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Six artificial recharge pilot replicates to gain insight into water quality enhancement processes

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HIGHLIGHTS

- Six artificial recharge systems replicates were built to study the role of diverse parameters.
- Contaminants and pathogen indicators decrease efficiently along the systems.
- Reactive barriers favor quality water improvement.
- The specific role of plants should further be investigated.

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ABSTRACT

The processes that control water quality improvement during artificial recharge (filtering, degradation, and adsorption) can be enhanced by adding a reactive barrier containing different types of sorption sites and promoting diverse redox states along the flow path, which increases the range of pollutants degraded. While this option looks attractive for renaturazing reclaimed water, three issues have to be analyzed prior to broad scale application: (1) a fair comparison between the system with and without reactive barrier; (2) the role of plants in prevention of clogging and addition of organic carbon; and (3) the removal of pathogens. Here, we describe a pilot installation built to address these issues within a waste water treatment plant that feeds on water reclaimed from the secondary outflow. The installation consists of six systems of recharge basin and aquifer with some variations in the design of the reactive barrier and the heterogeneity of the aquifer. We report preliminary results after one year of operation. We find that (1) the systems are efficient in obtaining a broad range of redox conditions (at least iron and manganese reducing), (2) contaminants of emerging concern are significantly removed (around 80% removal, but very sensitive to the compound), (3) pathogen indicators (*E. coli* and Enterococci) drop by some 3–5 log units, and (4) the recharge systems maintained infiltration capacity after one year of operation (only the system without plants and the one without reactive barrier displayed some clogging). Overall, the reactive barrier enhances somewhat the performance of the system, but the gain is not dramatic, which suggests that barrier composition needs to be improved.

1. Introduction

Groundwater pumping is increasing globally in response to the need of good quality water, the population increase and the subsequent need for irrigation. While pumping is still a relatively low fraction of global recharge, water levels are decreasing globally (Konikow and Kendy, 2005; Wada et al., 2010), regionally (e.g., North Africa, the Middle East and South Asia) (Aeschbach-Hertig and Gleeson, 2012; Konikow and Kendy, 2005) and locally, often accentuated by climate change (Gurdak, 2017).

The problem is made worse by point and diffuse contamination (Asano and Cotruvo, 2004; Konikow and Kendy, 2005; Taylor et al.,

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2012; Molins-Delgado et al., 2016b). Beyond human pollution, lowered water levels contribute to seawater intrusion in coastal aquifers, and loss of groundwater discharge to springs, streams, and wetlands, which lose a significant portion of their environmental services (Konikow and Kendy, 2005; Wada et al., 2010).

Reclaimed water is currently seen as an alternative or complementary source of water, especially for applications other than drinking water. The upgrade of techniques applied in wastewater treatment plants (WWTPs) to improve the quality of the effluents is, therefore, an urgent need (Molins-Delgado et al., 2016b, a). Nevertheless, the use of reclaimed wastewaters is hindered by the lack of confidence of citizens (Smith et al., 2018). An excellent option is to increase available water resources through Artificial Recharge, preferably termed Managed Aquifer Recharge (MAR) or Soil Aquifer Treatment (SAT), when the recharge water is a WWTP effluent. Artificial recharge (AR) via infiltration basins consists on stimulating the water to infiltrate through the vadose zone and subsequent transit travel along the aquifer.

Recharged water quality improves due to the decrease of the levels of pathogens (Dillon et al., 2006), chemical contaminants (Hoppe-Jones et al., 2010; Patterson et al., 2011; Valhondo et al., 2014, 2018), nutrients (Bekele et al., 2011), and organic matter (Bekele et al., 2011; Vanderzalm et al., 2018). Specifically, the contaminants concentrations has been observed to decrease during MAR/SAT mainly due to biodegradation, while their transport is retarded as a consequence of adsorption onto the particulate matter (Greskowiak et al., 2006; Henzler et al., 2014; Maeng et al., 2011; Regnery et al., 2015). MAR characteristics make it an environment friendly, efficient, and cost-effective technique to improve recharge water quality while increasing fresh water reserves, and maintain wetlands and hyporheic exchange in rivers (Asano and Cotruvo, 2004; Konikow and Kendy, 2005).

Despite its benefits, the implementation of MAR, and especially SAT/MAR, is still under debate. Most contaminants of emerging concern (CECs), pharmaceuticals and personal care products, illicit drugs, and micro- and nano-plastics, among others, and antibiotic resistance gens and antibiotic resistance bacteria are recalcitrant to current wastewater treatments. As a result, typical WWTPs effluents composition include pathogens and CECs (Amy and Drewes, 2007; Díaz-Cruz and Barceló, 2008; Joss et al., 2006; Köck-Schulmeyer et al., 2011; Mansell and Drewes, 2004; Molins-Delgado et al., 2015, 2017; Pärnänen et al., 2019). It was generally believed that pathogens did not move through porous media and that natural degradation processes removed most contaminants. However, outbreaks have shown that pathogens may reach pumping wells (Hrudey et al., 2003). Fear that these pollutants might contaminate groundwater suggests strict limits on water to be used for recharge. But too strict limits would have made illegal numerous systems that have worked properly in several European cities for more than 50 years. The debate caused the JRC (Alcalde Sanz et al., 2018) to abstain from producing recommendations for MAR at the European Union scale.

