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Impact of endogenous organic matter in the performance of a Managed Aquifer Recharge pond system: dynamics of bioclogging and redox conditions

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Impact of endogenous organic matter in the performance of a Managed Aquifer Recharge pond system: dynamics of bioclogging and redox conditions

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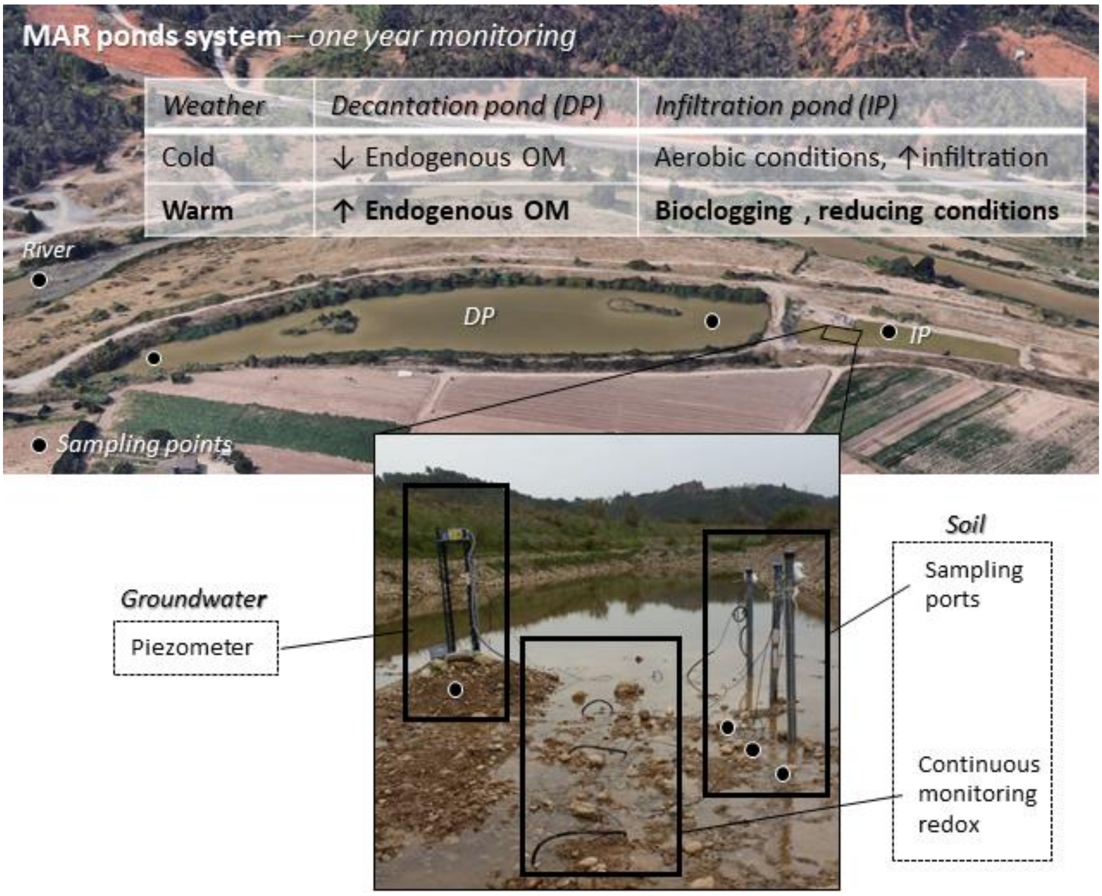
Graphical abstract



MAR ponds system – *one year monitoring*

Weather	*Decantation pond (DP)*	*Infiltration pond (IP)*
Cold	↓ Endogenous OM	Aerobic conditions, ↑infiltration
Warm	**↑ Endogenous OM**	**Bioclogging , reducing conditions**

Abstract

Understanding and characterizing changes in infiltration rates and water quality is key for a proper management and efficiency of MAR systems. Here, we present an integral characterization of a MAR surface infiltration pond system (river, decantation and infiltration ponds, soil and aquifer) in a Mediterranenan climate to investigate the origin and fate of organic matter in the facility, which is presumed to trigger clogging events, and reducing conditions. We performed four sampling surveys in different seasons, to obtain the hydrochemical signature of water and the concentrations and characterization of organic matter (OM) by fluorescence spectroscopy. This allowed the differentiation of OM recently generated (endogenous OM, that is, generated within the MAR system), which fuel microbial respiration processes, from allochthonous OM (imported with the raw water and less prone to degradation). These snapshot campaigns were combined with continuous measurements during one year (every 12 minutes) of redox potential at several points of the topsoil (1 m) of the infiltration pond, and daily measurements of the infiltration rate. Results show that OM is generated within the MAR system during spring and summer, mainly in the decantation pond and to a lesser extent in the infiltration pond. These endogenous organic matter boosts the microbial activity during warmer seasons, inducing reducing conditions in the topsoil of the infiltration pond and diminishing the infiltration rate due to bioclogging. Therefore, the design and management of surface MAR systems in seasonal climates such as the Mediterranean must consider the seasonal effects of endogenous biological activity on water quality and infiltration capacity of the system. Implications of the findings in the design and the management and planning of surface MAR systems are also discussed.

Keywords

Decantation pond; infiltration pond; bioclogging; Redox reactions; soil aquifer treatment

Highlights

- OM is a key parameter influencing bioclogging and redox potential in infiltration ponds
- Endogenous OM is generated within the MAR facility, mainly in the decantation pond
- Bioclogging and reducing conditions occurred in warmer months due to OM production
- MAR systems may be designed and managed to modify endogenous OM growth

1 Introduction

Surface infiltration ponds are engineered solutions widely used in Managed Aquifer Recharge (MAR). MAR facilities typically aim at increasing groundwater resources by storing water in the subsurface. Besides, water increases its residence time, which results in a quality increase of the recharging water through natural or enhanced attenuation processes (Dillon et al., 2018). When this occurs, MAR is considered as a passive water treatment, called Soil Aquifer Treatment (SAT) (Schaffer et al., 2015). Infiltration ponds, as well as other MAR solutions (such as surface spreading, bank filtration and deep wells) might be implemented coupled with a set of water pre-treatments in order to optimize the full infiltration system, in terms of the overall water quality at the reclaim or target point (e.g. for supply or irrigation or to remediate ecosystems).

