent), and CW effluent sampling points based on the concentrations of the detected OMCs in the water samples and the listed EC50 values for *Daphnia magna*, green algae, and fish (Sanderson et al., 2004). The HQs were calculated as the quotient between the MEC (measured environmental concentration at each sampling point) and the PNEC (predicted no-effect concentration). The PNEC values were estimated dividing the EC50 values (48 h) by a recommended arbitrary safety factor of 1000. The EC50 values were estimated for *Daphnia magna*, green algae, and fish with ECOSAR v1.10 (EPI Suite software, US EPA) (Table 1-Supplementary Material, SM). The cumulative HQ for each water sample was calculated as the sum of each individual HQ (Ginebreda et al., 2010).

2.5. Data analysis

The mass balance budget of the CW was calculated taking into consideration the water flow at the different sampling points (influent, intermediate point 1, intermediate point 2, and effluent) and the concentration of each OMC. The outflow of the wetland was directly obtained from the pumping evacuation station, whereas water flow at the different intermediate points was calculated from the measured water level at different sections of the CW, considering evapotranspiration, infiltration and rain episodes. Only OMCs with a frequency of detection (FOD) greater than 50% at the CW influent were assessed. The experimental results were statistically evaluated using the SPSS v. 22 package (SPSS Inc., Chicago, IL, US). SigmaPlot software v. 14.0 for Windows (Systat Software, Chicago, USA) was used for graphs.

3. Results and discussion

3.1. Water quality parameters

Table 1 shows the water quality parameters collected throughout the whole period of the monitoring program (2016-2018) for the different Embut CW sampling sites. The results show a positive redox potential and a relatively low oxygen concentration of around 3 mg/L across the CW. Nutrient concentrations were similar to those previously found in rice-field drainage water from the Ebro Delta (Calvo-Cubero et al., 2014). Although the TN concentration was only moderately reduced by the CW (40%), the concentration of dissolved certain N species was reduced by more than 80% ($N-NH_4$, 85%; $N-NO_2$, 94%; $N-NO_3$, 92%). Similarly, TP was only reduced by 9%, but $P-PO_4$ was reduced by 58%. The removal efficiencies were relevant considering the low influent concentration of N and P species (Table 1). The present results are similar to those previously found in small-scale wetland systems from the Ebro Delta treating rice-field irrigation-water drainage. Calvo-Cubero et al. (2014) observed that experimental wetland systems (100 m^2, each) reduced TN by 50%, $N-NH_4$ by 96%, $N-NO_3$ by 81%, TP by 50%, and $P-PO_4$ by 18% on average, whereas larger restored marshes (150 m long × 75 m wide) usually reduced N by 50–98% and soluble phosphorus by less than 50% (Comín et al., 2001). The main reduction of the nutrient concentration occurred in the first section of the CW. This is not surprising since it has been reported elsewhere that nutrients are normally reduced in this part, where most of the CW biodegradation processes take place, due to the organic matter consumption (Vymazal, 2007). It also agrees with the fact that the attenuation of nutrients in wetland systems follows a first order kinetic rate. The relatively high attenuation of nutrient species may be related to the positive redox potential and oxygen availability (Table 1), allowing a denitrification process ($N-NH_4$ oxidation) to take place, but also to denitrification ($N-NO_3$ and $N-NO_2$ reduction) due to anaerobic conditions in the bottom layers and sediments of the CW (Chen, 2011). Furthermore, the abundance of periphyton (Dodds, 2003), together with the presence of macrophytes (Greenway, 2007) in the CW, has also been shown to enhance nutrient attenuation.

3.2. Occurrence of OMCs in the Ebro Delta

Table 2 shows the FOD and abundance of the selected OMCs at the different sampling sites. The highest FOD and concentration levels for pesticides were observed in the RFDW (77% and 1973 ng/L, on average). This is consistent with the use of pesticides for rice agriculture. Conversely, the highest FOD and concentration levels for CECs were observed in the RIW (86% and 14 ng/L, on average). This is likewise consistent with the fact that CECs are released by WWTPs into the river waters (Gogoi et al., 2018). The concentration of pesticides at all sampling sites was greater than that of the CECs (1028 ng/L vs 10 ng/L, on average). Bentazone showed the highest concentration in the RFDW, with an average value of 21,318 ng/L, followed by MCPA. This is consistent both with the fact that these two herbicides are applied simultaneously in rice paddy fields and with previous monitoring studies of drainage canals from the same area (30,510 and 1,877 ng/L, on average, for bentazone and MCPA respectively) (Kuster et al., 2008). In the case of CECs, the greatest concentration levels were found for caffeine, benzotriazoles, and bisphenol A (20-71 ng/L, on average), whereas the average concentrations of the other studied CECs, especially pharmaceuticals, were below 10 ng/L. This is consistent with the fact that the river irrigation water was collected from a canal 30 km upstream from the Ebro Delta (Fig. 1), and that benzotriazoles (anticorrosive agents used in paint) can be released from paint covering irrigation systems or boats, whereas bisphenol A (a plasticizer agent) can be released from plastics or microplastics. Previous monitoring studies showed that the concentration of pharmaceuticals in this section of the Ebro River was very low, in the range of ng/L (Silva et al., 2011). Therefore, the present results show that pesticides due to rice farming are the most abundant OMCs in the Ebro Delta.

