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Please find enclosed the manuscript **The case of Mar Menor eutrophication: state of the art and description of previously tested Nature Based Solutions** by Álvarez-Rogel, J., Barberá, G.G., Maxwell, B., Guerrero-Brotons, M., Díaz-García, C., Martínez-Sánchez, J.J., Sallent, A., Martínez-Ródenas, J., González-Alcaraz, M.N., Jiménez-Cárceles, F.J., Tercero, M.C., Gómez, R.

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Cartagena 29 of June 2020

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*Research Highlights

Highlights

Mar Menor receives nutrients, mainly from agricultural discharges

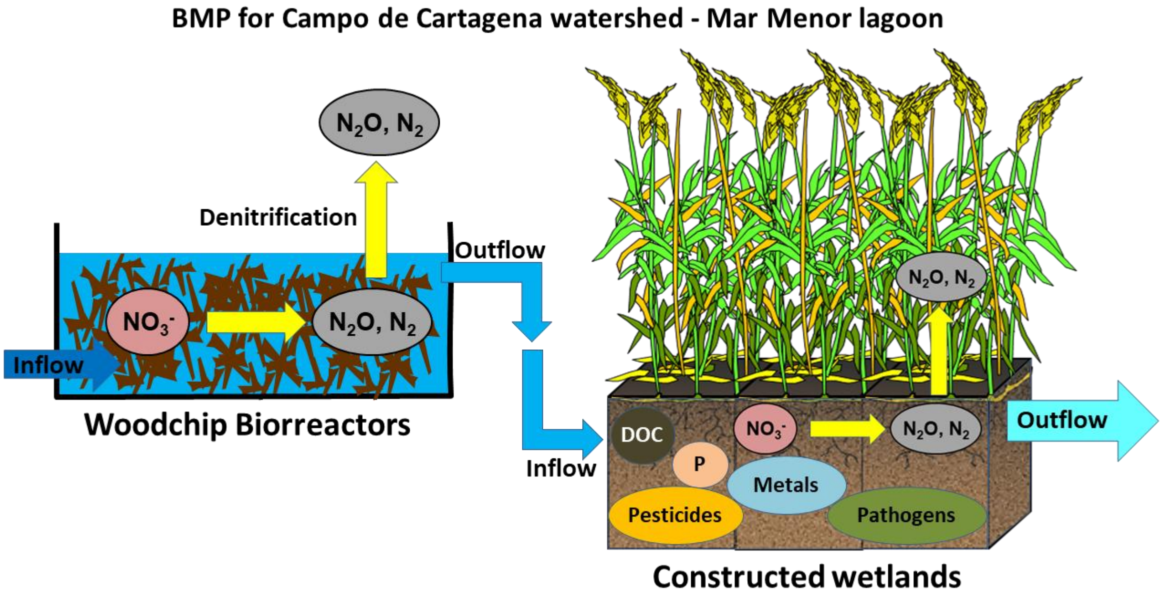
Coastal wetlands acts as buffers protecting the Mar Menor from nutrient inputs

Bioreactors and CWs are recommended BMP for treatment of nutrient enriched discharges

In the Campo de Cartagena BMP should be addressed on a watershed specific basis

BMP should address fertilization and irrigation protocols and soil conservation

Graphical Abstract (for review)



Essential title page information

The case of Mar Menor eutrophication: state of the art and description of previously tested Nature Based Solutions

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The case of Mar Menor eutrophication: state of the art and description of previously tested Nature Based Solutions

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Abstract

The Mar Menor (SE Spain), the largest hypersaline coastal lagoon of the Mediterranean basin, suffers a severe eutrophication crisis due to the nutrients (mainly nitrate from agricultural origin) that receives from the Campo de Cartagena watershed. This paper update the state of the art in relation with nutrient discharges to the Mar Menor, reviews the role of the coastal wetlands as buffers protecting the lagoon from nutrient inputs, summarize some results of a pilot plant with woodchip bioreactors for nitrate-enriched brine denitrification, and shows the first results obtained in a pilot plant with woodchip bioreactors

and constructed wetlands for treatment of agricultural drainage water and leachates, as well as other effluents, flowing in the Campo de Cartagena. Four strategies are considered for reducing nutrient inputs into the Mar Menor. 1) Reducing the leaching of nitrate to the aquifer and export of nutrients and sediments following heavy rains. This strategy requires improving fertilization practices, soil conditioning and irrigation routines as well as real soil conservation measures in agricultural areas. 2) Development of effective and scalable tools for denitrification of nitrate-rich brine produced by on-farm desalination plants. 3) Capture and treatment of nitrate-polluted water discharged to the Mar Menor via hydrologic networks, subsurface flow, drainage ditches, and others. 4) Preservation and restoration of coastal wetlands. Results obtained in field studies and in our pilot plants support that restoration of coastal wetlands, and construction of woodchip bioreactors and constructed wetlands are effective best management practices to reduce the negative effects of point and no-point source pollution affecting the Mar Menor.

Key words: eutrophication crisis, constructed wetlands, woodchip bioreactors, nitrate pollution, littoral lagoon, non-point pollution source

1. General characteristics of the Mar Menor lagoon and the Campo de Cartagena watershed and main environmental impacts

1.1. The lagoon and the watershed

The Mar Menor lagoon (135 km^2) and its adjacent watershed (Campo de Cartagena; 1316 km^2) are located in the Region of Murcia, southeast Spain (Figure S1). The climate is Mediterranean semiarid; mean annual temperature, precipitation and potential evapotranspiration are 18˚C, 300 mm and 1275 mm, respectively (Jiménez-Martínez et al., 2011).

The lagoon is the largest coastal hypersaline one in the Mediterranean basin. It has a volume of 645 hm^3 and a mean depth of ≈ 4.5 m. It is separated from the Mediterranean Sea by a narrow sand bar. Currently, there are three inlets connecting the lagoon with the Mediterranean. One of them was dredged in 1975 to allow the transit of recreational boats, enhancing water exchange with the Mediterranean and decreasing the lagoon salinity from >50 PSU to 42-46 PSU. This change altered population levels of the main aquatic species and allowed the entrance of new species with lower salinity tolerance (Scientific Advisory Group for el Mar Menor, 2017).

The Mar Menor was originally mostly surrounded by a belt of associated salt marshes, which were reduced in extent by urban development from 1960-2000. The lagoon and the remnant wetlands are included in the Ramsar Convention. Other declaration of protection are: Specially Protected Areas of Mediterranean Importance (SPAMI), Site of Community Importance (SCI) and Special Protection Area (SPA).

The lagoon and the wetlands experienced heavy pressure from mining wastes since the end of 19^{th} century, pressure from the development of local tourism since the 1960s and direct and indirect effects of intensive agriculture since the 1970s. Both, development from tourism and agricultural intensification, were responsible for pouring large amounts of nutrients into the lagoon. Tourism and population increase associated to intensive agriculture expansion produced poorly-treated wastewater, rich both in N and P compounds, however this situation was mostly corrected by the mid-2000s and over the last 10 years has not been a major source of nutrients.

Agricultural activities deserve particular attention. Until the early 1970s the agrarian system was mainly drylands, with scattered irrigated agriculture fed by wells, powered first by windmills and later by electric pumps. The inauguration of the Tagus–Segura aqueduct in 1979from central to SE Spain allocated up to 120 $hm^3\ y^{-1}$ for irrigation in the Campo de Cartagena. For comparison, water as natural precipitation over the entire watershed amounts to ≈ 400 $hm^3\ y^{-1}$. In the last 40 years agricultural land under irrigation grew by ten-fold, currently covering about 30-38% of the basin (≈ 40,000-50,000 ha). The Campo de Cartagena nowadays is an important supply point of agricultural products to European markets, especially for vegetables during winter. The extremely high intensity of agricultural production is sustained by fertigation although high amounts of manure are also applied, particularly in order to condition the soils of vegetable-oriented farms prior planting.

Presently, irrigation is maintained by a combination of Tagus-Segura water from the Tagus-Segura aqueduct, desalinated seawater, reused wastewater and groundwater withdrawal primarily sourced from the Quaternary aquifer. However, since the aquifer is salinized (≈3.9 to ≈6.5 dS m^{-1}) it is necessary to lower the salinity to the extracted groundwater by mixing with freshwater supplies or desalination. This desalination is usually performed in small reverse-osmosis (RO) desalination plants installed on local farms. Since the end of the 1990s, the brine produced from these small RO has been collected in a > 60 km network of pipes which usually has discharged the brine to the Mar Menor lagoon. García-Pintado et al. (2007) found an average of 62 mg L^{-1} N-NO_3^- in these brines over a 14-month monitoring period between (February 2003 to April 2004), and observed concentrations as high as > 130 mg L^{-1}.