Clogging is a common operational problem in MAR activities (see Rodríguez-Escales et al., 2018 and references therein for a full discussion on problems leading to system failure in MAR facilities). The main reasons for clogging are particle deposition (physical clogging), growth of biofilms (bioclogging), mineral precipitation (chemical clogging), and gas formation (hydraulic conductivity reduction). In the case of infiltration ponds, the most significant causes are physical and biological. The former is minimized by the presence of a pre-treatment pond which is aimed at promoting the settling of suspended solids thus reducing water turbidity, and the clogging risk (e.g., by introducing a decantation pond). Bioclogging is more difficult to manage since it depends on biological activity, being itself a function of complex interactions between temperature, light, carbon, and nutrient availability (Dou et al.2019), but also the actual design of the MAR facility, and the hydrogeologic conditions. There are several strategies to minimize the overall effect of clogging, from the alternation of dry and wet cycles of recharge (Rodriguez-Escales et al. 2016) to periodic scrapping of the pond surface in order to recover its initial infiltration capacity (e.g., Pedretti et al., 2012a).

Within the MAR facility, water is present in different compartments, from raw (recharge water), pre-treatment, topsoil, unsaturated zone, aquifer, and exit or reclaim point. Water quality keeps changing as a function of location along the MAR system and the infiltration path, or equivalently, with residence time. In quantitative terms, the most significant processes involved in the degradation of pollutants that are initially dissolved in the raw water are those mediated by reduction-oxidation (redox) chemical reactions (Massmann et al. 2006; Rodríguez-Escales et al. 2017). The transference of electrons in redox reactions involves a large number of microbial metabolic processes, contributing to nutrient degradation (Maeng et al., 2011; Massmann et al., 2006), such as Dissolved Organic Carbon (DOC) (Hoppe-Jones et al., 2010), nitrate (Rodríguez-Escales et al., 2016; Grau-Martínez et al., 2018), or ammonium (Canelles et al. 2021). Moreover, the oxidation of organic pollutants in natural environments, such as hydrocarbons (van Breukelen et al., 2004) or emerging organic compounds (EOCs) (Greskowiak et al., 2017) occurs thanks to different metabolic or co-metabolic degradation processes (Rodríguez-Escales et al., 2017). Therefore, understanding the redox dynamics in a recharge facility, both in space and in time, is key to know its actual depuration capacity. The occurrence of redox reactions is mainly conditioned by the presence of an electron donor, usually in the form of organic carbon, which tends to be the limiting reactive in aquifers (Rivett et al., 2008).

The presence of organic carbon in a MAR facility is related to the presence of natural organic matter (OM) and, especially, to the origin of the recharged water. If the water comes from an unpolluted river, the OM is present at low organic carbon concentrations, and composed mainly by dissolved humic and fulvic materials leached from soils (thus, rich in the so-called “humic-like” organic matter), which are recalcritant to degradation (Hudson et al., 2007). If rivers are polluted with wastewater, both Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) concentrations may be high and mostly labile, that is, prone to degradation by the microbial community. Last, if recharge water comes from wetlands (ponds, deep or shallow lakes, reservoirs), the OM may show a considerable fraction of dissolved and particulate compounds endogenously produced by both autotrophic and heterotrophic organisms (Panno et al., 2008). Endogenous organic matter results from anabolic and catabolic reactions, constituting a recently produced carbon, frequently rich in the so-called “protein-like” organic matter which can potentially fuel intense respiration processes (Hudson et al., 2007). We called this organic matter as endogenous carbon since it is originated within the recharge facility itself.

The formation of biomass blooms in MAR facilities are not anecdotal (Noh et al. 2020). When warm temperatures coincide with availability of light and nutrients, both algae and cyanobacteria may grow exponentially, becoming a new source of endogenous POC that becomes available at the MAR system. As this carbon is recently produced, it is more labile than the one present in the river water (Hyung et al., 2020). In a MAR system, biomass blooms may occur in places with longer water residence times (e.g. decantation ponds or pre-treatment wetlands), eventually reaching the topsoil of the infiltration pond (Dutta et al., 2015; Pedretti et al., 2012b). Once POC is produced, it can be hydrolyzed and transformed into labile dissolved organic carbon, becoming a new source of electron donor and boosting microbial communities in the soil and aquifer (Barba et al., 2019a and, 2019b) , which control the reduction-oxidation potential in the unsaturated zone (Rodríguez-Escales et al., 2020; Grau-Martínez et al., 2018).

Despite the relevance of organic matter in biogeochemical processes occurring at MAR facilities, most studies are focused at laboratory scale (Fichtner et al., 2019; Hyung et al., 2020; Takabe et al., 2019; Trussel et al., 2018; Wei et al., 2015, among others). The ones working at the field scale are only concerned about the removal of organic matter in the infiltration pond and limited to systems fed by treated wastewater (Ascúntar-Ríos et al., 2014; Wei et al., 2014; Zhang et al., 2014), with only a few recharged with natural waters (e.g., Jokela et al., 2017). Currently, there is a knowledge gap on the behavior of OM in the whole MAR facility understood as a unit. Even more, the role of endogenous carbon in the different MAR compartments (decantation pond, infiltration pond, etc.) is poorly understood. This is relevant because understanding OM dynamics in MAR systems would allow for the anticipation of bioclogging events, facilitating proper management of the facility, with implications for both the infiltration performance evolution and the water quality at the reclaim point.

The goal of this work is to investigate the origin and the evolution of organic matter along a whole MAR facility and its role in the generation of bioclogging events, and as a controller of the redox processes in the soil below the infiltration pond. For that, we intensively monitored a real recharge facility fed by river water located in Castellbisbal (Barcelona, Spain) during one year. The infiltration rate was recorded daily, while redox state was monitored every 15 minutes in the top soil of the infiltration pond at several depths. Water from the different system compartments (river-recharging water, entrance and exit of the pre-treatment system (decantation pond/wetland), the infiltration pond, the first meter of the unsaturated zone, and the aquifer), were sampled in different seasonal surveys. Implications of the findings in the design and the management and planning of surface MAR systems in the Mediterranean region are then discussed.

2 Methodology

2.1 Castellbisbal site description

The study area is located in Castellbisbal, in the outskirts of Barcelona (Figure 1). It feeds the Cubeta de Sant Andreu's aquifer, a well characterized area from the hydrogeological standpoint, constituted by quaternary sedimentary materials associated to the evolution of the Llobregat River. Different levels of stepped alluvial terraces compose the aquifer. The actual recharge facility used in this study is located in a river meander, in the T0-T1 Terrace, that sits on Cenozoic red mudstones (Martín and López, 2001).