3.3 Temporal dynamics of OMCs

Figure 2 shows the total concentration changes of pesticides and CECs in the different sampling days and sites. Whereas the concentration of pesticides did not significantly change in the irrigation water, it had a maximum peak in the first week of July in the drainage water, following the period of the most intensive pesticide treatments. The results show that bentazone was the most abundant pesticide (maximum peak concentration of 113,092 ng/L), followed by MCPA (5,076 ng/L). Figure 1-SM shows that the concentration profiles for the most abundant pesticides, such as bentazone and MCPA (herbicides used to control the spread of weeds) and tebuconazole (fungicide), were consistent with this peak; in contrast, oxadiazon (an herbicide intended for preemergence or early post-emergence application) showed two peaks, the first in early June (when the rice plants were in an early growing stage) and the second in early July. These peaks are consistent with previous results observed in the Rhône River Delta (France), where there were two main peaks of pesticide contamination. The first one corresponded to the use of pre-emergence herbicides (oxadiazon and pretilachlor), while the second one was related to the post-emergence herbicides (MCPA and bentazone) (Comoretto et al., 2007). Similar results were observed by Kuster et al. (2008), who found an increase in the concentration of bentazone in June, but they did not study the other pesticides or collect samples between July and October. Conversely, the concentration of CECs did not show many differences between sampling days. This is consistent with the fact that these compounds originated at WWTPs upstream in the river basin and the fact that their concentration in river waters is normally very stable over time (i.e., in the same season) (Kunkel and Radke, 2012; Matamoros and Rodríguez, 2017).

3.4. Attenuation of OMCs in the rice paddy fields

Results show that rice paddy fields are a source of pesticides due to their application during rice cultivation (Fig. 2), but recent studies have observed that they are also capable of removing pesticides (Moore et al., 2018). In the current study, all pesticides, except atrazine and terbuthylazine, increased in concentration, presumably due to their use in rice cultivation. In fact, these two triazine pesticides were already present in river water used to irrigate rice fields (Table 2). The present results show that rice fields were capable of reducing the concentration of atrazine and terbuthylazine by 75% and 26%, respectively. These results are consistent with those reported by More et al. (2018) showing that rice fields were capable of reducing atrazine and diazinon by more than 80%. Nevertheless, this is the first time that rice fields have been shown to be able to reduce CECs (Table 2). The CEC concentrations declined from 1% to 84%, with an average attenuation of 37%. Primidone and benzotriazole showed a poor removal (<2%), which is consistent with their poor attenuation in phytoremediation systems such as CWs (Matamoros and Hijosa-Valsero, 2018). Hence, rice fields should also be seen as a phytoremediation system to attenuate OMCs. Plant uptake and translocation to the rice grain cannot be ruled out for some of these compounds, as some have been observed to be uptaken by other crops (e.g., lettuces, carrots, tomatoes, and cucumber) (Miller et al., 2016). It should be noted that the attenuation of OMCs in the rice fields is an estimation carried out without a proper mass balance due to the lack of precise hydrological data. Hence, the real attenuation is expected to be greater than that found in this study, since the water output of rice fields is in the range of 30-40% of the water input (Liu et al., 2018).

3.5. Attenuation of OMCs in the CW

A mass balance analysis was performed in the CW to assess its effectiveness for reducing OMCs. Mass balance was calculated based on the water flow in each section and the concentration of each OMC, so evapotranspiration or water infiltration processes were included. Figure 3 shows the mass reduction of pesticides and CECs in the three sections of the CW. The mass removal efficiency was compound-dependent and ranged from 28% to 98%, with an average of 67%. The average mass removal for pesticides was 73% vs.

62% for CECs. This small difference can be accounted by the fact that pesticides were found at a much greater concentration and that the CECs were often below the limit of detection. In fact, various studies have suggested that there is a minimum concentration below which compounds may not be further degraded. This minimum threshold concentration mainly depends on the kinetic parameters of microorganism growth and metabolism, but also on the thermodynamics of the overall transformation reaction (Matamoros and Hijosa-Valsero, 2018). The first section (38%, on average) was more effective than the second (17%) and third (12%) for the attenuation of OMCs. This is a typical load-dependent phenomenon observed in wetland systems and can be explained by the fact that the first section of the system is where most of the sediments and organic matter accumulate and most nutrients are consumed by plants, algae, and other microorganisms (Haberl et al., 2003), but also due to the fact that degradation process in CWs follow a first order kinetic rate. This is also consistent with a previous study performed in a smaller CW spanning 2 ha treating a secondary wastewater effluent in which the first part of the system was observed to account for 90% of the MCPA and terbuthylazine removal (Matamoros et al., 2008). The present study shows that OMCs can be classified in three groups according to their removal efficiency: i) highly efficiently attenuated compounds (>80%), namely, chlorpyrifos, propanil, and MCPA; ii) moderately attenuated compounds (50-80%) namely, bentazone, molinate, oxadiazon, tebuconazole, terbuthylazine, tributyl phosphate, 5-TTri, carbamazepine, lorazepam, naproxen, oxazepam, primidone, and triclosan; and iii) poorly attenuated compounds (<40%), namely, alachlor, caffeine, and benzotriazole. These results are consistent with those reported in a compilation study, summarizing the results obtained in the attenuation of 87 pesticides by 47 restored and CW systems treating agricultural runoff water. In that study, the average attenuation was 95% for organophosphates (chlorpyrifos), 65% for triazine compounds (terbuthylazine), 62% for the triazole group (tebuconazole), and 35% for aryloxyalkanoic acids (MCPA, bentazone, and propanil) (Vymazal and Březinová, 2015). In the case of CECs, results from a 100 ha restored wetland system treating agricultural runoff and treated wastewater showed that the average attenuation of CECs was much lower (19%) (Matamoros et al., 2012) than that observed in the present study (62%), probably due to the fact that it was monitored from October to December (cold season). Nevertheless, the present results are consistent with previous studies also conducted during the warm season in a surface flow CW treating secondary treated wastewater (71%, on average) (Matamoros and Salvadó, 2012). Biodegradation and photodegradation of CECs in wetland systems are two attenuation processes in which seasonal changes in temperature and sunlight radiation play a very important role (Matamoros and Bayona, 2008). Different studies have proven that pesticides can be removed by biodegradation and photodegradation, but in some cases hydrolysis or sorption to the organic matter can also play a relevant role (Vymazal and Březinová, 2015). Nevertheless, the latter is less likely as most of the studied pesticides were polar.