To address these concerns, Valhondo et al. (2014) designed, as part of the ENSAT project (LIFE08 ENV/E/000117), a system to recharge across a reactive barrier, which contains diverse type of sorption surfaces (organic matter, clay and iron oxides) to enhance retention time and which adds organic carbon to favor a broad range of redox states, favoring the degradation of recalcitrant compounds (Barbieri et al., 2011; Christensen et al., 2001; Patterson et al., 2011; Rauch-Williams et al., 2010). The reactive barrier prototype proved efficient regarding CECs degradation, and generating a redox zonation in the aquifer beneath (Valhondo et al., 2014, 2015; 2018; Schaffer et al., 2015; Grau-Martínez et al., 2018). However, uncertainties emerged during the experiment. For one thing, the ENSAT project was a real scale one, hindering fair comparison between the system operating with and without reactive barrier. Second, the system worked well during the first two years, when plants grew in the recharge basing, but clogged after two additional years without plants, which suggested that plants contributed to prevent clogging while adding organic carbon. Finally, ENSAT project did not consider pathogens behavior. However, growing concerns make it clear that the fate of pathogens needs examination.

In this study, we constructed six pilot recharge systems to gain insight into the effectiveness of the reactive barrier, the fate of pathogens, and the role of plants. The systems mimic the infiltration and subsequent flow along the aquifer. One of the systems is used as a reference (no reactive barrier) and the rest introduce a particular variation regarding type of reactive barrier, absence of plants, and heterogeneity.

The objective of this work is to describe the systems and to present preliminary results after one year of operation.

2. Materials and methods

2.1. Site, pilot recharge system, and reactive barriers description

The pilot recharge systems were built in a WWTP facility, in the Nord-East Spanish Mediterranean coast. The WWTP regularly receives wastewater from 90,000 inhabitants, but inflow triples during the summer touristic season. The WWTP was designed for 165,000 equivalent-inhabitants, i.e. 33,000 m^3/d incoming flowrate and a treatment retention time of some 24 h. The plant approaches full capacity only in summer. The intensive seasonal behavior of the plant may result in different qualities of the effluent over the year. The implemented processes include pre-treatment (waste retention), primary treatment, a biologic secondary treatment (activated sludge) and tertiary treatment (sand filter), but the latter is only applied for green areas' irrigation within the facility.

The climate in this area is typically Mediterranean but with strong winds, usually in winter. Daily mean temperatures range between 14 and 20 °C, with typical minimum of 3 °C and maximum 36 °C (summer). July and August are the hottest months and from December to February the coldest. Annual mean precipitation is about 450 mm, concentrated in autumn season (Oct—Nov) and spring (April—May).

The structure consist of a 15×15 m^2 construction excavated 1.5 m into the ground, except for the discharge wall, which has been excavated to facilitate access for sampling and water level control (Fig. 1A). This structure is divided into 6 identical 2.38 m wide 15 m long canals that emulate an aquifer (referred hereafter as “aquifer”). Each “aquifer” is coupled to a 1.15 m high and 1.5 m long box that emerges over the aquifer and emulate an infiltration basin (referred hereafter as “recharge area”, Fig. 1B). Therefore, each recharge area is 1.5×2.38 m^2. The systems are named T1 through T6 (Fig. 1A). All six aquifers consist of fine sand (0.1—0.2 mm grain size), but two of them include $80 \times 40 \times 40$ cm^3 coarse sand (0.4—2.5 mm grain size) lenses at different depths to simulate aquifer heterogeneities.

Three different 1 m thick reactive barriers were designed and installed in five of the six systems. Reactive barrier 1 (referred as RB1 hereafter), is based on vegetal compost blended with sand (equal volume) and with little clay volume (2%), and was installed in three of the systems. Reactive barrier 2 (RB2), is based on woodchips blended with sand (equal volume) and with little amount of clay (2%), and was installed also in one of the systems. Reactive barrier 3 (RB3) is similar to RB1 but the volumetric portion of sand is 60% and the volumetric portion of vegetable compost is 40%, and it was installed in one of the systems. The reactive barriers were installed over 1.1 m thickness of aquifer separated by 15 cm