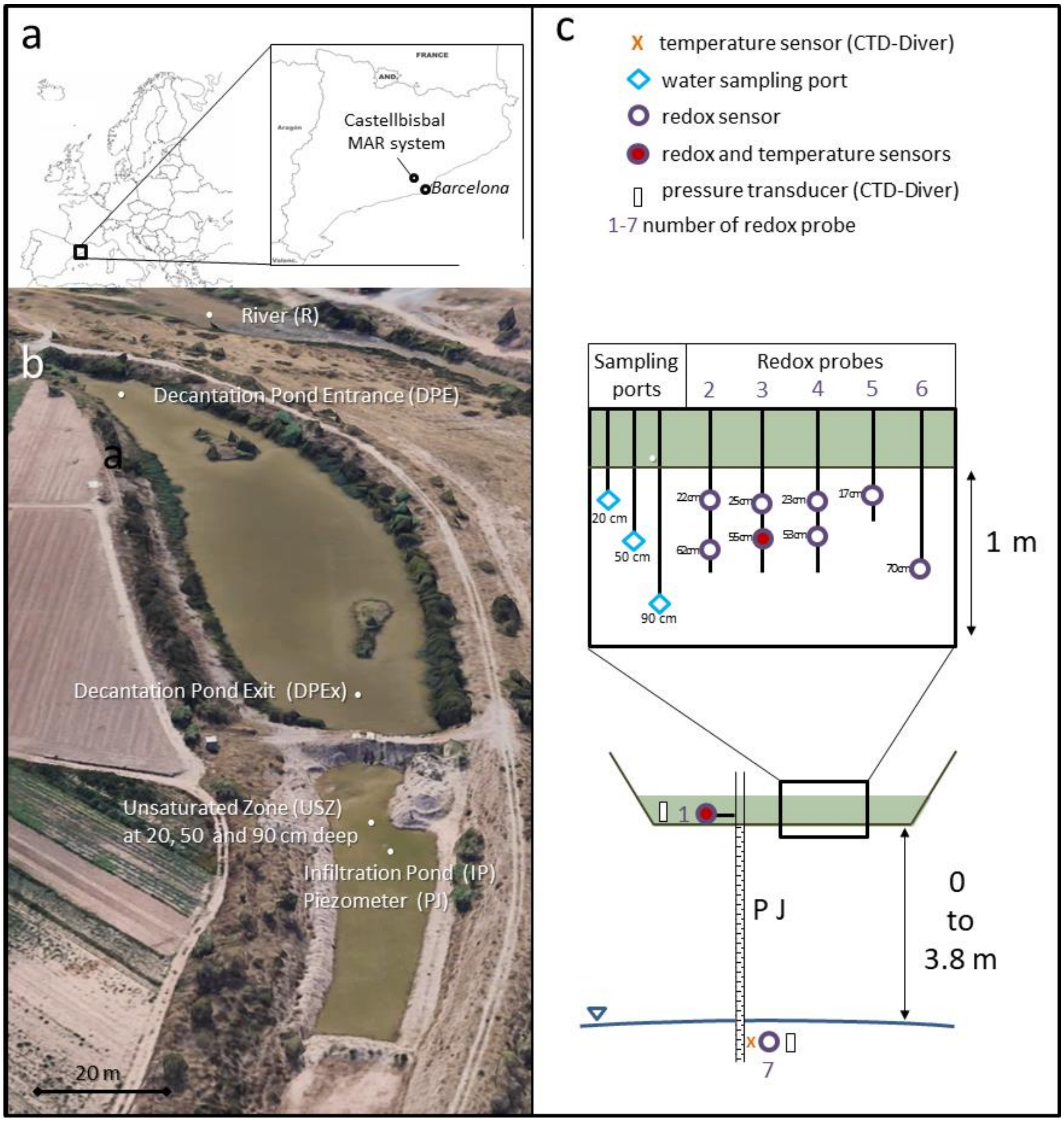


Figure 1. Castellbisbal MAR site description. a) General location of the site; b) Close-up of the facility and location of the sampling points; and c) Detail of the location of the different monitoring points and sensors in cross section.

The MAR system is formed by a permanent-regime decantation pond (acting as wetland) of 14500 m^2, and an infiltration pond of 1400 m^2. The source of water is the Llobregat River, captured some 300 m upstream of the decantation pond. The depth of the aquifer is around 10 m, and the water table lies between 0 – 3.8 m below the bottom of the pond depending on the time of the year. The lithology of the area is composed by gravels in a sandy matrix, with a porosity between 0.2 and 0.3, and an estimated transmissivity of around 4100 m^2/d (Martín and López, 2001). Recharge is mostly continuous over the year, but interrupted by management protocols when the turbidity of the river water reaches 150 NTUs and/or due to maintenance operations or summer holidays. There is a piezometer (PJ) inside the infiltration pond, that crosses the vadose-zone and it is screened only at the permanently saturated part of the aquifer.

2.2 Field site monitoring

2.2.1 Operational conditions during the study

The daily infiltration rate (m/d) was calculated through water balance within the infiltration pond. Storage accumulation in the pond was calculated as the daily cumulative difference in water level (actually measured every 30 minutes). Storage was equated to the difference between water supplied and infiltration, with the area as a function of water depth being known. Inlet flowrate was provided by the water user's community managers (CUACSA), from daily measurements at the interconnection between the decantation and the infiltration pond. Evaporation was considered negligible when compared to the infiltration volumes. Water level, temperature and electrical conductivity were measured at 30 min intervals (CTD-Diver, Schlumberger) in the piezometer PJ (see Figure 1 for location) at a depth of around 6 m from the bottom of the pond. All pressure measurements were compensated with atmospheric pressure values (Baro Diver, Schlumberger).

2.2.2 Non-intrusive continuous monitoring of temperature and redox potential

The non-intrusive redox measurements were taken in three multilevel and seven simple redox potential probes (Hypnos III, MVH Consult, The Netherlands). Their location is provided in Figure 1c. The probes consisted of platinum sensors located at different depths of a fiberglass epoxy tube. The simple sensor probes were installed at the infiltration pond water (probe 1), at 17 cm (probe 5), at 70 cm (probe 6) and inside PJ (depth of 6 m) (probe 7), all reported distances measured from the bottom of the pond. The three multilevel probes (two sensors in each one) measured redox potential at 22 and 62 cm (probe 2), 25 and 55 cm (probe 3) and at 23 and 53 cm (probe 4). A reference electrode (Ag/AgCl) was placed inside piezometer PJ, in order to ensure electrically conductive paths between the reference electrode and the redox probes. The platinum sensors and the reference electrode were connected to Hypnos III (Vorenhout et al., 2004), which recorded the measured potentials every 12 min. Previous to the installation, sensors were calibrated and revised according to the ORP values of a multi-parameter probe (YSI Professional Plus). The ORP values were adjusted to values of a standard hydrogen electrode following the expression obtained in the specifications of a Hamilton 271 mV redox solution, $Eh = ORP - 0.7309T + 225$. Two temperature sensors were integrated into the redox probes, one at the water pond (probe 1) and the other at 55 cm depth of the soil (probe 3, Figure 1c).