The CW was capable of reducing the discharge of 37 kg of pesticides and 0.12 kg of CECs into Alfacs Bay from June to October. Nevertheless, it should be noted that its current HRT was set to approximately 1 month and only treats a small proportion of the canal's rice drainage water. Therefore, further studies should explore its capacity to operate at much lower HRTs, increasing the volume of treated water. This may help to considerably reduce the mass discharge of OMCs from rice drainage water into the coastal ecosystems, but it may also reduce the effectiveness of the CW. Nevertheless, further studies are needed on that as the reduction of the HRT will also decrease the amount of pesticides released to the coastal ecosystem.

3.6. Combined effect of rice fields and CWs

Additionally, it is worth noting that although rice fields were observed to be a source of pesticides (8 out of the 12 studied compounds increased in concentration; see Table 2), their use in combination with the CW enhanced the attenuation of all the studied CECs and 2 pesticides. Therefore, their combined use was capable of achieving a cumulative attenuation of 63±21% for the CECs and 40±21% for the two pesticides. Nevertheless, the individual effect on the attenuation of CECs was similar in both systems, with an average attenuation of 37±23% for the rice fields and of 45±23% for the CW. Similar behavior was observed for atrazine and terbuthylazine, with a reduction in both the rice fields (75% and 26%, respectively) and the CW system (34% and 44%, respectively), and a combined attenuation of 83% and 60%, respectively. Therefore, the present results suggest that the combination of rice fields and CWs is useful for attenuating OMCs in rivers and, thus, reducing the discharge of OMCs into the coastal areas.

3.7. Ecotoxicological risk assessment

Figure 4 shows the cumulative HQ for *Daphnia magna* at the RIW, RFDW, and CW effluent. The cumulative HQ was much lower than 1 at the RIW (0.06, on average), but was greater than 1 (1.1., on average) after the water had passed through the rice fields for more than 2 months in a continuous flow mode, with a maximum peak of 2.4. It should be noted that an HQ greater than 1 indicates that the risk for *Daphnia magna* is significant. This is due to the application of pesticides in the rice fields. The present data show that pesticides had a greater contribution to the HQ than CECs at all the sampling points (90%, on average). Oxadiazon had the greatest HQ contribution at all the sampling sites (65%, on average), followed by tebuconazole (16%), and chlorpyriphos (4%). Despite the high concentration of bentazone (Table 1), its contribution to the HQ was low, as its EC50 value for *Daphnia magna* was high. The cumulative HQ profile showed two peaks, one in early June and the other in July. This is consistent with the concentration profile of oxadiazon (Fig. 1-SM). Toxicity approach studies for green algae and fish showed similar profiles (Figs. 2 and 3-SM), but with lower cumulative HQs (0.64 and 0.76, on average, for green algae and fish in the RFDW). The temporal toxicity pattern observed in the drainage channels is consistent with previous studies indicating that they were probably responsible for the mortality in shellfish in Alfacs Bay (Köck et al., 2010; Ochoa et al., 2012).

The attenuation of the risk in the CW was very high. The risk was greater than 1 in 9 (*Daphnia magna*), 4 (green algae) and 7 (fish) of the 21 sampling campaigns in the drainage water, but always less than 1 at the CW effluent, indicating that the risk is not significant. The average attenuation of the cumulative HQ ranged from 60% to 63% for the three studied trophic levels. These results are consistent with previous studies by Elsaesser et al. (2011), who observed that wetland systems were capable of reducing pesticide toxicity by more than 90%, as well as other studies by Matamoros et al. (2017) showing that CWs can reduce toxicity associated with CECs by 60%. Therefore, the use of CWs as a nature-based solution for reducing pesticide toxicity seems to be a very promising eco-technology that should be implemented in rice agriculture. Their deployment in deltaic and estuarine areas is very important since it could prevent adverse effects on aquatic ecosystems and fish and shellfish resources.

4. Conclusions

This study demonstrated that rice paddy fields are a sink and a source of OMCs and that the use of CWs is useful for reducing the discharge of OMCs into estuarine and coastal areas. The following specific conclusions can be drawn:

-The CW reduced the concentration of N and P species by more than 80% and 50%, respectively.