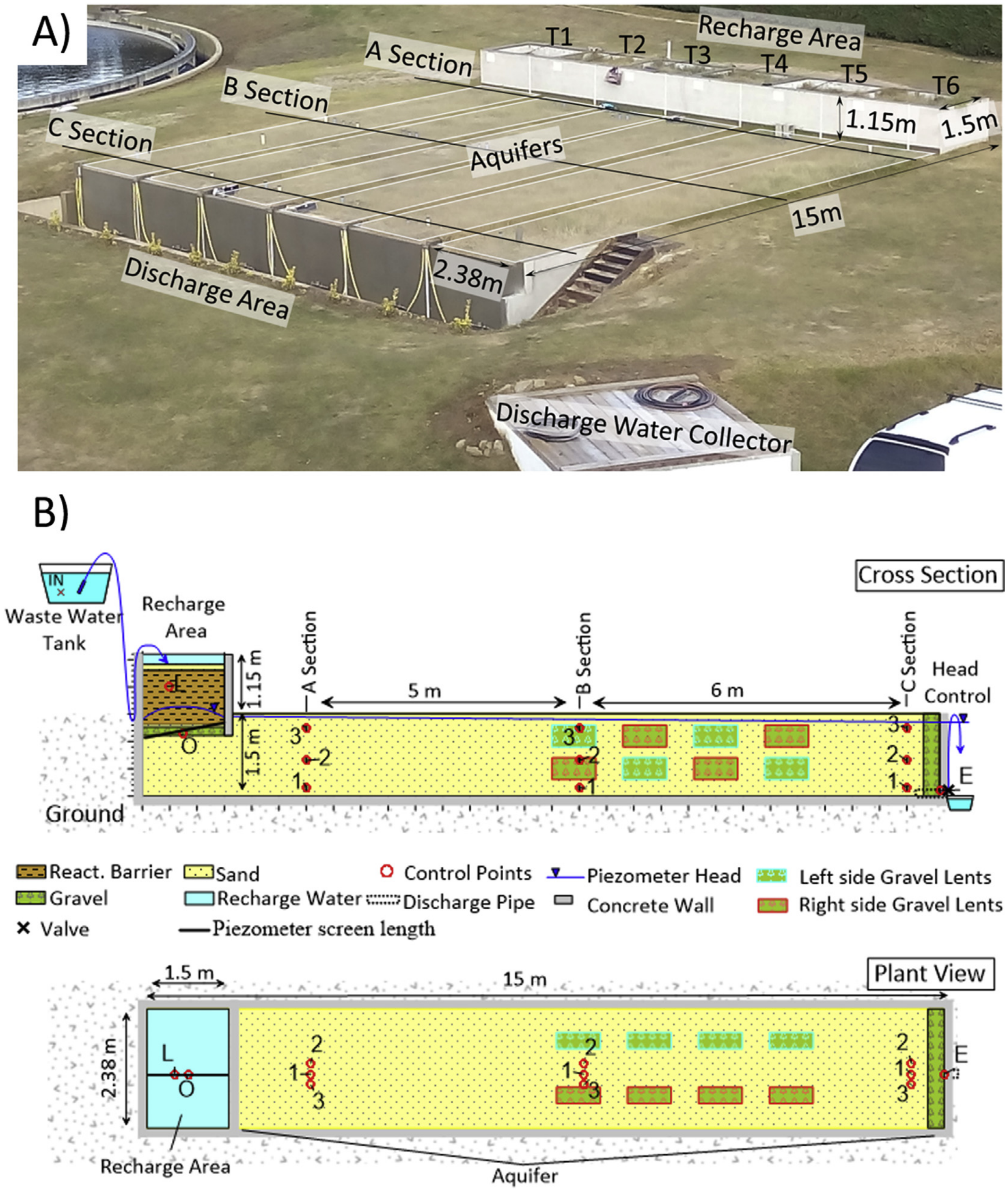

Fig. 1. General view of the experiment, recharge and discharge areas, piezometer sections and replicates T1 through T6 (A). Cross section and plant view scheme of one of the (generic) system with the recharge area, heterogeneity, and monitoring points: L-Lysimeter, and O-Crosswise, 1-Deep, 2-Middle, 3-Shallow piezometers (B).

thick layer of coarse sand, to facilitate the eventual development of an unsaturated zone, and covered by 10 cm thick layer of fine sand to prevent wood from floating.

The main role of the sand is to provide structural integrity to the barrier and to ensure high hydraulic conductivity, while the vegetal compost and woodchips provide sorption sites for neutral contaminants and contributes to release DOC into recharged water. The aim of clay is to provide sorption site for anionic compounds.

Taking this design as a basis, we have combined different barrier composition, aquifer heterogeneities and plant growths in the recharge area to compare different scenarios. T1 contains a heterogeneous aquifer, and RB1, and we have avoided the growth of plants in the recharge area. The second system, T2, (named “REF” hereafter) is homogeneous, without reactive barrier and plants in the recharge area. T3 has heterogeneities, RB1, and plants in the recharge area. T4 (named “RB1” hereafter) is homogeneous, has RB1 installed, and plants have grown in the recharge area. T5 (named “RB2” hereafter) is homogeneous, has RB2 installed, and plants have grown in the recharge area. Finally, T6 has heterogeneities, RB3 installed, and plants have grown in the recharge area.

The systems are controlled at both the inflow and outflow. Inflow into the recharge area can be fed with the WWTP secondary treatment effluent or with water from the sand filter tank. The flow rate is controlled with dosing pumps (PRIUS 7 bar) and monitored by electromagnetic flowmeters (ISOIL MS600) that account for the recharged volume. They pump the water from a reception tank with some 24 h retention time to homogenize daily fluctuations of water quality. The outflow water level is controlled by fixing the elevation of the discharge pipe that collects water from the bottom of the aquifer through a network covered with coarse sand to minimize head losses. The outflow pipes are equipped with meters that measure the cumulative discharge volume and with faucets for sampling.

Each system is equipped with thirteen monitoring points to measure pressure, temperature, electrical conductivity (EC) and to collect water samples at different depths and distances from the recharge area. Nine 10 cm screened piezometers (PVC 2″ ID) have been installed in each system at three distances from the recharge area, termed section A (1.5 m), B (5.5 m) and C (12.5 m) in Fig. 1A. Every section contains three piezometers screened at different depths: piezometer 1 (10–20 cm from the system base), piezometer 2 (60–70 cm from the system base) and piezometer 3 (110–120 cm from the system base) (Fig. 1B). Additionally, a 2.5 m long, inclined (as horizontally as possible, with angles between 12° and 15.2°) and completely screened piezometer was installed across the entire base of the recharge area (monitoring point O in Fig. 1B). Piezometers are equipped with CTD/CD-Diver (Schlumberger water services, Delf, The Netherlands) to measure pressure, temperature and EC. A barometric pressure Diver (Schlumberger water services, Delf, The Netherlands) was attached to the discharge wall to make corrections for atmospherical pressure measurements. Furthermore, stain steel lysimeters (Soil Measurement Systems, US Patent nº: 5035149), monitoring point L in 1, were installed horizontally, at 40 cm from the recharge area surface. Lysimeter has single chamber, welded construction with no glue or plastic, bubbling pressure of the porous steel is 0.6 bars, 7/8″ OD model have a porous steel section of 3.7" in length. Water is also monitored at the inflow and the outflow.