2.2.3 Sampling campaigns: hydrochemistry

During the study period of one year (Oct 2016 - Oct 2017), four sampling campaigns were performed: one in winter (December 2016), one in spring (April 2017) and two in summer (June and July 2017). Water sampling locations were: 1) river (R), 2) decantation pond at both entrance and exit (DP-E and DP-Ex), 3) infiltration pond (IP), 4) unsaturated zone at different depths (20, 50 and 90 cm, USZ) and 5) the aquifer just below the infiltration pond (PJ) (see Figure 1c).

The samples of the vadose zone were extracted with a vacuum pump connected to the three sampling ports. In PJ, water was purged before sampling until field parameters stabilized. Field parameters (electrical conductivity, pressure, temperature, dissolved oxygen, carbon dioxide partial pressure, redox potential, and pH) were measured *in situ* with a multi-parameter probe (YSI Professional Plus) and an infrared gas analyzer (EGM-4 PPSystems) connected to a membrane contactor (Liqui-Cell); measurements were performed in a flow cell in order to preserve the pressurization of water during sampling. Alkalinity was measured in the field using test kit. Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), major cations and anions, nutrients and metals were also analyzed from the water samples.

Water samples for DOC determination were filtered in the field through pre-combusted and pre-rinsed 0.7 µm glass fiber filters (GF/F; Whatman, UK). DOC/TOC concentrations were analyzed by high-temperature catalytic oxidation on a Shimadzu TOC-V- CSH analyzer (Shimadzu Co., Japan). The samples for anion and cation analyses were filtered with 0.2 µm nylon filters (Whatman, UK), kept in dark at 4º C, and analyzed in the laboratory within the following 24 h. DOC samples from July 2017 campaign were lost due to instrument malfunctioning. Nitrate, nitrite, major anions and major cations were determined by liquid phase ionic chromatography (IC5000, Dionex, Thermo Fisher Scientific, USA). Phosphate was determined by spectrophotometry (Smartchem 140, AMS Alliance). Samples for metal determination were filtered in the field through a 0.2 µm nylon filters (Whatman, UK), acidified with nitric acid to a pH = 2-3, and analyzed within 72 h by ICP- OES using a Perkin Elmer Optima 3200DV.

2.2.4 Sampling campaigns: organic matter characterization

Dissolved Organic Matter (DOM) composition was characterized by absorbance-fluorescence spectroscopy (AFS) as in Casas-Ruiz et al. (2016). AFS is a semi-quantitative technique that takes advantage of the contrasting fluorescence properties of different pools of DOM (proteins, humic and fulvic acids) (Kothawala et al 2014). Fluorescence Excitation-Emission matrices (EEMs) were obtained measuring samples filtered through a 0.2 µm nylon filter in a 1-cm quartz cuvette, using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Samples were excited using wavelengths from 248 to 449 nm (with 3 nm increments) and the resulting emissions were measured at 250 to 550 nm (3 nm increments). Excitation and emission slit widths were set to 5 nm. All EEMs were corrected for instrument-specific bias and blank subtracted using the EEM of Milli-Q water run every ten samples. Spectra were corrected for inner filter effects following Kothawala et al. (2014) using UV–Visible absorbance spectra (190–800 nm) measured on an

Agilent 8453 diode array spectrophotometer (Agilent Technologies, Germany). The integral of the Raman scatter peak of Milli-Q blanks was used for EEMs intensity calibration to Raman Units (Murphy et al. 2010).

We used several features of the EEMs for characterization of the DOM pools. First, we used the value of fluorescent emission at different excitation peaks in the EEMs traditionally used to differentiate between humic-like DOM (coming from the leaching of organic matter stored in the watershed soils and mostly refractory to microbial degradation) and protein-like DOM (coming from recent anabolic or catabolic biological activity and mostly easily degradable, e.g., proteins). We considered peaks A and C as indicative of humic-like components, and peaks T, B, M of those of protein-like components (Hudson et al., 2007). We also determined two common fluorescent indices: the Humification Index (HIX) and the Biological Index (BIX). HIX index aims at estimating the maturity of soil DOM, whereas BIX is proportional to the content of recently produced organic matter. The Fluorescence Index (FI), widely used for DOM characterization (McKnight et al., 2001) was unresponsive to changes in DOM in our samples, and thus not reported. The integral of the fluorescence signal across the whole EEM was calculated as a semi-quantitative proxy of the amount of fluorescent DOM in the samples.

Organic carbon content in the first 2 cm of the sediment below the infiltration pond was estimated by sampling sediment cores with a plastic syringe in 5 locations selected randomly, and then measured by loss on ignition from the difference between the weight of samples dried at 50ºC in an oven for 48h and after combustion of the samples at 450ºC for 4h. We assumed a ratio of organic matter to carbon of 1.724 (Elosegui and Sabater, 2009). Organic carbon in the biofilm growing on the surface of stones exposed to sunlight in the infiltration pond was measured collecting all biomass in a known surface of 5 randomly selected stones, and subsequently processed in a similar way as the sediment cores.

3 Results

3.1 Infiltration rate, Eh and groundwater level variations

The infiltration rate had strong variations along the one-year observation period (Figure 2a). In general terms, it was highest during cold seasons (autumn and winter). Temporal variations responded to different clogging events and management tasks, which allowed us to define five characteristic periods of infiltration (Reodríguez-Escales et al. 2020). Period I started (initial conditions) in October, after a scrapping operation, and lasted until December (64 days in total). Period II, Dec-Mar (83 d), displayed an intermediate infiltration rate. Period III, Mar-Jun (75 d), started right after a heavy rainfall event, and showed low infiltration rates that we attributed to clogging. Period IV, up to the end of June (27 d), started after a scrapping operation which promoted a period of high infiltration rate. Finally, Period V, Jul-Oct (116 d), displayed fluctuations in the infiltration rate, with flow discontinued in the middle of the period (August) due to summer holidays.