-The pesticides bentazone and MCPA are the most abundant OMCs in the Ebro Delta, with an application peak at the beginning of July.

-Rice paddy fields are capable of reducing the concentration of CECs by 37%, on average, but they are also a source of pesticides in the Ebro Delta.

-The mass balance study showed that the CW was capable of removing 67% of OMCs, on average, with the first section being the most effective.

-The contribution of pesticides to the cumulative HQ was greater than 90%, but the cumulative HQ (*Daphnia magna*, green algae, and fish) was only greater than 1 in the RFDW.

-The CW was capable of reducing the cumulative HQ by 60-63%, resulting in values below 1, which indicates that the risk for the three trophic levels studied at the effluent was not significant.

Although further studies are necessary to confirm that these levels of OMCs do not affect the aquatic biota, the use of CWs seems to be a feasible strategy to avoid the discharge of harmful OMCs into estuarine and coastal areas, which may be magnified by increasing the CW inflow.

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Table 1-SM. EC50 values (mg/L) for *Daphnia magna* (48 hours), algae (96h) and fish (96h) used to calculate PNEC based on QSAR models (The Ecological Structure Activity Relationships, ECOSAR Version 1.11).

	Daphnia	Algae	Fish
Surfynol 104	4.39	6.05	6.67
Alachor	8.44	10.597	1.1
Atrazine	20	20	32
Bentazone	215	141	390
Chlorpyrifos	0.35	0.859	0.465
DEET	53	44	92
Molinate	14	15	23
Oxadiazone	0.622	1.36	0.846
Propanil	17	18.6	29
Tebuconazole	3.44	5.27	5.089
Terbutylazine	8.7	10.5	13.6
MCPA	334	304	562
Caffeine	3458	1274	7220
Tributyl phosphate	3.42	5.1	5.09
5TTri	288	156	548
Bisphenol A	4.14	5.78	6.27
Benzotriazole	109	72	197
Carbamazepine	67.5	55.3	116.1
Diclofenac	25.8	41.4	37.7
Ibuprofen	27.8	41.1	41.6
Lorazepam	66.9	58	113
Naproxen	121.5	137.9	193.3
Oxazepam	70.7	59.6	120
Primidone	1261	212	2498
Triclosan	0.701	1.443	0.965