A consequence of expansion and intensification of agriculture was the enhanced recharge of aquifers (due to increase infiltration from irrigation inputs), which in turns increased submarine groundwater discharge (SGD) to the lagoon and produced deep changes on hydrology close to the coast where ephemeral surface watercourses (named *ramblas*) turned to permanent flow. Intense fertigation and addition of manure led to the pollution of surface and subsurface waters with nitrate. Groundwater in the Quaternary aquifer ranges from 22-34 mg L^{-1} N-NO_3^- (Jiménez-Martínez et al., 2011, 2016, although closer to the coast the water can contain 30-45 mg L^{-1} (Tragsatec, 2020).

1.2. Eutrophication crisis

The impacts of increased nutrient input to the Mar Menor lagoon were initially buffered by the self-regulatory, functional mechanisms. This ended when the lagoon was pushed beyond a threshold point, taking the system from the original oligotrophic state to a eutrophic state (Ruiz-Fernández et al., 2019). Beginning in the summer of 2015 a phytoplankton bloom was triggered, which later peaked in 2016 (Ruiz-Fernández et al., 2019) turning water turbid and greenish throughout the lagoon. As a consequence, light did not reach the lagoon bottom during nine months of the year and 85% of the area typically covered by benthic macrophytes and their associated community was completely lost (Belando et al., 2019). After this event, the network of pipes transporting brines to the lagoon was closed by the regional government, and the use of on-farm desalination plants without a process for brine denitrification was forbidden. However, some of the authors of this paper found evidences that brines were still being discharged into hydrologic network through subterranean drains and other concealed pathways. Between 2016 and September 2019 the lagoon alternates between clearer (Secchi depth 4-5 m) and low transparency states (1-2 m; www.canalmarmenor.es). In September 2019 a storm event yielding $\approx$ 250 mm over 24 h led to the discharge of large amounts of freshwater, sediments and nutrients to the lagoon. In the weeks immediately following the event, atmospheric conditions were relatively stable, limiting the mixing of water between the less saline surficial water and the more saline deep water. The stratification of the water column and the priming of the system by nutrient input provoked oxygen depletion at lower depths of the water column leading to an euxinic episode (anaerobic and sulfidic conditions) that killed most of the plants and animals present.

1.3. Water and nutrient routing from the watershed to the lagoon, the present situation

Between November of 2016 and January 2018 an exhaustive inventory of surface water reaching the lagoon was carried out by some of the authors of this paper (https://www.canalmarmenor.es/monitorizacion-actividad-hidrologica). The routes of the water in the watershed were also tracked and indirect indicators of SGD were measured at 100-m resolution in the lagoon coast. From January 2018 until June 2020 water sampling was still conducted, although less frequently and at a fewer number of sites. The study revealed that the whole hydrological system is significantly impacted by artificial drainage and flows. A total of > 30 surface water locations were found to be discharging into the lagoon. Their typology, flow volume and persistence are highly variable. Some of these sources of discharge into the lagoon include: natural discharges in beaches which appear following large rain events, municipal stormwater networks, drainage channels from infrastructure (e.g., an airport), overflow systems for subterranean drains, and outlets of hydrological networks (e.g., open channel watercourses).

Most of the discharges at these points were attributable to lateral groundwater discharge in the drainage network, drains, stormwater pipes, etc. This water had a typical N-NO_3^- concentration of 30-40 mg L^{-1} and < 1 mg L^{-1} of total P; similar to that of the Quaternary aquifer close to the coast. However, lower and higher concentrations were also found. Lower nitrate concentrations (≈ 20 mg N-NO_3^- L^{-1}) were found in seawater pumped out of commercial and residential spaces below the level of the aquifer, which was pumped into the stormwater network. Higher concentration (55-80 mg N-NO_3^- L^{-1}) were possibly associated with concealed brine discharges from on-farm desalination plants.

Total water flow from these sources and, hence, their associated N load into the lagoon are highly variable. In the early 2000s García-Pintado et al. (2007) found discharge in the largest regional hydrologic network (Albujón) to lag large rain events by about two months. However, the presence of human activities is essential to explain flow dynamics and N load. In January 2017, maximum flow and load were 31908 m^3 d^{-1} and 1084 kg N-NO_3^- d^{-1}, respectively. This high discharge was associated to 3-day, 200 mm rain event occurred in December 2016. Minimum flow and load were found in October 2017, which measured 4713 m^3 d^{-1} and 119 kg N-NO_3^- d^{-1}. The difference was attributable not only to seasonal drought but also to the pumping of flow from the outlet of the Albujón to a desalination plant 16 km north of the outlet, where raw water and/or brines were discharged into the Mediterranean.

This information relates only to the surficial discharges, to the lagoon although SGD is the most important source of nitrate inputs to the lagoon. In our monitoring, indirect indicators of groundwater discharge (pore water salinity in the beach 1-m inland to the shoreline) showed evidences of subsurface water flowing to the lagoon along most of the 35 km of the coast, although uncertainty about water discharge and N loads remains high. The two most recent estimations of subsurface discharge to the lagoon are 40 hm^3 y^{-1} (Domingo Pinillos et al., 2018) and 8.5-11.6 hm^3 y^{-1} (Tragsatec, 2020). Taking 35 mg as the mean N-NO_3^- concentration on the Quaternary aquifer close to the lagoon (Tragsatec, 2020) these two estimations of discharge would result in a load of 3836 kg N-NO_3 d^{-1} and 815-1112 kg N-NO_3^- d^{-1}, respectively. However, based on field works (Álvarez-Rogel et al., 2006) it is feasible that this flow experiences denitrification processes in anoxic soils and sediments of the coastal wetlands and in the beaches, where artificial sand covers usually contain anoxic sediments. If this is the case, the true load of $N\text{-}NO_3^-$ flowing to the lagoon through groundwater discharge would be less than these estimates.

Finally, the third component of water and nutrient inputs into the lagoon are flood events. Between 2015 and 2020 there were two >200 mm events occurring in December 2016 and September 2019. The latter was especially relevant as it discharged > 60 hm^3 to the Mar Menor and triggered the anoxia event previously described. In the sampling carried about by the authors during this event gave a 95% confidence interval for $N\text{-}NO_3^-$ concentration of water discharging to the lagoon of 4.05 - 7.70 mg L^{-1}. Extrapolated to the total volume of discharge during this event, this would amount to a load of 243-462 Mg $N\text{-}NO_3^-$. For soluble reactive phosphorus (SRP, $P\text{-}PO_4^{3-}$) the confidence interval was 0.85-1.02 mg P L^{-1} and a load of 51-61 Mg SRP. These inputs are clearly huge sources of nutrients, especially so for P as surface waters in during 'baseflow' and subsurface groundwater discharges have much lower P concentrations. To give a sense of the impact of SRP inputs from this flood, estimates of total dissolved SRP in the lagoon in June 2019, prior to the September 2019 event, was < 0.5 Mg SRP. The recovery of the lagoon is expected to be a long and very complex process, in which the improvement of agricultural practices must be necessarily involved. The latter should be complemented with the implementation of best management practices (BMPs) in the watershed to protect the lagoon against the effects of point and non-point pollution. The following sections describe the application of woodchips bioreactors and constructed wetlands for pollution mitigation, review former field and greenhouse studies that demonstrated the effective role of coastal wetlands in reducing the flow of nutrient-enriched water to the Mar Menor, and summarize recent works with denitrifying bioreactors and constructed wetlands for treatment of polluted waters in the study area. Finally, a proposal for implementation of these techniques at watershed scale is discussed.

2. Woodchips bioreactors and constructed wetlands: best management practices to improve environmental quality in agricultural watersheds with intensive use

2.1. Woodchips bioreactors

Woodchip bioreactors (also known as denitrifying bioreactors) consist of trenches or containers filled with a carbonaceous material (usually woodchips or other plant residue) through which the nitrate-enriched water is passed at an established hydraulic residence time (HRT). The carbonaceous material provides a substrate for biofilm growth and an organic carbon source for anaerobe microorganisms to complete denitrification. Woodchip bioreactors provide a practical, low-cost means of nitrate reduction (Christianson et al., 2009), are easy to install require low maintenance (Schipper et al., 2010; Christianson and Helmers, 2011; von Ahnen et al., 2016) and their use can increase the value of local organic wastes which serve as the carbon media for these systems. While bioreactors have high denitrification capacity, they are specifically designed for the retention of SRP, pesticides and pathogens (Christianson and Helmers, 2011). Moreover, high DOC concentrations and other compounds (e.g. sulphides, SRP) leached from the woodchips have been observed, mainly during the start-up period when woodchips are fresh (Healy et al., 2012; Malá et al., 2017). However, this excess pool of potential pollutants is usually washed away after the first weeks, until the system reaches steady-state operation conditions (Fenton et al., 2014; Malá et al., 2017). Since these bioreactors can operate for periods longer than one decade (Schipper et al., 2010b; Fenton et al., 2014), the initial release of undesirable compounds is not considered a drawback. Some possible pollutants from bioreactors (e.g., H_2S) should be monitored in the case that bioreactors suffer any malfunctioning (e.g., excessive retention time; Lepine et al., 2016).