Regardless the variations in the infiltration dynamics, the groundwater level (GWL) was not significantly disturbed (Figure 2b) during the period, attributed to the very high aquifer transmissivity, buffering the mounding effect below the pond. The most important GWL change occurred in Period III, after day 150 (spring), due to an important rain event that produced an increase of river flow that flooded the recharge facilities and induced a significant increase in the regional aquifer levels. For about 3 weeks at the beginning of April, the GWL rose above the bottom of the pond. After this extreme event the GWL slightly and steadily decreased until the end of Period III with some minor increase due to high infiltration rates in periods IV and V.

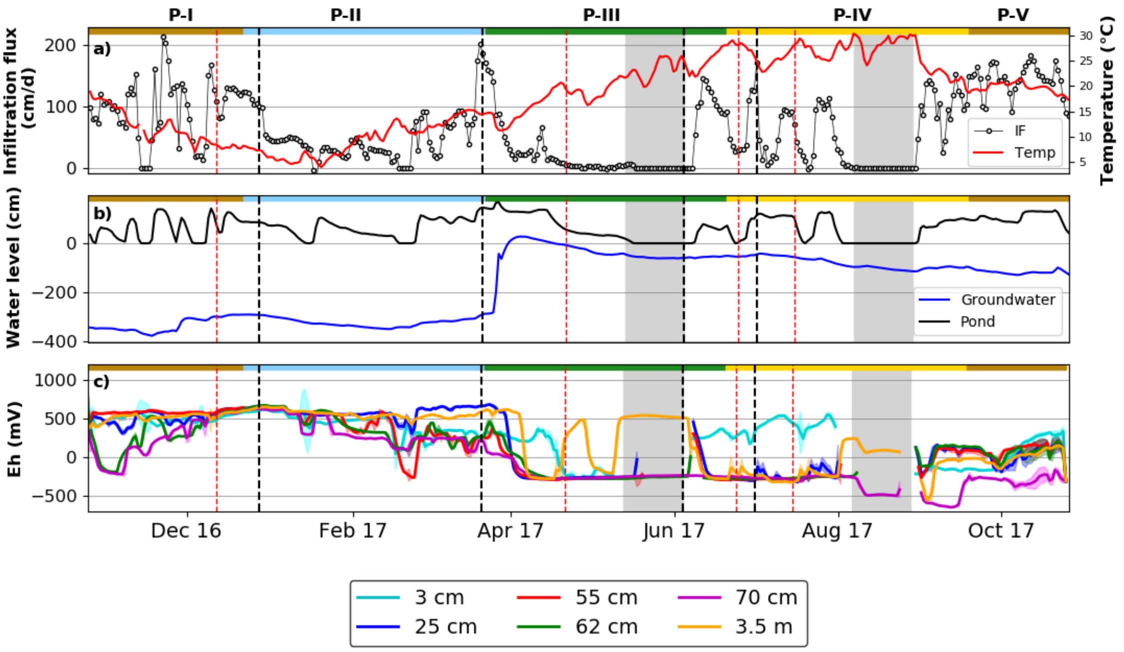


Figure 2. Temporal evolution of the different continuous measurements. a) Infiltration flux in cm/d (black) and temperature within the infiltration pond (red solid line); b) Water level at piezometer PJ (blue) and the infiltration pond (black); c) Redox potential (from sensor redox probes) at different depths. Grey zones are periods where infiltration was discontinued, either due to scrapping operations (June), or for summer holidays (August).

The redox potential (Figure 2c) displays some clear trends. In general terms, the redox potential during autumn and winter (Periods I-II) showed higher values than during spring and summer (Periods III-IV-V). Note that the transition from aerobic conditions (topsoil) to anaerobic ones occurred right below the infiltration pond and within the first meter of the unsaturated zone, a phenomenon also observed elsewhere (e.g., Massmann et al., 2004). The behavior is similar at all depths, except for the redox potential in the shallowest point (3 cm), which was more oxidative at the beginning of summer, this attributed to the immediate scrapping operation.

3.2 Evolution of water quality in depth along seasons

In the winter 2016 survey, most water quality parameters showed slight changes along the different compartments composing the MAR system (Figure 3). In April, there was a slight decrease of nitrogen and phosphorous in the Decantation Pond (DP), but the most important changes occurred in the Infiltration Pond (IP) and the topsoil, with an increase in ammonia, phosphate, manganese and iron, and a decrease in sulfate. In summer, the most significant changes took place in the topsoil, although sulfate and pH variations were observed at DP and IP.

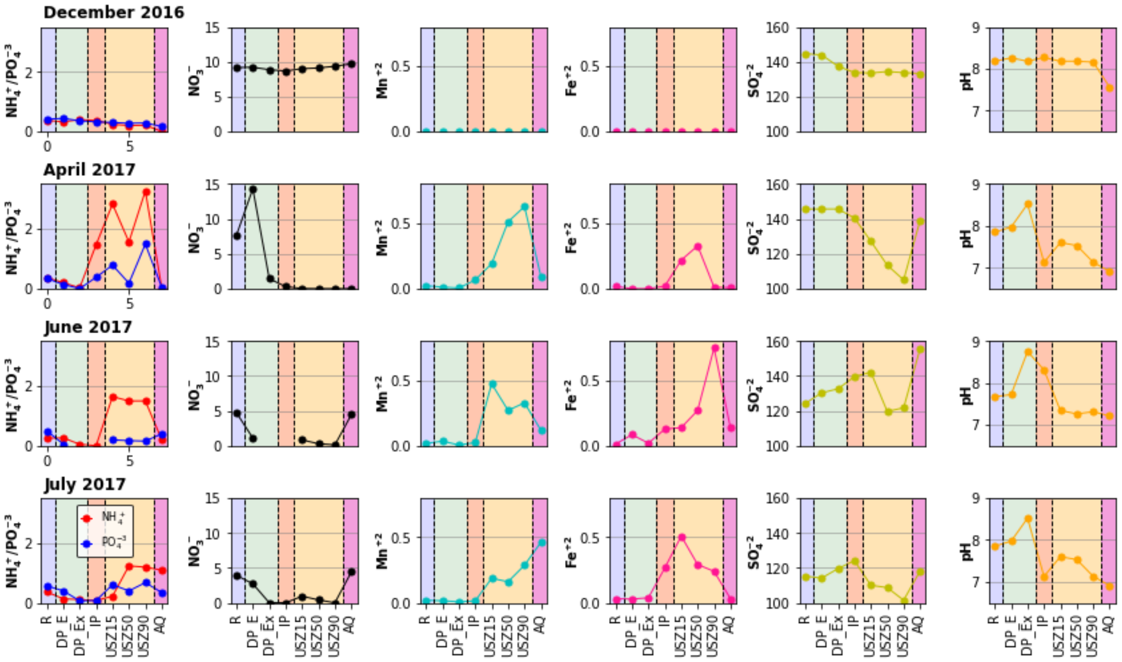


Figure 3. Hydrochemical results of the four sampling campaigns. All units (except pH) are in mg/L. The color pattern relates to the different places within the recharge facility: blue, river (sample denoted by R); green, decantation pond (samples DP-E at the entrance, and DP-EX at the exit); orange, infiltration pond (IP); light orange, unsaturated zone-soil (samples USZ 15, 50 and 0, with numbers indicating depth in cm); and magenta, aquifer (AQ, measured in PJ).