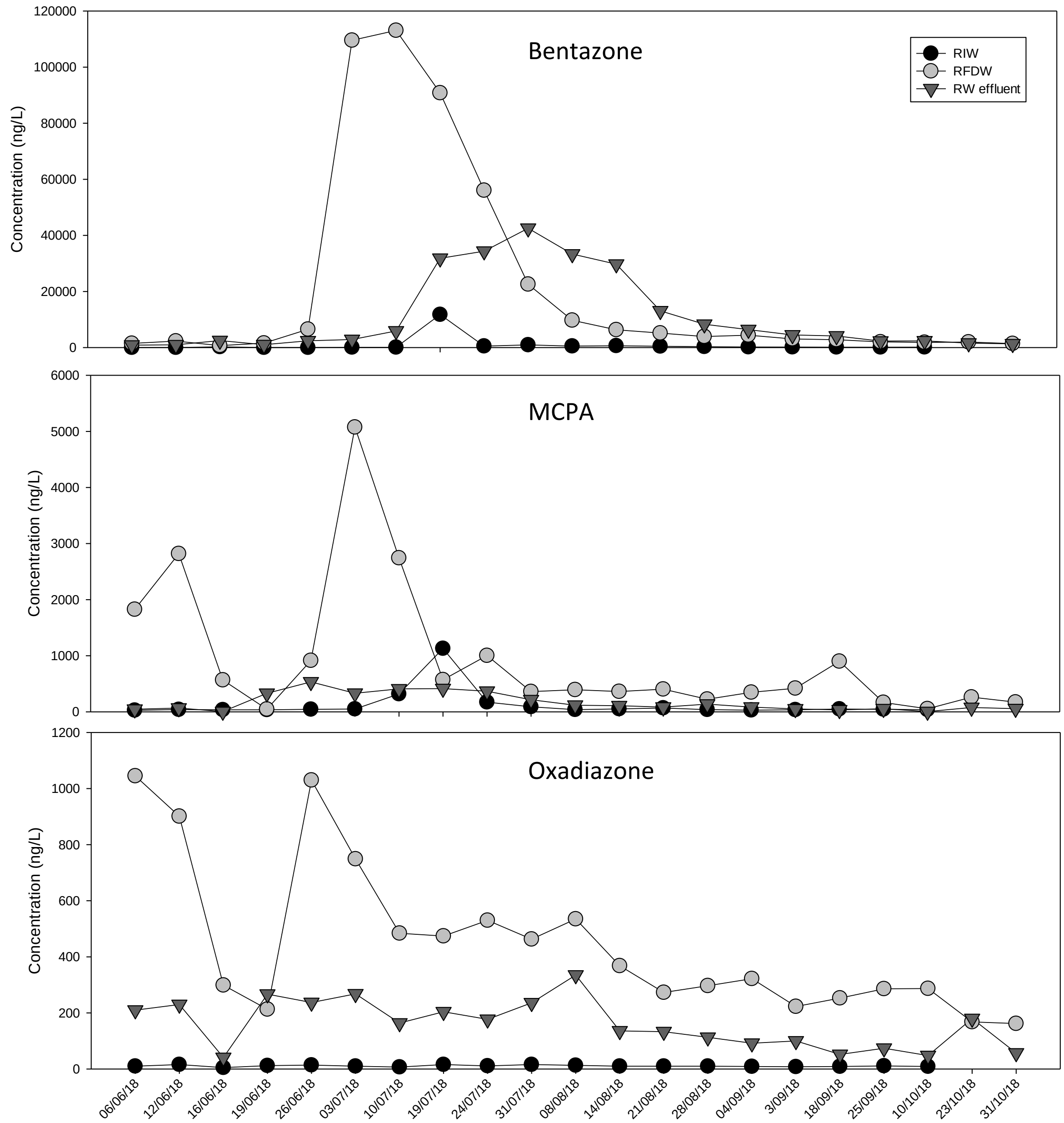

Figure 1-SM. Temporal trend of the concentration of bentazone, MCPA nad oxadiazone in the RIW, RFDW and RW effluent.

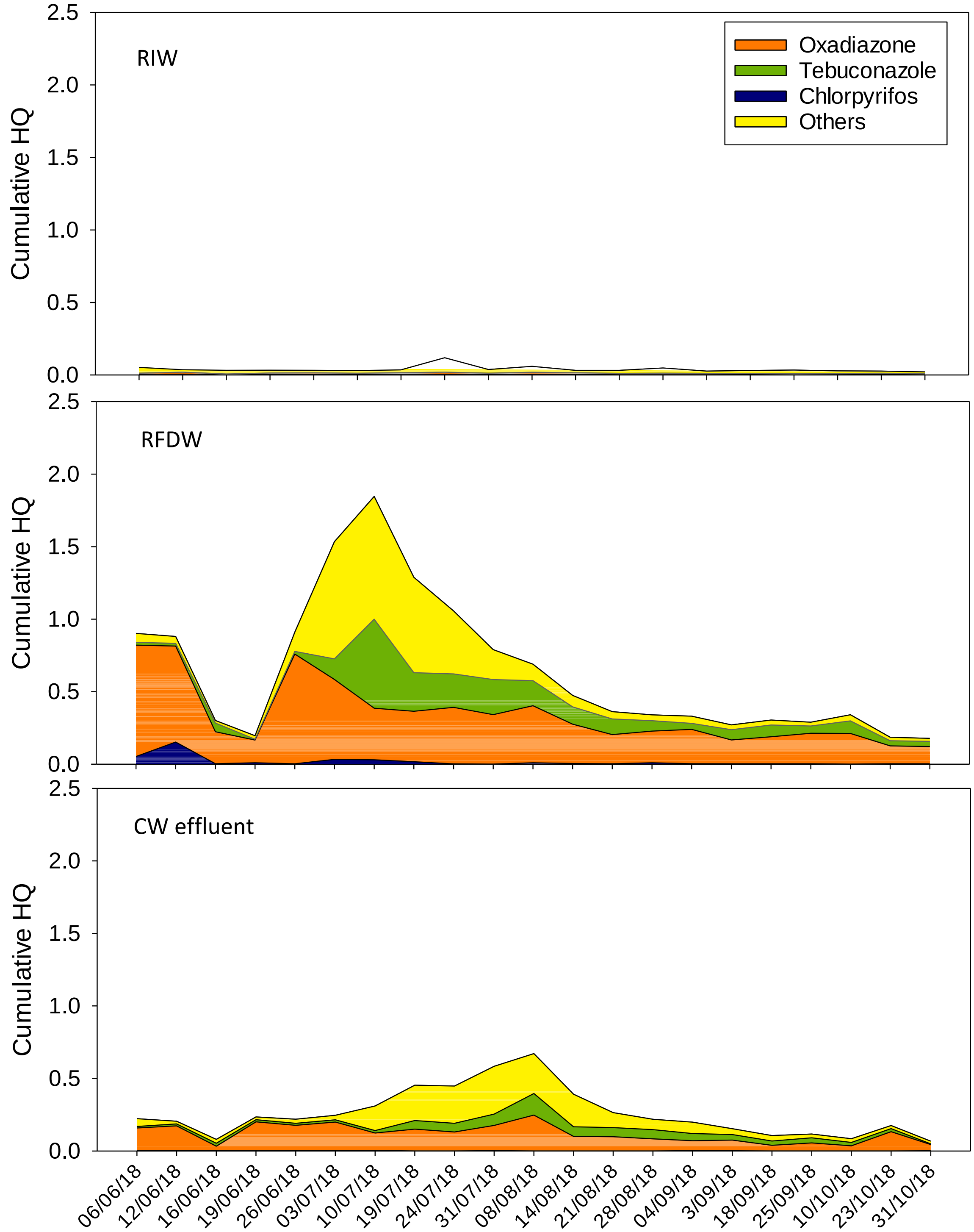

Fig 2-SM. Cumulative HQ for Green algae (96h) in the RIW, RFDW and CW effluent.