2.2. Constructed wetlands

Constructed wetlands have been shown to be effective for wastewater depuration from a number of different sources (e.g., Knight et al., 1993), including the treatment of agricultural non-point source pollution worldwide (Mitch et al., 2014; Tournebize et al., 2017; Vymazal, 2017). In constructed wetlands, essential processes that take place in natural wetlands are recreated through specific engineering designs. As results, retention, transformation, degradation and removal of pollutants occur (Howard-Williams 1985). Design parameters, such as hydrological load and regime (continuous *vs* flood pulse), type of flowpath (free water surface *vs* subsurface flow system), hydraulic retention time, type of substrate plant species, and vegetation coverage, all highly affect wetland performance and are considered in the wetland design according to the inflow water quality (Hammer, 1989; Reed et al., 1995; Verhoeven and Meuleman, 1999). Subsurface flow wetlands are more appropriate when nitrate removal through denitrification is a priority (e.g., Reed and Brown, 1995). A substrate with medium grain size (e.g., gravel), perform better than sand which offers a lower hydraulic conductivity and increased risk of clogging (e.g., Sandford et al., 1995). The use of inert mineral substrates, in comparison to biologically active media (e.g., soils) slow down the growth of microorganisms, an essential biotic element for water depuration. With a secondary role, vegetation is important because it offers a root system that has a positive effect on the growth of microorganisms. Vegetation also increases oxygen availability in the rhizosphere (Stottmeister et al., 2003) which can be especially important in subsurface flow systems that have been proven to be essential for NO_3^- and other pollutant removal (Tercero et al., 2015; Álvarez-Rogel et al., 2016). In addition to all these variables of wetland design, wetland performance will also depend on local conditions such as chemical composition of agricultural waters and climatic conditions (Surface et al., 1993; Diaz et al., 2012; Tournebize et al., 2017).

3. The role of the coastal wetlands of the Mar Menor lagoon buffering eutrophication

This section summarizes main results obtained from a number of field and greenhouse studies carried out between 2002 and 2017 to evaluate the extent of nutrient enrichment in two ramblas and the role of the Marina del Carmolí and Lo Poyo salt marsh (Figure S1), to protect the Mar Menor against nutrient enrichment.

3.1. Characteristics of the studied wetlands

The Marina del Carmolí is the largest salt marsh (≈320 ha) on the coast of the Mar Menor lagoon. The salt marsh receives water from the Rambla de Miedo and Rambla de Miranda, which flow across the marsh before reaching the lagoon. The first has suffered urban waste water discharges from a wastewater treatment plant over a long period of time and, since the rambla originates in the old La Unión-Sierra de Cartagena mining district transports metal mine wastes to the salt marsh (Jiménez-Cárceles et al., 2008b). The second rambla flows across areas of intensive fertigation areas in the Campo de Cartagena.

Lo Poyo salt marsh (≈ 211 ha) is strongly affected by metal mine wastes carried out from the old mining district of La Unión-Sierra de Cartagena. Concentrations of metals and metalloids in some sectors of the salt marsh and in the submerged sediments adjacent to the shoreline are extremely high (188-530 mg kg^{-1} As, 11-51 mg kg^{-1} Cd, 56-137 mg kg^{-1} Cu, 708-5640 mg kg^{-1} Mn, 4990-11600 mg kg^{-1} Pb, and 3550-20600 mg kg^{-1} Zn) and part of these metals are bioavailable and transferred to biota (Álvarez-Rogel et al., 2004; María-Cervantes et al., 2009; Conesa et al., 2011). In the area most affected by mining wastes vegetation is scattered or even absent, leaving large areas of bare soil, which favours the dispersion of polluted particles by water and wind erosion. Hence, while Marina del Carmolí works as an active buffer protecting the Mar Menor from nutrient inputs, the functioning of Lo Poyo salt marsh is compromised and it is a source of pollution by itself.

3.2. Field studies

Between July 2002 and July 2003, water samples were collected bimonthly from Rambla de Miranda and Rambla de Miedo just before reaching the Marina del Carmolí. Additionally, sampling plots were established across the salt marsh in two transects perpendicular to the shoreline following the channel bed of the two ramblas (Figure S1), for collecting water samples seasonally. For more details see Álvarez-Rogel et al. (2006, 2007) and Jiménez-Cárceles and Álvarez-Rogel (2008). Between September 2005 and November 2006, new water samples were collected from the Rambla de Miranda and Rambla de Miedo in the same locations as previous sample collection (Figure S1). In addition to regular monthly sampling (considered as base flow regime) extra samples were collected immediately after three storm events (considered as flash-flood events). Water discharges were measured and the instantaneous nutrient load estimated for each sampling time. Annual loads of nutrients were calculated separately for base flow and flash flood events according to the criteria of García-Pintado et al. (2007). Additional information about the study site is given in González-Alcaraz et al. (2012b).

Between July 2002 and July 2003 the N-NO_3^- concentrations in Miranda (≈25-62 mg L^{-1} N-NO_3^-) exceeded the critical level of 15 mg L^{-1} N-NO_3^- stablished by the EU Directive 91/271/CEE to consider eutrophication risks (Table 1). By contrast, concentrations in the water from Miedo were almost always < 11.3 mg L^{-1} N-NO_3^-. However, P concentration in Miranda (≈ 0.1-0.2 mg L^{-1} SRP) were much lower than in Miedo (≈0.8-2.6 mg L^{-1} SRP). As was the case for $N\text{-}NO_3^-$, SRP concentrations were also higher than the critical levels of the EU Directive 91/271/CEE (1-2 mg L^{-1} of total P).

Between September 2005 and November 2006 discharge of Miedo was 0.154 hm^{-3} y^{-1} and on Miranda 1.201 hm^{-3} y^{-1}. Annual amounts of water flowing during the three storms events were lower (0.005 h m^{-3} y^{-1} for Miedo and 0.010 for Miranda) than base flow (0.148 hm^{-3} y^{-1} for Miedo and 1.04 hm^{-3} y^{-1} for Miranda). Although for both ramblas N-NO3$^-$ concentrations under base flow (≈60 mg L^{-1} in Miranda and ≈1.13 in Miedo) and storm events (≈50 mg L^{-1} in Miranda and ≈1.35 in Miedo) were similar, the continuous discharges led to a total $N\text{-}NO_3^-$ load discharged during base flow two orders of magnitude higher than was discharged during storm events (Table 2). Regarding SRP, although the concentrations in Miranda were much lower than in Miedo, the higher total annual discharge of Miranda resulted in similar annual total SRP loads in both ramblas (0.16 Mg y^{-1} and 0.19 Mg y^{-1}).

The results of both field campaigns indicated different pollution sources affecting both ramblas and showed that the continuous flow was much more relevant in $N\text{-}NO_3^-$ discharges than punctual events during the study period. Miranda received nutrient inputs from agricultural sources while Miedo was mainly affected by dumping of insufficient treated urban waste water. The results indicated that the base flow sustained a substantial discharge of $N\text{-}NO_3^-$ enriched water from agricultural origin into the salt marsh, while inputs from wastewater-treatment plants were of much lower magnitude.

Within the salt marsh, as the water was flowing through the Marina del Carmolí the wetland was found reduction of $N\text{-}NO_3^-$ and RSP concentrations of nearly 100%, although some seasonal variation was observed. In the driest months, when the surface discharge decreased and water circulated slowly, the processes involved in reduction of nutrients were more efficient than in rainy periods in which water velocity increased and residence time of water in the wetland decreased, as observed in other wetlands (Woltemade, 2000; Darviche-Cridao , 2017).

3.3. Greenhouse studies

Greenhouse experiments helped to understand what mechanisms were more relevant for nutrient removal in the studied salt marshes. Experiments were carried out with metal-polluted and non-polluted soils, collected from the Marina del Carmolí and Lo Poyo salt marsh. More details can be found in González-Alcaraz et al. (2011, 2012a, 2013), Álvarez-Rogel et al. (2016), and Tercero et al. (2015, 2016).