3.3 Organic matter dynamics along the system

The amount of DOC entering in the MAR system from the river (R) was relatively low, between 3 and 6 mg/L during all the monitored period (Figure 4). However, in the April and summer surveys, an increase in TOC and DOC was observed along decantation and infiltration ponds. In the Summer surveys, there was a clear decrease in TOC once the water passed through the topsoil (USZ samples, Figure 4), while in April this reduction started already in the IP. The organic carbon content in the surface sediments (Supplementary Material, TS5 and TS6) was largest in April (241.5±47.1 g C/m^2) and smallest in June (41.8±34.5 g C/m^2), which could be influenced by scrapping operations, while the organic carbon content in the surface biofilm of the infiltration pond fluctuated with no trend between 8.9 and 464.1 g C/m^2.

The intensity of peaks associated to protein-like DOM (peaks T, B, M) relative to those associated to humic-like components (peaks A, C) were lowest in winter with no clear trend, with the smallest variation of organic matter concentration along the system for all seasons. The maximum intensities were observed in June, with a high predominance of protein-like DOM in both ponds and in the vadose zone. In April, the relative intensity of protein-like DOM peaks moderately increased in the infiltration pond compared to the winter values, but being lower than in June; in July, the highest values were observed in the decantation pond. The BIX index (also indicator of recently produced DOM) showed slight variations along the system, while the HIX index (humic-like substances), correlated inversely to BIX following a negative power law (r^2=0.86, p<0.0001).

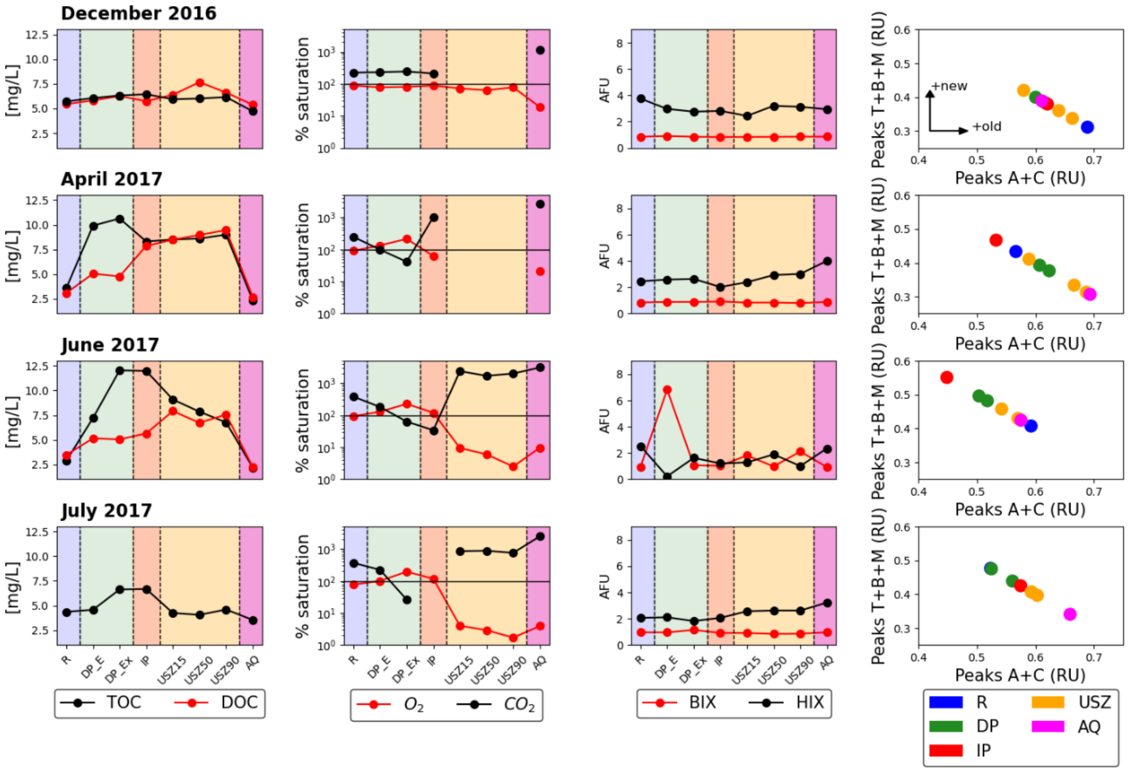


Figure 4. Evolution of TOC, oxygen, CO2 content, BIX, and HIX indices at the different sampling campaigns. See the notation for sampling points in the caption of Figure 3. The last column displays the proportion of fresh-like components (vertical) to humic-like ones (horizontal) corresponding to each sampling point and survey.

4 Discussion

The reported changes in the infiltration rate and the water quality in the different parts of the MAR system respond to a combination of environmental conditions together with managerial activities. Quantitative and qualitative aspects are affected by the redox dynamics below the infiltration pond (see also Goeren et al., 2014, Turkeltaub et al., 2022). Full understanding can only be achieved considering the evolution of the organic matter along the recharge system, linked to the seasonal conditions.

***Autumn and winter*: Low biological activity with high infiltration rate; recharge flow controlled by river water turbidity (Periods I and II)**

Monitoring started in October 2016, following a scrapping of the bottom of the infiltration pond, so with full recharging capacity. During Period I, significant variations in infiltration rate were observed (Figure 2, P-I and P-II), but not due to a decrease in infiltration capacity, but rather due to water availability, as river water turbidity frequently exceeded the threshold value of 150 NTU due to heavy rainfall events. During this high infiltration phase, the Eh values remained relatively constant at oxidant values (+500 mV) at shallow depths during most of the Period I and the beginning of the Period II, indicative of aerobic conditions and relatively few water quality changes in the system. This assumption was confirmed by the December survey where DOC and TOC remained stable in the full facility (Figure 4). The organic matter showed a large presence of humic-like peaks in the DOM samples, indicating preeminence of recalcitrant organic carbon coming from soil leachates in the watershed. Furthermore, the highest values of HIX compared with the other surveys supports the idea of low biological activity during this period, also confirmed by the lack of changes in DO and CO_2 saturation along the system (Figure 4). This low reactivity was also supported by the hydrochemistry, as it remained without significant changes along the MAR system (Figure 3). There was only a slight increase of nitrate with the corresponding decrease of ammonia along the upper soil and the aquifer (Figure 3) which was attributed to nitrification (see Rodríguez- Escales et al. 2020).