2.2. Recharge system operation and performance

The system started operation in January 5th, 2018. Fig. 2A displays the recharge episodes (W/D), the lasting (in days) of the wet periods, the sample collection for chemical and microbiological parameters and the hydraulic test performed during the study. Four recharge periods, from 27 to 118 operative days, have been performed (Fig. 2A). The wet/dry (W/D) periods duration was conditioned by the demands of the tests performed to characterize the systems. The WWTP secondary treatment effluent was used to feed the systems. The average inflow was set to 1 L/min (a recharge rate of 0.40 m/d) and the head of the outlet was set between 130 and 140 cm for all the six systems.

WWTP efficiency was characterized by collecting samples at the entrance of each applied treatment. Water quality evolution along the systems was assessed during the four wet periods by quantifying physicochemical, microbiological, and chemical parameters from samples collected at the inflow, piezometers, and effluent of the systems.

Variability of the secondary treatment effluent, and specifically electrical conductivity (EC), has been used occasionally as a tracer. Fig. 2B displays EC measurement at inflow (INF) and EC measurement vs. cumulative volume at RB1 system monitoring points. Inflow EC increased significantly during four days, moving along the aquifer at the advective flow velocity. On the one hand, first arrival was measured at the base of the barrier (Crosswise piezometer) almost immediately, which suggests that a portion of the inflow water is reaching the aquifer through preferential flow paths with very short residence time (had flow been uniform, a delay of some 0.3 m^3 would have been expected). On the other hand, the EC decay is smother in the crosswise piezometer than in the inflow water displaying the dispersion generated by the different velocity flow paths in the vadose zone. Evolution of breakthrough curves show an increase in dispersion with the distance to the recharge area from Cross to RB1-C1.

It is worth pointing that these data represent "resident concentrations" (i.e., the actual concentrations in the aquifer), which may be very different from flow averaged concentrations (i.e., the ones measured during pumping or at the outlet, when most water flows through preferential flow paths). For example, the total volume of water in the system is some 16 m^3. Therefore, under uniform flow, EC at RB1-C1 should have arrived for a somewhat smaller volume, whereas EC increases at some 22 m^3, which implies that this point belongs to a flow path somewhat slower than the average. The distinction between resident and flow averaged

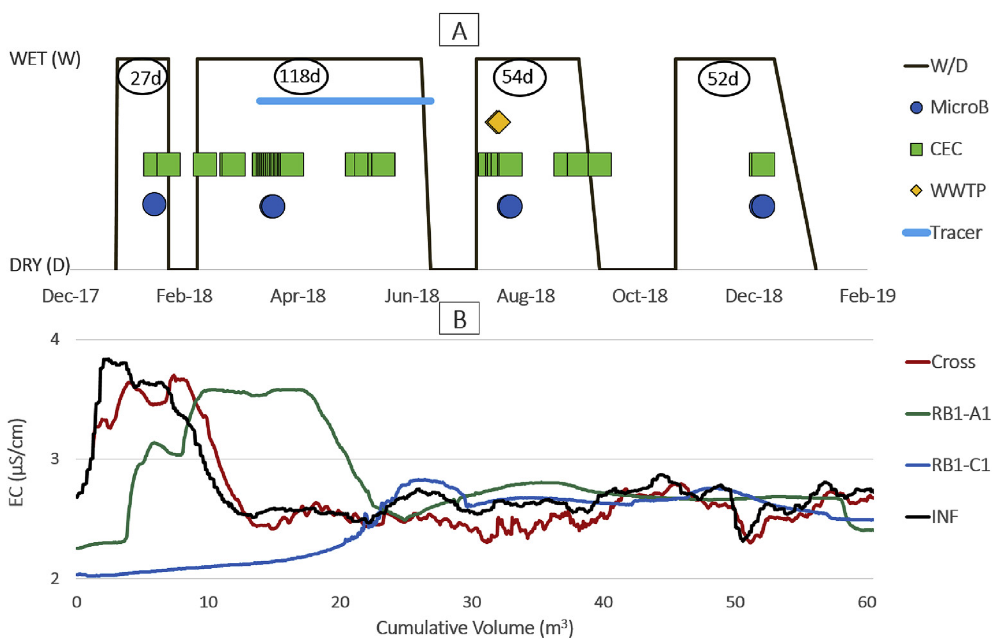

Fig. 2. Experimental set up: Wet/dry (W/D) periods and lasting days, sampling collection for chemical and biological analysis, microbiological parameters, and sampling collection for WWTP characterization (A), and EC evolution at the inflow and EC breakthrough curves measured at three monitoring points of RB1 system vs. cumulative inflow (m^3) during the last wet period, October 26th–December 17th(B).

concentrations is relevant because reactions occur in the aquifer as controlled by the water there (i.e., resident concentrations), which typically represent the largest portion of the volume, but a small fraction of the flow. Still, this small volumetric fraction of water in preferential flow paths represents the dominant fraction at the outlet, when averaging is made in terms of flow rates.