Pots (13.5 cm × 14 cm) experiments were performed with metal-polluted soils collected from the Marina del Carmolí (pH=7.8, water soluble (ws) Cd 18 ± 3 μg L^{-1}; ws Zn 2169 ± 1393 μg L^{-1}; ws Pb 6.6 ± 5.5 μg L^{-1}), and Lo Poyo salt marsh (pH=6.2, ws Cd 237 ± 133 μg L^{-1}; ws Zn 26 995 ± 13 680 μg L^{-1}; ws Pb 47 ± 27 μg L^{-1}). Unvegetated vs. vegetated (with *Sarcocornia fruticosa* or *Phragmites australis*) treatments were compared for both soils. Pots were flooded during 15 weeks with eutrophic water (dissolved organic carbon (DOC) ≈26 mg L^{-1}, SRP ≈7.5 mg L^{-1}, N-NO_3^- ≈ 41 mg L^{-1}) and then left two weeks drying. In the soil with pH=7.8, during the second day of flooding N-NO_3^- removal efficiencies were between 70% and 90% (≈ 1.01–1.12 g N-NO_3^- m^{-2} d^{-1}). These results indicated that in this soil denitrification (reduction of NO_3^- to gaseous end-products N_2O or N_2 via anaerobic microbial respiration) was the main mechanism associated with NO_3^- removal regardless of the presence of plants, in agreement with previous studies in wetlands (Xue et al., 1999; Vymazal, 2007). Similar results were obtained in the soil of pH=6.2 with plants, but not in this soil when plants were absent where removal efficiencies for N-NO_3^- concentrations were only lower than ≈45% after 15 weeks of flooding. In this acidic soil with higher water soluble metal concentrations, microbial activity could be hindered and plants could have played a more relevant role in two ways: 1) by absorbing NO_3^- and 2) by providing a physical support for denitrifiers in the rhizosphere (Hinsinger et al., 2009). Hence, revegetation of salt marsh zones affected by acidic mining wastes is paramount to improve their functions to act as buffer strips against excessive NO_3^- contents flowing to the Mar Menor.

Regarding SRP, pore water concentrations decreased rapidly in both soils (by ≈ 80–90 % during the first 3 h of flooding), with and without presence of plants. Hence, SRP retention by the soils was the main mechanism involved in removal of SRP from pore water, with plants playing a minor role.

A mesocosms experiment was performed with unpolluted soil collected from la Marina del Carmolí, unvegetated vs. vegetated (with *Phragmites australis*) treatments. The mesocosms (0.5 m × 0.5 m × 1 m containers), were flooded for ≈4 weeks and then left to dry for ≈3 weeks. This cycle was repeated six times over 44 weeks. Two eutrophication levels were assayed: 1) low nutrient levels (LN): N-NO_3^- 4.5 mg L^{-1}, SRP 0.19 mg L^{-1}, DOC 10 mg L^{-1}; and 2) high nutrients level levels (HN): a ten-fold increase in concentrations of N, P and DOC relative to the LN treatment. More details can be found in Tercero et al. (2015, 2016) and Álvarez-Rogel et al. (2016). The results showed that denitrification was the main mechanism for N-NO_3^- removal, regardless of the N-NO_3^- concentration in the flooding water (4.5 or 45 mg L^{-1}) or the presence of plants. However, the effectiveness of nitrate removal was modulated by the temperature (which varied with the seasons) and the flooding conditions. During warmer seasons (soil temperature ≈15 to ≈30 ºC) pore water N-NO_3^- removal reached ≈90% in one week, but during colder periods (soil temperature ≈10 to ≈15 ºC) it decreased to ≈40–50%. This was related with a higher microbial activity during the warmer months of the experiment. Denitrification was confirmed by the N_2O emissions detected in all the treatments (813 ± 1192 N-N2O µg m^{-2} h^{-1}, max= 81590, min=16), but emissions were modulated by *P. australis*, which had for the effect of reducing N_2O emissions during the first days of the drying phases.

More than 90% of the SRP added with the eutrophic water was removed during the first 24h of flooding, regardless of the nutrient load, the season of the year or the presence/absence of *P. australis*. A P fractionation showed that Ca/Mg compounds were the main contributors to soil P retention (≈34-53% of the total P in the soil was extracted from this fraction). The biomass of *P, australis* accumulated ≈27% of the total SRP added in the treatment with water of low P load, while the biomass accumulation accounted for ≈12% of total SRP added in the treatment with high P load.

4. Pilot experiences with woodchip bioreactors and constructed wetlands

Before their implementation as in-field management practices, pilot tests are necessary to optimize the functioning of bioreactors and wetlands according to each specific purpose. As described in previous sections, in the Campo de Cartagena there are three main target waters: brine from desalinations plants, agricultural drainage water and surface runoff flowing in surface watercourses. The first is exclusively connected to agricultural activities since brine is the waste resulting from desalination of groundwater for irrigation. The third is also mainly related with agricultural activities, but can be also influenced by occasional urban waste water disposal in the watercourses. Typical brine is highly saline (EC≈18 dS m^{-1}), heavily N-NO_3^- enriched (≈ 45 mg L^{-1}), contain negligible concentrations of DOC and SRP, and generally contain a lack of microorganisms. Water flowing in surface watercourses and drainage ditches can have a variable composition, but is typically less saline, than brine (EC ≈ 5-7 dS m^{-1}), had less N-NO_3^- (≈ 22-34 mg L^{-1}), and contains low concentrations of DOC (≈ 4-7 mg L^{-1}) and SRP (< ≈ 0.33 mg L^{-1}). Water in these surface watercourses can often contain microorganisms (e.g. coliforms and *Escherichia coli*) as well as pesticides.

Salinity may negatively affect the activity of those microbes involved in water treatment processes by forcing them to divert energy from other essential processes (organic matter mineralization, nitrification, denitrification) to control their osmotic balance. Additionally, low DOC concentrations, typical of both the brine and surface drainage water, may negatively affect NO_3^- removal by making denitrification carbon limited, as has been shown in both natural and constructed wetlands (Pochana et al., 1999; Bachand and Horne, 1999, Arango et al., 2007; Inwood et al., 2007).

6.1. Pilot plant with woodchip bioreactors for denitrification of brine from desalination plants

While woodchip bioreactors have been used extensively for denitrification of freshwater, a recently novel application of woodchip bioreactors is their use in the treatment of highly saline brine from desalination plants treating groundwater. Preliminary investigations were performed to determine the suitability of woodchip bioreactors for this application (Díaz-García et al., 2020). After determining woodchips were the most suitable carbon media for denitrifying bioreactors, field experiments of woodchip bioreactors were conducted. These experiments took place at the Agri-food Experimental Station Tomás Ferro (ESEA) of the School of Agricultural Engineering of Technical University of Cartagena (ETSIA-UPCT) located in the Campo de Cartagena. The research station is an open-air facility and includes a desalination pilot plant using reverse osmosis (RO), that withdraws water from the polluted Quaternary aquifer, with a treatment capacity of 130 m^{-3} d^{-1}. Typical brine obtained in this facility from the one- and two-stage RO processes have EC values of 17 ±

1 to 39 ± 3 dS m^{-1}, respectively, and N-NO_3^- concentrations of 48 ± 2 to 154 ± 33 mg L^{-1}. The brine also contains high levels of other salts, including Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, and Mg^{2+}.

In 2017 pilot-scale woodchip bioreactors were constructed at the ESEA station. A total of 18 woodchip bioreactors were constructed using above-ground tanks. All bioreactors were filled with fresh woodchips sourced from local citrus trees, a mixture of fine and coarse shredded woodchips (mean length = 35 mm).

A number of different experiments were performed in the pilot-scale bioreactors, with experiments varying in duration and nature (Díaz-García et al., 2020; Maxwell et al., 2020a and b). Three tanks were used in a long-term experiment (840 days) observing seasonal variation in N-NO_3^- removal rates as well as declines in efficiency over time. Woodchip bioreactors were run in batch mode, with untreated brine added to the bioreactor, and woodchips remaining saturated for a period of 24 h. Other tanks were used in a number of experiments with shorter duration (2 – 10 weeks) testing the effect of drying-rewetting (DRW) cycles on N-NO_3^- removal performance. These bioreactors were also used to determine differences in N-NO_3^- removal rates between brine from the one-stage RO process and the higher strength brine produced during two-stage RO. In some cases, batch experiments were done with a 48 h HRT. Experiments with 24 h HRT had a total of three batch experiments each week, with woodchips being left unsaturated after the third batch for 96 h until the first batch of the following week. Experiments with 48 h HRT had only two batches performed each week, with an unsaturated period of 72 h. At the end of each batch with 24 or 48 h HRT, woodchips were drained, samples collected from the effluent, and woodchips immediately resaturated with untreated brine. The use of a batch process at this research station is not typical for woodchip bioreactors, which more frequently are continuous flow systems, however batch mode was preferred for this application for ease of use by farmers producing regular, discrete volumes of brine.