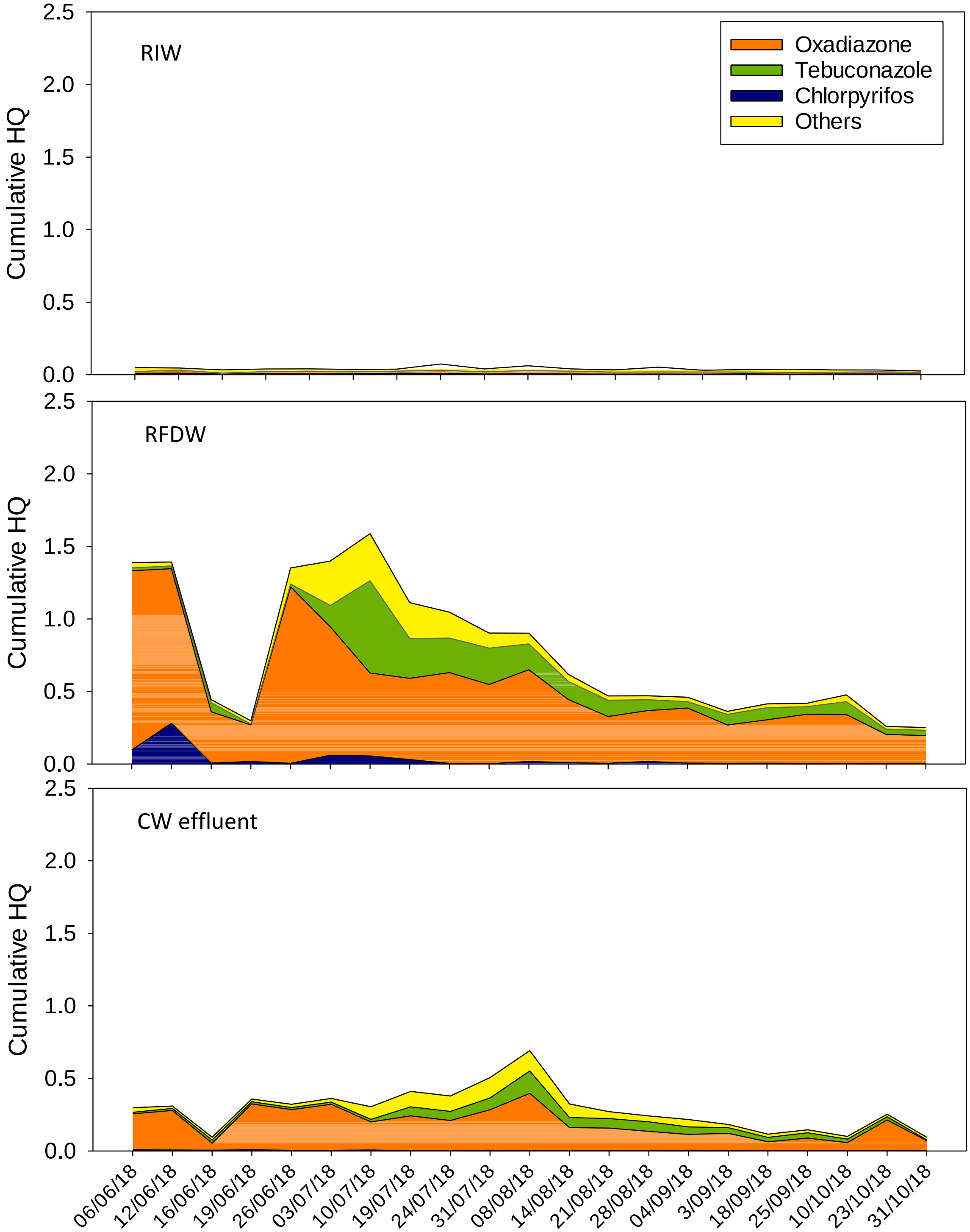

Fig 3-SM. Cumulative HQ for Fish (96 h) in the RIW, RFDW and CW effluent.

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Lorazepam	66.9	58	113
Naproxen	121.5	137.9	193.3
Oxazepam	70.7	59.6	120
Primidone	1261	212	2498
Triclosan	0.701	1.443	0.965