During Period II, the infiltration capacity decreased slowly, attributed to several factors: 1) a slight increase in physical clogging due to an incomplete elimination of fine materials in the DP during the heavy rainy events described in Period I; 2) a compaction of the materials present at the bottom of the IP; and 3) a decrease in water temperature, which implicitly implied a reduction of hydraulic conductivity and, consequently, of the infiltration rate (Vandenbohede and Van Houtte, 2012). During this Period II, there was also a decrease in the redox potential (between +500 and 0 mV) indicating that denitrification and manganese reduction were the main processes, as also confirmed by hydrochemistry (Figure 3). This behavior is consistent with the small but continuous increase of temperature (end of winter in a Mediterranean climate) which could have triggered some slight microbial activity in the system, as observed in warmer periods.

Spring: Flooding event disturbing the system with a progressive increase in the biological activity (Period III)

Period III started after a flooding event following a big rain episode at the end of March. An immediate observation was a drastic reduction in infiltration capacity at the beginning of the period (Figure 2a), probably caused by physical clogging from the entrance of suspended solids in both ponds. Physical clogging was also postulated from the outcome of a flow model of the infiltration pond developed in parallel (Rodríguez- Escales et al. 2020). At the same time, the flooding event caused a significant increase of the regional GWL that overflowed the bottom of the infiltration pond during three weeks, followed by a slight decrease with time (Figure 2b).

During this period, the combination of a practically null infiltration rate for two weeks and warm temperatures, enhanced the biological activity of the system. This resulted in a decrease in redox potential from an average of 600 mV to -200 mV in two weeks at the topsoil (Figure 3c) and in three weeks in the aquifer (PJ, Figure 3 (3.5m depth)). The hydrochemical survey carried after the rain event at the infiltration pond showed a null concentration of nitrate, as well as the presence of Mn(II), Fe(II) and sulfur, indicative of reducing conditions, coherent with the reported Eh (Figure 3). Achieving reducing conditions during wet periods and warm temperatures is in agreement with previous works (Moshe et al., 2020). The increase of the biological activity was not restricted to the infiltration pond and the topsoil, but we observed some differences in the metabolic balance for the different MAR facility compartments:

i) In the DP, an important increase of TOC and in less extent of DOC, with very high DO and extremely low CO_2 saturation values, indicating high primary production from photoautotrophs, (Goren et al., 2014; Turkeltaub et al., 2022). TOC peaks were associated to protein-like organic matter, produced *in situ* by primary producers observed in the MAR (algae, cyanobacteria) mainly synthetized in the DP (Figure 4). Indeed, accumulation of algae biomass was visually observed during the field survey. This was coherent with pH dynamics (Figure 3), showing more basified conditions in the decantation pond than in the infiltration one, the topsoil and the aquifer. The OM increase from the river water to the exit of the DP was accompanied with the highest protein-like peaks, supporting the view that OM generation was endogenous and recently produced.

ii) The role of the infiltration pond as generator of endogenous organic matter by photosynthesis was not clear during this season. Despite the IP showed the highest protein-like DOM signal of the April survey, as well as the highest carbon content in the sediments (Supplementary Material), compared with the DP there were a similar TOC values, a decrease in the saturation of O_2, and an increase in CO_2 d (Figure 4). These values indicates that respiration was also occurring in the IP. This would be coherent with the fact that this survey was performed when the infiltration pond was nearly clogged with a GWL above the bottom of the pond (Figure 2). Consequently, the observations were the result of the mixing of groundwater and surface water, where respiration was more important in groundwater whereas photosynthesis in surface water.

iii) In the topsoil of the infiltration pond (USZ) and the aquifer, the dominant process was respiration. This implied DOC degradation and a low pH value, consistant with low oxygen and nitrate concentrations and Eh data (Figures 2, 3 and 4). The steady increase of DOC (and total DOM fluorescence) from the infiltration pond to the vadose zone indicates a transfer from the TOC to the DOC pool, probably biologically mediated. This assumption is consistent with the fact that protein-like DOM peaks moderately increased only in the infiltration pond, where an important reduction TOC together with a decrease of DOC took place. It is interesting to see how DOC properties were modified along the infiltration path, as there was a significant progressive decrease of the protein-like DOM peaks between the top sample (USZ-15), the deep (USZ-90) and the aquifer (PJ). This indicated that the labile organic matter was consumed along the water circulation path through the soil due to the microbiological activity (also consistent with the reduction of Eh, Figures 2 and 3) .

4.3 Summer: Infiltration rate controlled by the biological activity of the system (Periods IV and V) with reducing conditions in the topsoil of the Infiltration Pond.

At the end of Period III (end of spring), the infiltration pond was totally clogged, and scrapping was performed as a mitigation measure. At the beginning of Period IV, the infiltration capacity was fully recovered, which induced during some days a short increase of up to aerobic conditions except at the bottom of the topsoil (70 cm depth) (Figure 2). After two weeks, Eh went down again to values of -200 mV at all depths except the shallowest point (3 cm depth) until the starting of Period V (beginning of July). Further, the infiltration capacity was significantly reduced, this time attributed to bioclogging since: 1) low turbidity in the water daily monitored at the Llobregat River (data not shown); and 2) the infiltration rate was recovered after the summer breaks without any need for additional scrapping actions.

The reported observations were consistent with high biological activity in all MAR compartments. The June survey showed a TOC increase along the system, even higher than in April, with concentrations up to 12 mg/l at the outlet of the decantation pond. Similar to the spring survey, high DO and extremely low CO_2 saturations indicated high primary production in the DP. However, same conditions were also observed in the IP, confirming that primary production occurred in the infiltration pond. This was also coherent with more basified pH than in spring (Figure 3). Once water crossed the infiltration pond, the situation switched, and respiration metabolism took over (DO saturation dramatically decreased, while CO_2 saturation increased). Note that in the spring survey sampling was a mixing between groundwater and surface water as reported, whereas in June this mixing was not expected since GWL did not reach the bottom of the IP.