Additionally, a tracer test was performed during the spring of 2018. In order to understand the systems, we have initially focused on those homogeneous and with plants in the recharge area, REF, RB1 and RB2.

2.3. Analytical methods

Samples for chemical and biological analysis were collected from the inlet, the piezometers installed along the systems, and the six outlets. Before sampling, piezometers were purged until the field parameters, i.e. electrical conductivity (EC), dissolved oxygen (DO), pH, Redox potential, and temperature, were stable. These parameters were measured using a YSI multiparameter sonde (YSI, Yellow Springs, OH, USA).

The samples for DOC, metals, and main cationic substances determination were collected in muffled glass bottles, transported to the lab under cool conditions (4 °C) and upon arrival, filtered through 0.22 μm membrane filters and acidified with HCl (for DOC analysis) or HNO_3 (for metals and cations determination), and stored at 4 °C until their further analysis (max. two days). DOC was measured with a TOC-VCSH analyzer Shimadzu (Kyoto, Japan). Metals were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS) using an iCAP-Q instrument (Thermo Fisher Scientific, Massachusetts, USA). Cationic species were analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using an iCAP 6500 instrument (Thermo Fisher Scientific).

In the filtered water samples, ammonium was analyzed using an ORION Ion Selective Electrode (ISE, Thermo Fisher Scientific, Massachusetts, USA). Main anionic substances were determined by ion chromatography using a Dionex AQUION (Dionex, Sunnyvale, CA, USA) with an Ionpack AS9 2 × 250 mm column and Na^2CO_3 9 mM solution as eluent. Samples for chemical contaminants analysis, i.e. CECs, were collected in precleaned amber glass bottles to avoid potential photodegradation. The samples were shipped to the laboratory under cool conditions. Once in the lab, samples were vacuum filtered twice, first using 1 μm glass fibre filters (Whatman, Fairfield, CT, USA) and then through 0.45 μm nylon membrane filters (Teknokroma, Barcelona, Spain) and stored at −20 °C in the dark until analysis.

The analytical determinations were performed by on-line solid phase extraction coupled to high performance liquid chromatography-tandem mass spectrometry (on-line-SPE-HPLC-MS/MS), as described in our previous papers (Gago-Ferrero et al., 2013; García-Gil et al., 2018). Briefly, 5 ml of the water samples were extracted and purified in an automated on-line SPE-LC SymbiosisTM Pico (Spark Holland. Emmen, The Netherlands) instrument using PLRPs on-line SPE cartridges. The trapped analytes were eluted from the SPE cartridge and introduced into the LC analytical column with the chromatographic mobile phase consisting of HPLC-grade water and acetonitrile (ACN). MS/MS detection was performed in a 4000 QTRAPTM MS/MS mass spectrometer (Applied Biosystems-Sciex. Foster City, California, USA) under selected reaction monitoring mode (SRM) for improved selectivity and sensitivity. Analyses were run in both positive and negative modes using an electrospray ionization source (ESI+, ESI-). Quantification was performed using isotopically labelled internal standards (isotopic dilution). Method limits of detection (LODs) ranged from 0.2 to 3.0 ng/L.

Gram-positive and gram-negative bacterial indicators of fecal origin were analyzed by standardized MPN detection tests following manufacture instructions (Colilert and Enterolert IDEXX, US). Water samples (100 ml) were collected in sterile buckets, stored at 4 °C, and processed within 24 h. The log removal values were calculated considering the average *E. coli* and Enterococci concentrations in the infiltration water, crosswise piezometer water, and final effluent of three sampling campaigns (January, March, and July 2018).

3. Results and discussion

We discuss water quality profiles from REF, RB1, and RB2 systems. The only significant difference among the three systems is the lack of reactive barrier (REF) and the type of material added as organic carbon source (compost for RB1 and woodchips for RB2). Water quality improvement will be described by comparing the evolution of sensitive redox species, chemical pollutants and pathogen indicators.

3.1. Redox sensitive species

Fig. 3 displays the concentrations of Dissolved Organic Carbon (DOC), Manganese, Ammonium (NH^+4), and Nitrate (NO^-3) measured in samples from the infiltration water, the crosswise piezometer and the effluent of the REF, RB1, and RB2 systems during the July−August wet period (Fig. 2).

DOC (Fig. 3A) is gradually consumed along the flow path in REF and RB2 systems, while it increases at the crosswise piezometer of RB1 system, indicating that reactive barrier 1, based on compost, released higher amounts of DOC than reactive barrier 2, based on woodchips. The DOC concentration at the effluents is close to 10 mg/L suggesting that at least part of the DOC from the influent water is not easily degradable.

Manganese concentration (Fig. 3B) increases along the flow path of both three systems indicating than at least Manganese reducing conditions are reached (Manganese is not mobile under oxidizing conditions).