Results obtained from the pilot-scale bioreactors showed the ability of woodchip bioreactors to successfully denitrify brine. Removal rates in the tanks over 840 days were 5 – 40 g N m^{-3} of saturated woodchips d^{-1}, showing significant seasonal variability and clear decrease in efficiency with time. Rates were highest in the warmer summer months (24.6 ± 0.9 °C) ranging from 18 – 40 g N-NO_3^- m^{-3} d^{-1}, and lowest (18 – 40 g N-NO_3^- m^{-3} d^{-1}) in the cooler, winter months (12.7±1.7 °C). Results from the shorter duration experiments showed that duration of DRW cycles increased subsequent rates of N-NO_3^- removal upon resaturation of the woodchips. Nitrate removal rates were also higher when treating brine from the two-stage RO process, relative to one-stage RO, although effluent from treating the higher strength brine had higher concentrations of dissolved organics at the end of the batch. Further research is needed to determine the usable lifetime of woodchips when used for this application, however the early results from the pilot plant indicate woodchip bioreactors are a suitable tool for denitrification of brine.

6.2. Pilot plant with woodchip bioreactors and constructed wetlands for treatment of water flowing in drainage ditches

6.2.1. Design and characteristics of the pilot plant

This pilot plant is located in the Campo de Cartagena, about 3 km inland from the Mar Menor lagoon (Figure S1), within the facilities of the Los Alcázares urban wastewater treatment plant (UWWTP). Water treated at the pilot plant is obtained from the nearby D7 drainage ditch. The D7 is one of the main channels collecting agricultural drainage water and leachates, as well as other effluents, flowing in the Campo de Cartagena. The water was mainly characterized as having pH ≈ 7.5 - 8.0, EC ≈ 5 - 8 dS m^{-1}, DOC ≈ 6 -10 mg L^{-1}, SRP ≈ 0.03 - 0.16 mg L^{-1}, and N-NO_3^- ≈ 22 - 45 mg L^{-1}.

Bioreactors at pilot plant consist of three excavated trenches (6 m long x 0.98 m wide x 1.2 m depth filled with citrus woodchips through which untreated water from D7 (3 m^3 d^{-1} per bioreactor) is routed to achieve denitrification at 8h, 16h and 24h HRT respectively (Figure S2). Bioreactors were installed at the pilot plant to evaluate their performance under continuous flow, in contrast with the brine denitrification in batch mode as previously described. Because woodchip bioreactors primarily target the reduction of NO_3^-, and due to their potential for leaching other compounds in their effluent (e.g., DOC), the pilot plant was designed with the intention of combining bioreactors and wetlands, two best management practices (BMPs) that can be complementary for pollutant removal.

Constructed wetlands at the pilot plant are designed in a multi-stage treatment system, consisting of three series working in parallel with three treatment phases each (Figures 3 and S1). It is well known that effective nutrient removal in constructed wetlands can be reached only after several growing seasons in which enough below-ground and above-ground plant–microbial interactions have been developed (Mitsch and Jørgensen, 2004). This is a further handicap for denitrification of waters poor in DOC and SRP in conventional constructed wetlands with an inert substrate such as gravel. For that reason, the pilot plant was designed to 1) explore alternatives to conventional gravel wetlands and 2) to analyze the efficiency in pollutant removal of the separate phases which differed in their design.

Phase I of each series consists of three identical subsurface flow cells (40 m^2) planted with *P. australis* and with a media depth of 0.6 m which consists of: limestone gravel with a mean diameter of 12 mm (Series 1); a 7:3 mix (by volume) of gravel+wetland silty soil (Series 2); a 9:1 mix (by volume) of gravel+biochar (Series 3). These proportions were previously tested experimentally to ensure a proper hydraulic conductivity. As an alternative to the use of gravel, which is a conventional substrate for constructed wetlands, we tested the performance of a mixture of gravel and soil obtained from an adjacent wetland with the twofold aim of 1) ensuring the presence of a well stablished community of microorganisms adapted to saline conditions and 2) providing a natural source of DOC during the initial stage of the wetland start-up. Alternatively, a mix of gravel and biochar was used due to reports in the literature of biochar as a promising natural product for water treatment. Biochar has been shown to be effective for the immobilization and retention of pollutants in soil, including organic contaminants (Mohan et al., 2014; Ahmed et al., 2016; Rajapaksha et al., 2016; Li et al., 2017). In addition, it is a source of both recalcitrant and labile carbon (Sohi et al., 2010), with a positive effect on denitrification rates in constructed wetlands (Barchand and Horne, 1999). A positive effect on plant growth has also been described (Hussain et al., 2017). Each cell of Phase 1 receives 5 m^3 d^{-1} of water from the adjacent D7 drainage channel D7 (Figure S3). Water flow from Phase I to Phase III is continuous. Morphometrical and hydraulic features of each treatment Phase are shown in Table 2.

Phase 2 of each series consisted of a free surface flow cell (Figure S3 and S4), whereas Phase 3 of each series is a subsurface flow cell filled with limestone gravel and planted with *Juncus maritimus*.

6.2.2. First results obtained during the starting-up of the pilot plant

Bioreactors

Use of woodchip bioreactors began in May 2019. Based on the previous concerns of leaching of potential pollutants during the bioreactor start-up period, an initial 30-day period of woodchips washing was established. This was necessary to remove the extremely high DOC (≈ 100-1000 mg L^{-1}), SRP (≈ 5 - 20 mg L^{-1}), N-NH_4^+ (≈ 1.5 - 7 mg L^{-1}) and sulphide (≈ 1 - 5 mg L^{-1}) leached from the woodchips during the first weeks. After this initial period, several parameters (e.g., temperature, EC, pH) were measured on a weekly basis in the internal sampling wells of the bioreactor, and effluent samples collected and analysed for

EC, DOC and concentrations of ionic species including NO_3^-. N-NO_3^- removal efficiency (%) was calculated as the ratio between N-NO_3^- concentration in the effluent and N-NO_3^- concentration in the inflow.

Bioreactors did not increase the salinity of the treated water, as shown by the similar EC in the inflow (7.37 ± 0.88 dS m^{-1}) and in the bioreactor effluent (7.46 ± 0.71 dS m^{-1}). After the 30th day of operation, effluent DOC concentrations were lower than ≈20 mg L^{-1} in all three bioreactors with separate HRT, outside of three unusual events on days 10, 82, and 84 at in the 8 h HRT bioreactor (Figure 1), although there was no clear explanation for these high DOC concentrations. The low DOC concentrations in the effluent indicate that after the initial period of ≈30 days, effluents from the bioreactors were not particularly enriched in DOC, but the results also show that unexpected peaks in discharge of soluble organic material could occur. Certain operational issues (e.g., clogged distributor pipes, broken pump) could result in stagnated water remaining inside the bioreactors for periods longer than the desired HRT, which may lead to peaks in DOC discharge as effluent becomes enriched in DOC or other undesirable compounds (e.g., H_2S) under excessively long HRT (Lepine et al., 2016).

Between days 30-84, when temperatures were < 23 ºC (spring and early summer), NO_3^- removal efficiency increased with increasing HRT, with the highest removal at 24 h HRT (Figure 2). However, between days 84-180, when temperatures were > 25 ºC (early summer to middle of fall), N-NO_3^- concentrations in the effluents dropped (≈ 1.35-13 mg L^{-1}) and removal efficiency increased (≈ 92 – 95 %) at 16h and 24h HRT. During this period the behaviour of the bioreactor with 8 h HRT was irregular, some days reaching similar removal efficiency relative to 16 and 24 h HRT, other times showing peaks in effluent N-NO_3^- concentrations of 13-22 mg L^{-1}. From day 180 until the end of the study period (day 252, late fall and winter) efficiency drastically decreased at all three HRT, with values as low as < 50 %, coinciding with a period of lower temperatures (≈ 16 ºC).

There are a number of factors which have been shown to influence NO_3^- removal efficiency in woodchip bioreactors. These include, but are not limited to, temperature (David et al., 2016; Hoover et al., 2016; Addy et al., 2016), HRT (Greenan et al., 2009; David et al., 2016; Lepine et al., 2016), influent NO_3^- concentration (Chun et al., 2009; Ghane et al., 2015; Addy et al., 2016), and age of woodchips (Cameron and Schipper, 2010; Robertson, 2010; Addy et al., 2016). Temperature increases microbial metabolic activity (e.g., denitrification) (Braker et al., 2010), a trend similarly reported for NO_3^- removal efficiency in woodchips bioreactors (Cameron and Schipper, 2010; Addy et al., 2016; Hoover et al., 2016).