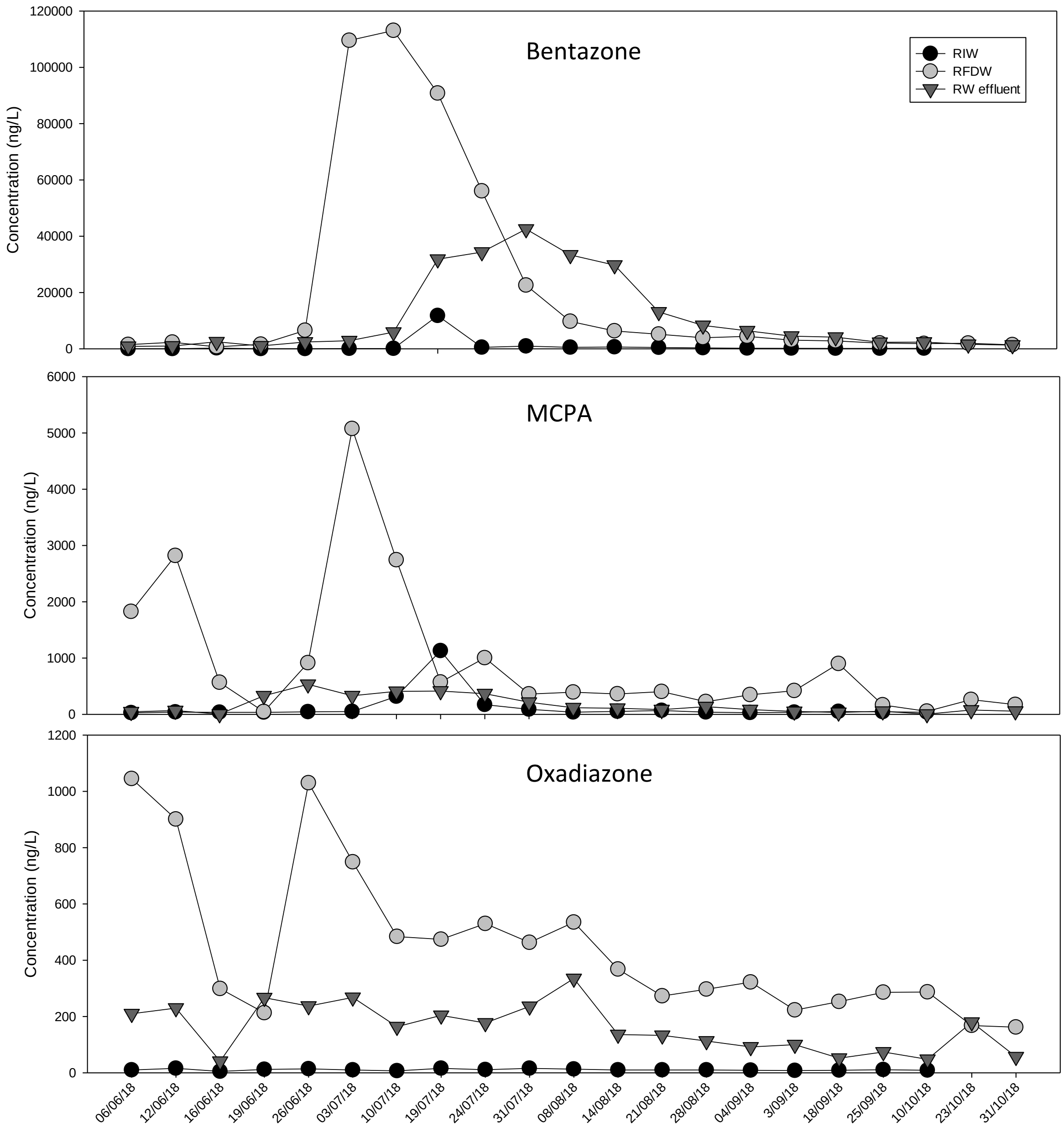


Figure 1-SM. Temporal trend of the concentration of bentazone, MCPA nad oxadiazone in the RIW, RFDW and RW effluent.