All the Nitrogen detected at the inflow water was in form of Ammonium (Fig. 3C and D). Ammonium decreases along the flow path while Nitrate concentration increases. This might suggest that nitrification is taking place. However, nitrification requires aerobic conditions, which were not observed. In fact, it is somewhat surprising to find high Manganese (a suggestion of highly reducing conditions) and high Nitrate (somewhat oxidizing) in the same sample. The only explanation we find for this paradox, lies in the difference between outlet concentrations (flow averaged) and crosswise well samples, which represent resident concentrations. We had observed that at Sant Vicenç dels Horts, where water samples in the soil were more reducing than in the aquifer (Valhondo et al., 2014). However, the effect is much more significant here and requires further analysis.

The source water used for artificial recharge in the new site has a much larger amount of DOC that the recharge water at the previous study at Sant Vicenç dels Horts, in fact we can observe reducing conditions even in the REF system. Differences between the system running with and without reactive barrier are not so marked as we observed in Sant Vicenç dels Horts, where without the RB the available amount of DOC was not enough to consume the DO of the recharged water.

3.2. Contaminants of emerging concern

Considering the WWTP location and the initial chemical characterization of the wastewater treated in the facility (mainly urban origin, including a hospital) a selection of 52 CECs and their main

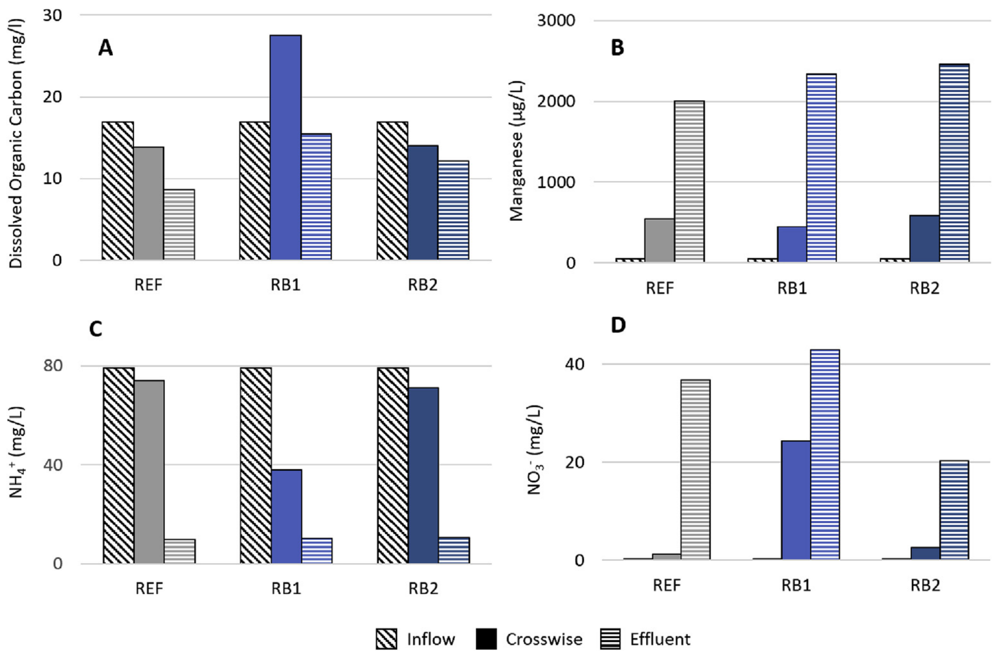

Fig. 3. Concentration of A) Dissolved organic carbon, B) Manganese, C) NH4+, and D) NO3- evolution along the REF, RB1, and RB2 systems.

human metabolites were investigated. The chemicals were classified into three groups, i.e. organic UV filters (14, UVF), preservatives (4, PBs) and pharmaceuticals (34, PhAcs). The target compounds were representatives of the selected groups and included: benzophenones, benzotriazoles, camphors, PABA-derivatives, parabens, antibiotics (quinolones, flouroquinolones, sulphonamides, tetracyclines, macrolides), analgesics, anti-inflammatories, lipid regulators, -blockers and anti-depressants.

Fig. 4A and B shows the cumulative loads of the organic UV filters (ΣUVF), the preservatives (ΣPB), the pharmaceuticals (ΣPhAC), and the total chemical contaminants load (ΣTOTAL). In order to have a more specific picture of the reactive barriers' performance, analyzed water samples represented in the graph are those collected during two successive wet periods (January 2018 and March 2018) at the inlet and at the crosswise piezometers from REF, RB1, and RB2 systems. The estimated CECs removal efficiencies of the barriers are shown in Fig. 4C and D.

The higher load of total chemical contaminants in March, compared to January (compare Fig. 4 A to B) can be easily correlated with the population increment that the municipalities in the area experiment during Easter holidays. In particular, the increase in the concentration of PhAcs draws special attention; it is almost 5 times higher in March. Likewise, the increasing concentrations of PBs observed may be attributed to the eventual increase in population