Performance of woodchip bioreactors also decreases with time due to aging of the woody carbon media. As woodchips age and are degraded through decomposition, lignin gradually comprises a greater proportion of the total woodchip biomass, relative to more labile hemicellulose and cellulose. Rates of consumption of the more recalcitrant lignin via anaerobic respiratory pathways (e.g., denitrification) are low or negligible (Zeikus et al., 1982; Holt and Jones, 1983; Odier and Monties, 1983). This decrease in carbon quality has been shown to cause NO_3^- removal rates in woodchip bioreactors to decrease with time (Addy et al., 2016; Nordström and Herbert, 2019), although most of the loss in performance happens early on, relative to the full lifespan of the bioreactor, as fresh, labile carbon is the first to be consumed or leached.

Constructed wetlands

Here we show the main results of removal efficiency for DOC, N-NO_3^- and SRP of the different treatment series that differ in substrate type (Figure 3). Results correspond to the performance of wetlands during their first months of operation, from April to November of

2019. The first sampling was performed three months after the plant pilot start-up. At this very early stage of wetland maturity, large fluctuations in removal of DOC and nutrients are expected (Figure 3), and high removal efficiencies are not expected, especially for N-NO_3^-. (Kadlec et al., 2000; Maine et al., 2009). It is well known that the development of a well-established community of denitrifying microorganisms, among other factors, is essential to reach high N-NO_3^- removal rates in wetlands. In addition, although plant uptake is secondary compared to denitrification for N-NO_3^- removing in wetlands (e.g., Pulou 2012), minimal plant development during the first months of operation negatively affect N-NO_3^- removal, as plants likely encourages denitrification by contributing substrate and organic carbon (Reddy and Patrick, 1984; Yepsen et al., 2014 Tournebize et al., 2017).

Carbon availability is especially important in wetlands treating agricultural drainage waters which are often characterized by a low ratio of available carbon to nitrogen (C/N) (Table 3). Removal efficiencies for N-NO_3^- during this early stage were low, however differences in removal efficiency between substrates types were significant (Figure 3). As predicted, the mix of conventional substrate (gravel) with soil from an adjacent natural wetland (Series 2) showed the highest removal efficiency (Table 4), whereas no differences were observed among gravel and the mix of gravel and biochar. Retention of SRP (Table 4) was in line with previous studies for constructed wetlands receiving agricultural runoff (Lu et al., 2009; Kadlec et al., 2010; Díaz et al. 2012). At this stage of operation wetlands performed better for phosphorus removal than for N-NO_3^-. Young wetlands can be more effective at removing P due to greater availability of P sorption sites in the substrate matrix (Jordan et al., 2003; Smith et al., 2006 en Díaz et al. 2012). No differences were observed between substrate types at this early stage of wetland operation.

DOC concentration in the influent was low (Table 3) and stable over time. Accordingly, as the efficiency of DOC removal depended, among other factors, on inflow loadings, average removal efficiencies were also very low (Figure 3). No differences were observed among the treatment series of gravel and gravel+soil for DOC removal, however the gravel+biochar series showed lower performance (Figure 3, Table 4). Punctual increases of DOC in outflow concentrations were observed in all treatment series, as was seen previously in constructed wetlands (e.g., Díaz et al., 2012). The increase in DOC concentrations are usually due to evapoconcentration processes, and secondly a consequence of both abiotic solubility of plant/sediment organic matter compounds and microbial degradation of plant material (Pinney et al., 2000). Considering the low plant development during this initial study period, both the evapoconcentration process and the solubilisation of organic matter from sediments are the main plausible explanations for the observed DOC concentration in effluents from wetlands. In addition to the increase in water electrical conductivity (EC)(Table 3) through the wetlands, analyses of Cl^-, used as a passive tracer, showed mean increases of Cl^- of 106 and 144% in outflow waters respect to the inflow concentration for October-November and July-September, respectively. The observed gradual increase in Cl^- concentration as inflow water flow through wetlands, is a clear evidence of the importance of evapotranspiration explaining DOC and nutrient concentration in the effluent (Table 3). To avoid this artefact when calculating wetland removal efficiency, the Cl^- concentration was used to correct the effect of evapotranspiration. Therefore, the removal efficiency (R%) for DOC and nutrients was calculated by considering Eq. 2 (Trudell et al. 1986):

$$R\% = \left(1 - \left(\frac{S_{out}}{Cl_{out}^-} \Big/ \frac{S_{in}}{Cl_{in}^-}\right)\right) \times 100 \qquad \text{Eq. 1}$$

where R% is the percentage of any solute removed by the constructed wetlands in relation to inflowing solute concentration, and S/C l^- out and S/Cl^- in are the concentration ratios of both solutes in the outlet and inlet of each treatment serie. A positive R% indicates retention and, conversely, a negative value indicates exportation.

In addition to the evapoconcentration process, the solubility of organic compounds from the substrate could be especially important in the treatment serie with biochar (gravel +biochar), according to the removal efficiency values (Table 4).

7. Concluding remarks and future perspectives

The task of reducing nutrient inputs into the Mar Menor is clearly a complex and expensive task. Four strategies for addressing this issue are worth considering. The first strategy, which is not the subject of this paper, relates to reducing the leaching of nitrate to the aquifer as well as limiting the export of nutrients and sediments following heavy rains. This strategy requires significant changes to fertilization practices, soil conditioning and irrigation routines as well as real soil conservation measures that have mostly been neglected in intensive agriculture in SE of Spain. Secondly, it is necessary that nitrate-rich brine produced by on-farm desalination plants needs effective and scalable tools for denitrification. Results the pilot scale bioreactors at the ESEA research station are promising, however next steps will include how to bring this water treatment practice to scale to serve the decentralized network of over 500 on-farm desalination plants in the Campo de Cartagena. Third, nitrate-polluted water discharged to the Mar Menor via various hydrologic pathways (hydrologic networks, subsurface flow, drainage ditches, etc) needs to be captured and treated. The ecological-based treatment tools proposed here (woodchip bioreactors, constructed wetlands) can be paired with existing infrastructure in the region to provide treatment to these discharges. Our pilot plant is only a prototype, and a nearly full interception of flows (surface and subsurface) along with rerouting intercepted water to various denitrification infrastructures is complex and expensive. Fourth, the role of natural coastal wetlands is vital. These systems need to be protected and, in some cases, restoration may be necessary in degraded areas.

Although many of these results from the pilot-scale experiments are preliminary, they indicate that the combination of woodchip bioreactors with wetlands could be a successful BMP strategy for the treatment of agricultural drainage in the Campo de Cartagena. Other BMP strategies may include other conventional approaches to reducing runoff and soil erosion. These strategies may include implementation of a Code of Good Agricultural Practices by farmers, the use of buffer strips and hedges, and the restoration of natural coastal wetlands. Each strategy targets a particular problem and often a combination of management practices is needed to properly address agricultural non-point pollution at the watershed scale (Woltemade, 2000).

On the basis of our preliminary results and in line with other studies (Zedler, 2003; Darviche-Criado et al., 2017) strategies focused on wetlands conservation and restoration will contribute to the mitigation of the Mar Manor eutrophication. Together with Marina del Carmoli and Lo Poyo salt marshes other small coastal wetlands persist in different states of degradation along the Mar Menor shoreline. Ensuring their conservation and implementation of specific restoration practices will ensure the existence of an active, although discontinuous, buffer strip around the Mar Menor whose action would contribute to the retention of sediments and pollutants.

With respect to the proposed ecological-based technologies (i.e., ecotechnologies, *sensu* Sukias, 2018), bioreactors show a high performance for $N\text{-}NO_3^-$ removal and are typically preferable to wetlands for nitrate removal in terms of cost and area required to provide sufficient HRT. Bioreactors have shown high efficiencies for nitrate removal even at the watershed scale, although some uncertainties still exist (Moorman et al., 2015; Rivas et al., 2019). Although low DOC concentrations are common in the effluent from bioreactors, unexpected peaks in discharge could occur during operational issues, and may produce other undesirable compounds (e.g., methane, sulphide). Similarly, the ability of bioreactors to reduce P concentrations is limited (Rivas et al., 2019), and their performance on coliforms or other pathogens may be low. Constructed wetlands perform well for phosphorus and pathogens and are also effective for DOC and pesticide removal (e.g., Gregoire et al., 2009; Tournebize et al., 2017). Wetlands also create an aesthetic environment and the provision of other ecosystem services with great value to society including biodiversity improvement, which may be particularly useful in heavily impacted, homogenous agricultural landscapes with low biodiversity. Considering the distinct advantages and drawbacks from these two technologies, it is possible that effluents from bioreactors could be treated by constructed wetlands, ensuring a high performance for removal of several pollutants. Moreover, unexpected high discharge of DOC from bioreactors could be removed in wetlands and at the same time that would increase denitrification rates in the latter, although this deserve further investigation due to the high recalcitrant lignine content in bioreactor effluents (Zeikus et al., 1982; Holt and Jones, 1983; Odier and Monties, 1983).