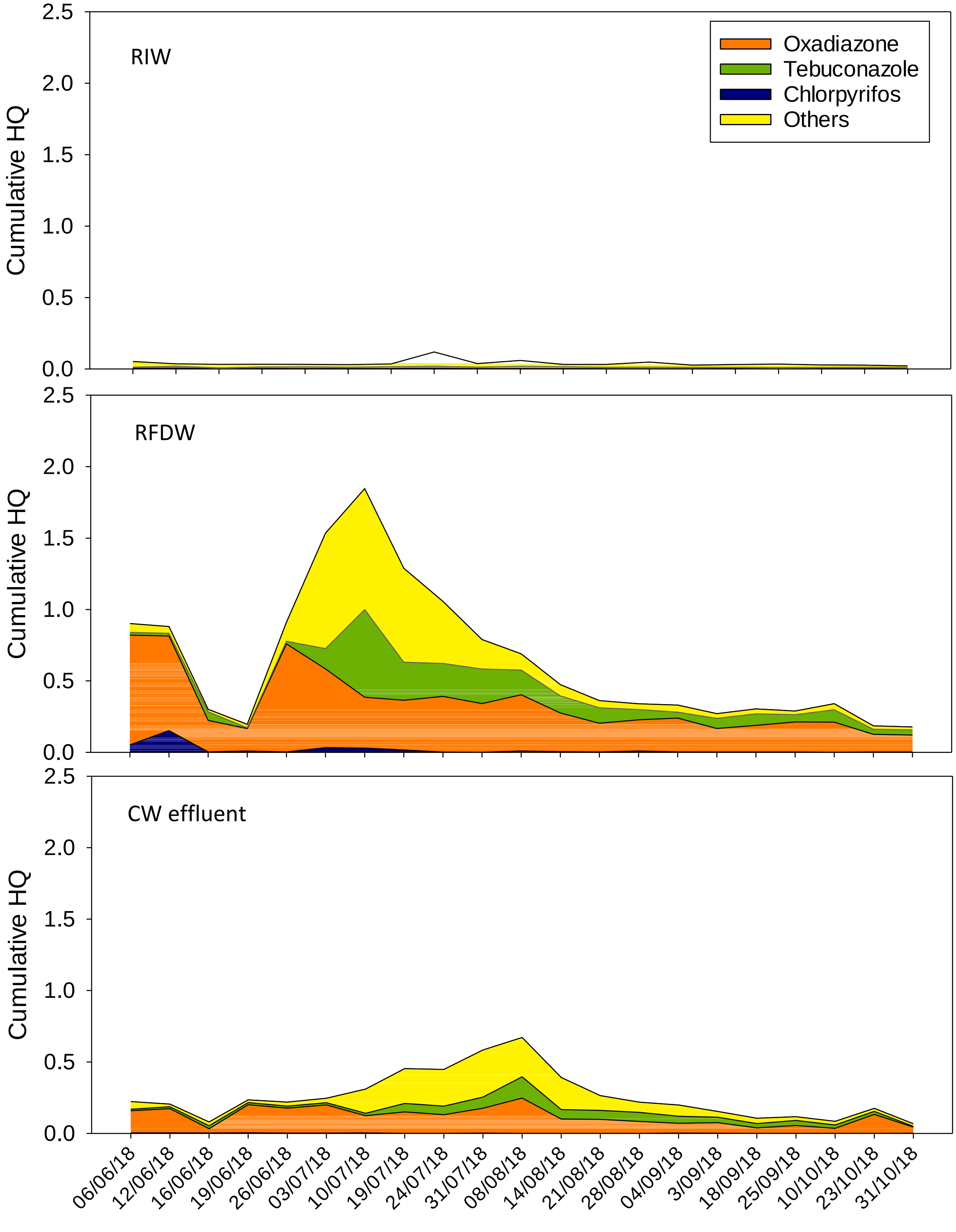
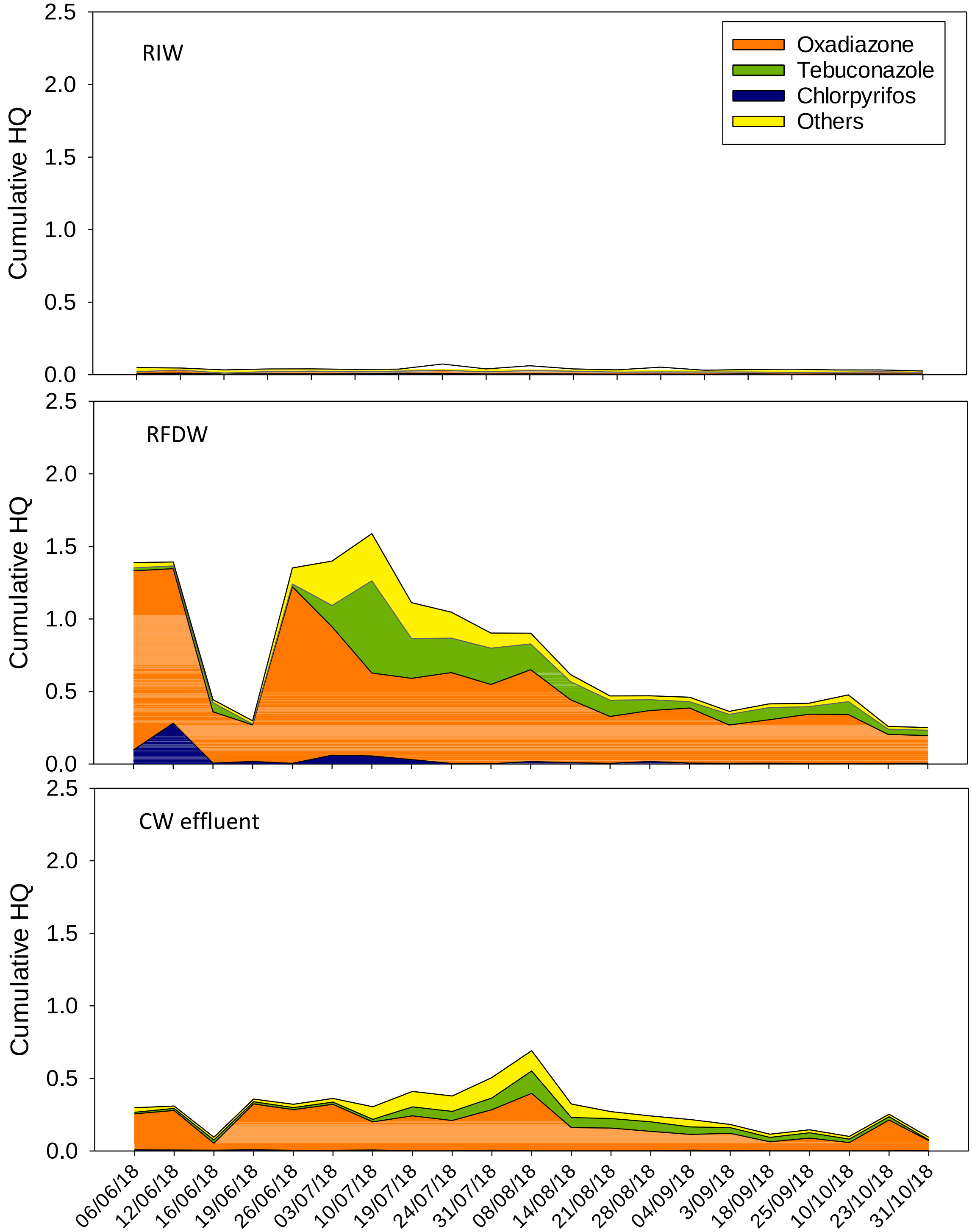


Fig 2-SM. Cumulative HQ for Green algae (96h) in the RIW, RFDW and CW effluent.



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