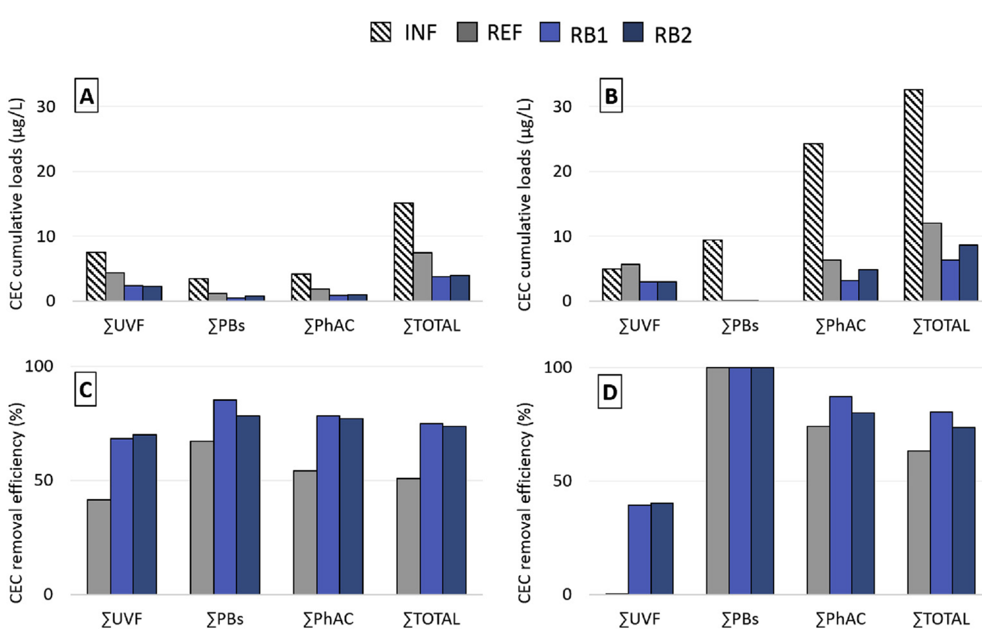

Fig. 4. Cumulative loads of organic UV filters, preservatives, pharmaceuticals, and total target chemicals loads determined at the inlet (infiltration) and at the crosswise piezometers of the REF, RB1, and RB2 systems in A) January 2018 and B) March 2018.

in this quite popular touristic destination in the Catalonian coast, because of their wide use as preservatives in food, beverages, cosmetics, pharmaceuticals, …According to the weather forecast service (www.eltiempo.es), temperatures were quite similar in January and March, and thus beach goers appeared to refrained from exposing themselves to the sun, and as a consequence, the concentrations of UVFs in both periods resulted quite similar.

CECs removal appeared to be quite satisfactory, even in the REF system (Fig. 4C and D). Overall, the three barriers displayed removal efficiency for the total loads of the chemicals analyzed in the range 40 to virtually 100%. In March, higher removal rates were calculated for PBs and PhAcs, whilst the opposite was observed for UVFs. The general removal increase is most likely due to the greater time elapsed since the beginning of the start-up of the recharging system, which means that the microbial population has adapted and developed in the medium. The different behavior of the UVFs was not well understood, but could be the result of a competitive process to access the adsorption sites of the barriers' materials with PBs and PhAcs, which were present at much higher concentrations in the infiltration waters from March, as aforementioned.

Despite that solely the infiltration process is pretty efficient at removing certain contaminants, it was proved that the addition of an organic source to the barrier improves CECs elimination. This increased removal performance is mainly observed for UVFs. RB1 (with compost as organic source) provides similar or slightly better removal rates for the target CECs than RB2 (with woodchips as organic substrate) proving that the addition of organic substrates in recharge systems is an efficient approach to reduce chemical contamination loads from recharge waters.

3.2.1. Pathogens indicators

Bacterial indicators of fecal contamination are the most applied parameters for the assessment of pathogen removal efficiency in water and wastewater treatments (Gerba and Pepper, 2009; Salgot et al., 2006). We assessed the occurrence of *E. coli* and Enterococci, which are widely accepted as reference parameters of fecal contamination, waterborne pathogens, and, generally, as bacteriological quality of water (Hendricks and Pool, 2012; Levantesi et al., 2010; Salgot et al., 2006).

Fig. 5 displays concentrations (MPN/100 ml) of *E. coli* (A) and Enterococci (B) measured in samples from the influent water (INF), Crosswise piezometer (Cross) and effluent (Eff) from REF, RB1, and RB2 systems. We observed a general reduction of fecal contamination indicators in all the three recharge systems. The overall removal efficiency varied between 2.4 and 4.3 log units. It worth noting that the *E. coli* removal efficiency (average = 4.1 log units) was higher than that reported for both conventional and advanced wastewater treatment systems (Sanctis et al., 2016). Although limited differences between systems operating with or without barrier were observed, the pilot plant allowed discriminating the effects of different composition of reactive barriers and of the hydrological properties of simulated aquifer on microbiological parameters of water quality.

3.3. Role of plants

Vegetation grew naturally in the recharge areas while we were discussing what to plant. We had planned to keep one recharge area without vegetation, but the fact is that hardly anything grew naturally in T1 system. It is not clear why vegetation did not grow in this system, which is somewhat warmer than the rest (it receives sunlight on the side) and possibly more exposed to wind.