The design of a strategy for effectively reducing discharge of nutrients will require other important considerations, such as sizing and proper location of BMPs in the watershed. Due to the uncertainty of discharges from agricultural watershed (e.g., volume, timing and chemistry), the optimal design for constructed wetlands will be a challenge, with retention time and wetland location in the watershed being recognized as critical elements (Woltemade, 2000; Mander et al., 2017).

Further, it has been demonstrated that the combination of both ecotechnologies improved the performance and resilience of water treatment under shock loading events (Sukias et al., 2018) (e.g., increases in waste water production when population increase during holidays or peaks in agricultural effluents during periods of maximum farming activities).

As in other agricultural landscapes, treatment of agricultural effluents in the Campo de Cartagena have to be addressed on a watershed specific basis. The siting of both ecotechnologies should be considered in strategic areas where drainage ditches may intercept a large percentage of the runoff which can be conducted to the systems, or where open channel watercourses impacted by agriculture could be rerouted through the BMPs period to direct discharge into the Mar Menor lagoon. This strategy, named "*on-stream interception*", has been previously discussed with regard to nitrate removal (Tournebize et al., 2017). Additionally, some authors pointed out that, depending on the parameter being targeted (nitrate or pesticides), constructed wetlands must be located near the pollution source or at the outlet of the subcatchment (< 100 ha) (Van der Valk and Jolly, 1992). It is important to find a balance between the percentage of the total agricultural effluent treated by the BMP and the ratio between the size of the created wetland relative to contributing drainage area. As this ratio increases, the removal efficiency of pollutants in wetlands improve (Jansson et al., 1994). Therefore, an analysis of the existing information about the water pathway and movement of pollutants is the first step for designing a strategy to mitigate the effect of agricultural effluents in the Mar Menor lagoon. This information is essential to determine i) the number of treatment systems needed, ii) where they should be located and iii) how they must be designed (in terms of size and, in the case of constructed wetlands, type of flowpath). The use of LIDAR topographic data has been shown to be a successful tool to identify suitable sites for wetland construction at watershed scale (Tomer et al., 2013).

In the Campo de Cartagena, agricultural discharges may come directly from desalinization plants or from drainage ditches. As was shown, water quality in both situations are quite different, as same as timing and volume of discharges. Accordingly, the design of the treatment system must be specific for particular effluents (Kadlec et al., 2017). Finally, a watershed treatment plan must be developed that takes into consideration local conditions as topography, incidence of floods or land ownership. Regarding the last aspect, and considering that public or non-agricultural spaces are scarce in the Campo de Cartagena, the possibility of acquiring agricultural land directly from farmers should be considered, as discussed by other authors (e.g., Tournebize et al., 2017). Three main social and economic aspects have been highlighted to be consider when planning, implementing, and administering treatment systems at watershed scale in agricultural landscapes: the attitude of farmers and rural leaders, legal and public policy implications, and economic costs and benefits (Van der Valk and Jolly, 1992). All these aspects must be considered during planning in order to achieve the successful mitigation of agricultural pollution in the Mar Menor lagoon.

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Figure legends

Figure 1. Dissolved organic carbon (DOC) concentrations in the bioreactor effluents. Samples were weekly collected. Mean DOC concentration of the inflow over the studied period is given.

Figure 2. A: $N\text{-}NO_3^-$ concentrations in the inflow and in the effluent of the bioreactors at 8 h, 16 h and 24 h HRT and temperature inside the bioreactors (average of the three HRT); B: efficiency in $N\text{-}NO_3^-$ removal at 8 h, 16 h and 24 h HRT.

Figure 3. Efficiency in DOC (dissolved organic carbon), $N\text{-}NO_3^-$ and SRP (soluble reactive phosphorus) removal in the three series of constructed wetlands of the pilot plant between July and November 2019.

Figure 1

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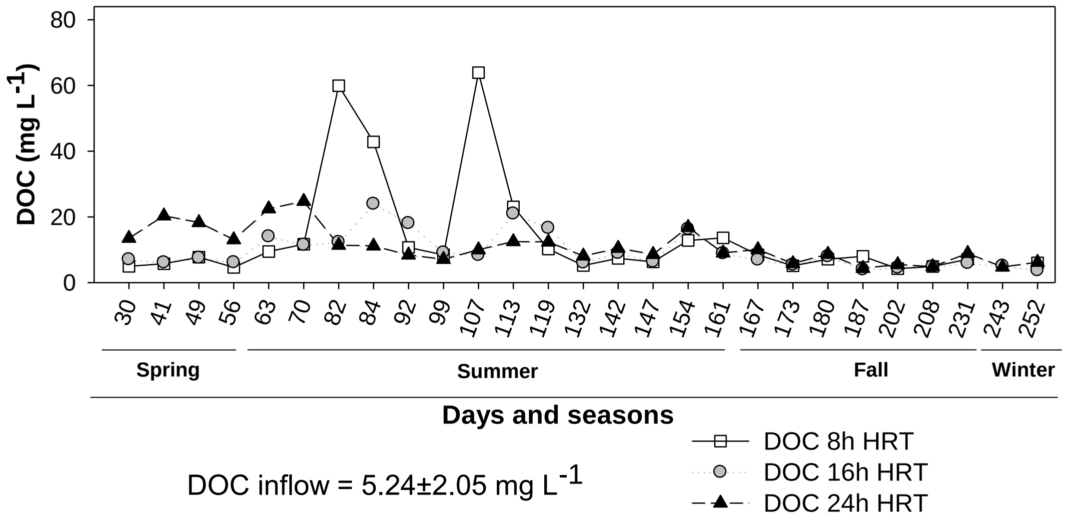

Figure 2

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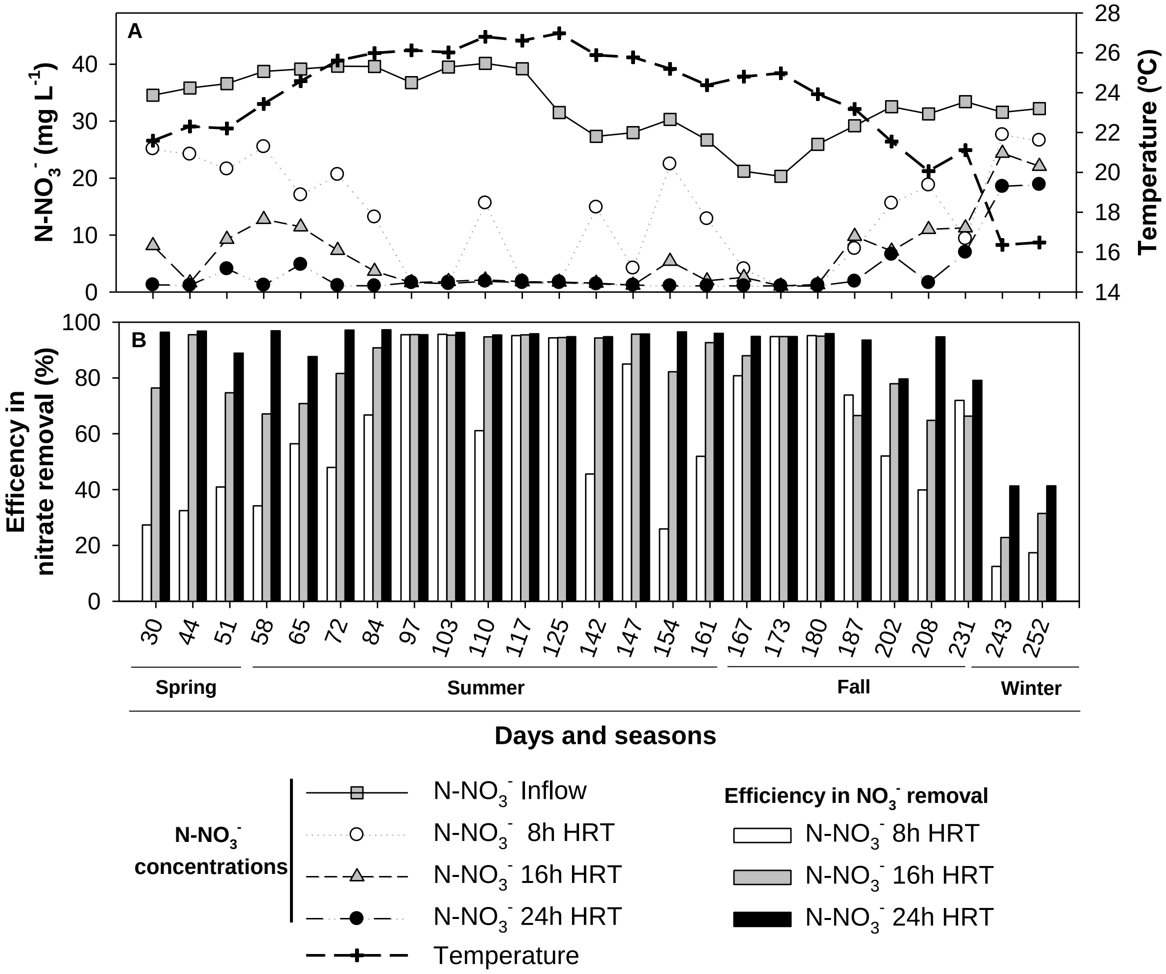

Figure 3

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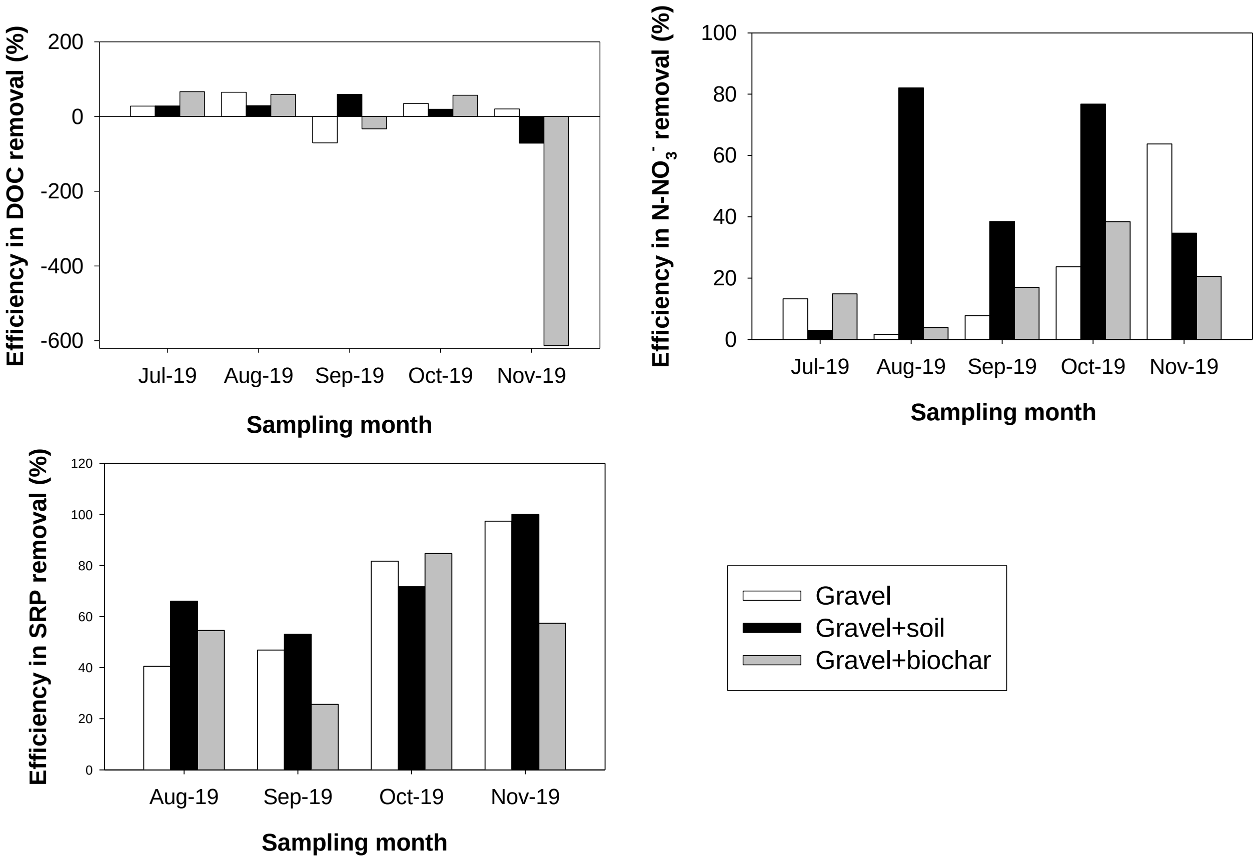

Table 1

Table 1. $N\text{-}NO_3^-$ and SRP (soluble reactive phosphorus) concentrations and loads found in previous works in watercourses of the Campo de Cartagena-Mar Menor area. BF: base flow; S: storm events. Values are average±SD (maximum between brackets).

Period	Rambla	$N\text{-}NO_3^-$ concentration (mg L^{-1})	$N\text{-}NO_3^-$ load (Mg y^{-1})	SRP concentration (mg L^{-1})	SRP load (Mg y^{-1})	Reference
Jul 2002	Miranda	25.3±17.1 (65.2)	n.m.	0.19±0.19 (0.56)	n.m.	Álvarez-Rogel et al. (2006)
Jul 2003	Miedo	1.97±4.52 (12.12)	n.m.	2.59±1.26 (3.92)	n.m.	Álvarez-Rogel et al. (2006)
Sep 2005	Miranda	BF: 62.7±22.8 (117)	BF: 67.1	BF: 0.16±0.06 (0.26)	BF: 0.19	González-Alcaraz et al. (2012b)
Nov 2006		S: 46.9±16.7 (63.6)	S: 0.49	S: 0.10±0.07 (0.18)	S: 0.001	
	Miedo	BF: 1.15±0.79 (2.62)	BF: 0.10	BF: 1.76±0.75 (3.0)	BF: 0.17	González-Alcaraz et al. (2012b)
		S: 1.41±1.52 (3.16)	S: 0.009	S: 0.89±0.87 (1.89)	S: 0.003	

Table 2

Table 2. Main morphometry and hydraulic features of different Phases in constructed wetlands

Parameter	Design criteria		
	Phase I	Phase II	Phase III
Bed size (m^2)	40	21	28
Lenght to width ratio	1.6:1	2.3:1	2.3:1
Water depth (m)	0.6	0.4	0.6
Bed slope (%)	1	1	1
Hydraulic loading rate (m d^{-1})	0.13	0.24	0.18
Hydraulic retention time (days)	2.2	1.7	1.7

Table 3

Table 3. Water quality parameters of the water influent to the pilot plant and effluents from the different Series between April and November 2019. Values are overall average ± standard error (n= 5, from August to November). EC: electrical conductivity; DOC: dissolved organic carbon; SRP: soluble reactive phosphorus.

	Influent	Gravel (Serie 1)	Gravel+soil (Serie 2)	Gravel+biochar (Serie3)
EC (dS m^{-1})	5.9 ± 0.2	7.0 ± 0.4	7.4 ± 0.6	7.4 ± 0.5
DOC (mg L^{-1})	3.9 ± 0.3	4.2 ± 1.3	3.8 ± 0.6	4.0 ± 1.5
N-NO_3^- (mg L^{-1})	26.4 ± 1.56	23.9 ± 4.47	17.52 ± 5.89	6.21 ± 1.17
SRP (µg L^{-1})	27.4 ± 2.1	15.9 ± 7.7	12.0 ± 5.8	17.4 ± 6.9

Table 4

Table 4. Overall average removal efficiency (%) of created wetland during the study period (July-November 2019). Minimum and maximum values are shown in brackets. First sampling was carried out after three months of the starting-up of the created wetland pilot plant. Negative values denote exportation. DOC: dissolved organic carbon; SRP: soluble reactive phosphorus.

Parameter	Gravel	Gravel + soil	Gravel + biochar
DOC	15.5	12.9	-92.7
	(-70.6 - 65.0)	(-71.5 - 59.4)	(-613.5 - 66.7)
NO_3^-	22.0	47.0	18.9
	(1.7 - 63.8)	(3.0 - 82.1)	(3.9 - 38.4)
SRP	66.6	69.8	71
	(40.5 – 97.4)	(53.1 - 100)	(57.4 - 84.7)

Supplementary Material

Click here to download Supplementary Material: Supplementary material Alvarez-Rogel et al. Mar Menor.docx

Credit Author Statement

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