The infiltration capacity of all the systems has remained relatively stable during the whole year. In fact, the applied flow rate is sufficiently small to prevent ponding. That is, the systems are

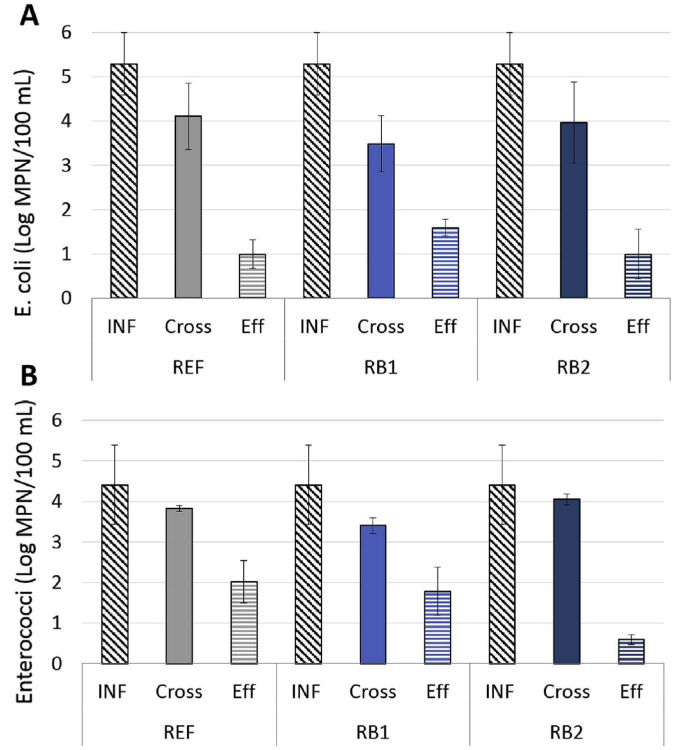

Fig. 5. Concentrations (Log MPN/100 ml) of *E. coli* (A), and Enterococci (B) measured at inflow (INF), Crosswise piezometer (Cross) and effluent (Eff) samples from REF, RB1, and RB2 systems.

operating below capacity, which favors the growth of a rich, almost luxurious, vegetation during spring (Fig. 6B). This vegetation dies in fall, so that vegetation is hardly present in winter (Fig. 6A).

Systems T3 through T6 never clogged and T1 and REF worked generally fine, but clogged one day during winter (Fig. 6C). Clogging of T1 is consistent with our conjecture that by growing roots, plants help in preventing clogging. Recent studies also support this conjecture. Coustumer et al. (2012) and Wu et al. (2017) documented that plants favor infiltration through macropores and root channels formation. Indeed, root biomass correlates positively with the measured infiltration rates during field experiments in a former coal mine (Li et al., 2019). However, the fact that REF system also clogged, despite the presence of plants, suggests that other factors should be relevant as well. Li et al. (2019) summarized factors controlling soil infiltrability as soil texture, moisture and mineral composition. The addition and blend of diverse materials to the sand can cause a variation in the soil texture, preventing the systems that work with the reactive barrier from clogging, in contrast to what happened in REF system.

4. Conclusion

Artificial Recharge through infiltration basins has demonstrate to be efficient improving recharged water quality, specifically regarding CECs and pathogen indicators.

The elimination efficiency of the four groups of CECs studied (UV filters, preservatives, pharmaceuticals, and total target chemicals) ranges between 40% and 100%. The elimination is consistently better in systems that work with reactive barriers than in the reference system.

Pathogen indicators, specifically *E. coli* and Enterococci, are reduced between three and five log units across the recharge systems, which, is higher than that observed for advanced and

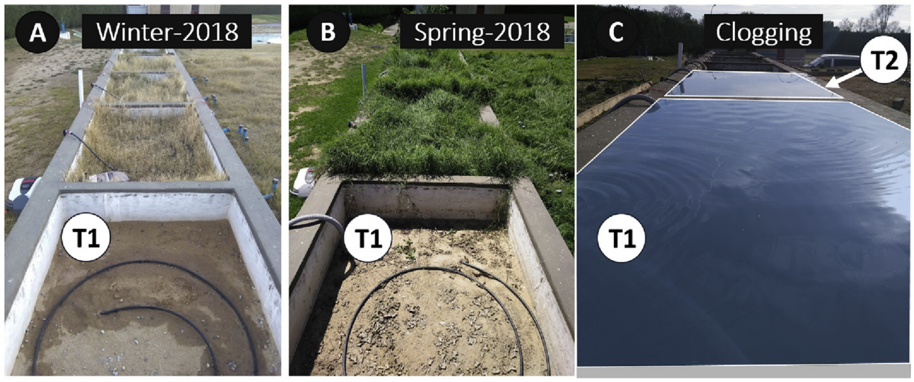

Fig. 6. Plans growth and clogging in T1 (no plants) and T2(REF-no barrier) systems during one recharge episode (A and B), Increase of water column at T1 (RB1-no plants) and T2 (REF-no barrier) During a recharge event.

conventional wastewater treatment systems. The installation of reactive barriers in the recharge areas favors the performance of the systems.

The presence of both plants and reactive barrier in the recharge zone seems to favor the infiltration rates by preventing clogging.

These results confirm that artificial recharge is a very attractive low-cost option to implement as a possible tertiary treatment in WWTP and that its performance is enhanced by the addition of a reactive barrier.

Nevertheless, further work is needed to clarify a number of issues:

1) Results presented here refer to integrated flow average measurements. But suitable understanding of in situ processes requires clarifying sampling procedures to properly distinguish resident concentrations (the ones that control actual reactions) from flow averaged concentrations (the ones that control outflow water quality).

2) Outflowing water was anaerobic because our aquifers do not have a natural flux which with to mix. Recovery of aerobic conditions by mixing reducing recharged water and aerobic native groundwater might help with the quality improvement and generate some Fe precipitates in the aquifer further improving the retention of pathogens. While the systems with reactive barriers performed better than the Reference system, the impact of the barrier was not as dramatic as we had expected. This suggests than other organic substances must be tested to boost the microbial community activity.

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