Summer surveys showed DOM protein-like peaks indicating that the organic matter was generated along both the DP and IP, inducing reducing conditions in the topsoil with a production of manganese and iron, sulfate reduction, and null concentration of nitrate. The intensity of peaks associated to protein-like DOM relative to the intensity of peaks associated to humic-like components showed a maximum in June, mostly in both ponds (in July, being only in DP). Despite in July the system was stopped for 5 days, the infiltration capacity was not recovered until August (grey period in Figure 2) after the MAR system was discontinued for one month (and no scrapping). Finally, in the last part of Period V, the redox potential raised slightly to a low positive value and it seemed to recover the initial conditions (October, 2016).

4.4 Considerations to improve MAR ponds systems planning and management

Understanding changes in the infiltration rate and water quality due to the combination of environmental factors together with management actions allows improving the efficiency of MAR systems. That means water quality is improved without hampering the target infiltration rate. The characterization of organic matter, the hydrochemical signature, plus the continuous monitoring of Eh and infiltration rate indicates that the studied MAR system can produce its own organic carbon on top of the actual carbon present in the raw recharge water. This self-produced organic carbon affects the infiltration rate and induces changes in water quality, both being strongly dependent on climate conditions.

As observed in the Castellbisbal site, for a MAR system in a Mediterranean climate, the biological activity in the MAR ponds in winter with lower temperatures is expected to be minimal, reducing the capability of the system to induce biological clogging and keeping the redox potential in the aerobic zone. During this period, the occurrence of rain events is higher, increasing river turbidity giving as a result an important significance to physical clogging and the need for intense managing operations (discontinuing operation frequently or needing for clogging removal whenever the system is flooded). During warm periods, the biological activity of the system will increase, generating organic matter in the ponds, and enhancing microbiological activity in the topsoil. Such activity results in more reducing conditions of recharge water with higher concentrations of ammonium and metals, especially, during the first meters of the unsaturated zone. Although, at the first moment, this represents a loss in water quality, these conditions enhance the depuration capacity of the MAR facility for more recalcitrant compounds (EOCs). Reducing conditions of the recharged water would be mitigated along the unsaturated zone and/or once it is mixed with groundwater, getting the target with enough quality. It has been widely demonstrated that lower residence times, as well as, more diversity in the redox conditions promoted by a higher biological activity enhances the removal capacity of EOCs in MAR facilities (Valhondo et al. 2014, Rodríguez-Escales et al. 2017). Nevertheless, during this period the system needs to be managed carefully considering the higher risk of clogging. At this point, we strongly recommend a continuous, non-intrusive, and *in-situ* monitoring of the different compartments of the full MAR system. Measurements should include not only infiltration rates (or accumulated volumes), but also the main physicochemical and hydrochemical parameters, the redox potential and the source of the organic matter. Oppositely to winter, infiltration may be maintained without periodic scrapping, provided infiltration is discontinued and allowing the pond to be dried and exposed to the sun to provide unfavourable conditions for biofilm formation. The required drying time for the studied system needs to be properly established in any given facility (in Castellbisbal, it lies between five days and one month), also conditioned to local factors (geology, type and hydraulic characteristics of the soil, climatology, etc.).

Another important point is that the management of the decantation pond may have an important effect on the quality and quantity of the infiltrated water. That is, the organic matter generated in a MAR system with a continuously flooded DP (thus, functioning as a wetland), is expected to be much more significant than in systems where the pond is periodically dried (e.g., when recharge water is supplied in a discontinuous way). For that, the current design of the decantation ponds needs to be rethought. Currently, the main factors to consider when designing it are two: availability of space and enough residence time of water to ensure a proper deposition of the suspended materials. This study indicates that a third factor should be considered, that of the appropriate design (e.g. surface area/depth ratio) in order to increase (if quality is prioritized) or decrease (if quantity is prioritized) the generation of organic matter along the pond. However, it is necessary to stress that in each climatic zone, the variation of the environmental conditions will be different (temperature, light, available nutrients), so that the detailed evolution of the biological activity of a given system should be studied in a case-by-case consideration. Altogether, we believe that proper monitoring will reduce maintenance costs of MAR facilities in the mid and long term.

5 Conclusions

In this work, we have characterized a MAR surface infiltration pond system (river, decantation and infiltration ponds, soil and aquifer) to investigate the origin and the fate of organic matter in the facility and to relate it to the clogging events during a whole year. This characterization has been based on an intensive and continuously monitoring of the infiltration rate, the reduction oxidation potential in the first meter of the unsaturated zone as well as four hydrochemical surveys characterizing, as well, the properties of the organic matter.

The characterization of organic matter has allowed us to distinguish the recent organic matter (endogenous organic matter, that is, generated within the MAR system), which fuel microbial respiration processes, from allochthonous organic matter (imported with the raw water and less prone to degradation). Results show that OM is generated within the MAR system during spring and summer, mainly in the decantation pond and to a lesser extent in the infiltration pond. These endogenous organic matter boosts the microbial activity in the topsoil of the infiltration pond, inducing reducing conditions and diminishing the infiltration rate due to bioclogging. In general terms, the biological activity of surface water was more associated to photosynthesis, whereas infiltrated water to respiration. On the other hand, during cooler seasons, biological activity is diminished and the organic matter present in the MAR facility is more recalcitrant coming from water river. Therefore, clogging events were associated to river water turbidity (with higher values of 150 NTU), which was associated, at the same time, to heavy rainfall events characteristics of Mediterranean region.

Therefore, to fully understand the dynamics and biogeochemical taking place in a MAR system, the full system needs to be considered, from raw water to the aquifer including both ponds and the topsoil. The generation of endogenous organic matter in MAR systems should be considered for managing purposes in order to improve water quality, increase quantity or both, but also the for MAR systems planning and design.

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Abstract

Understanding and characterizing changes in infiltration rates and water quality is key for a proper management and efficiency of MAR systems. Here, we present an integral characterization of a MAR surface infiltration pond system (river, decantation and infiltration ponds, soil and aquifer) in a Mediterranenan climate to investigate the origin and fate of organic matter in the facility, which is presumed to trigger clogging events, and reducing conditions. We performed four sampling surveys in different seasons, to obtain the hydrochemical signature of water and the concentrations and characterization of organic matter (OM) by fluorescence spectroscopy. This allowed the differentiation of OM recently generated (endogenous OM, that is, generated within the MAR system), which fuel microbial respiration processes, from allochthonous OM (imported with the raw water and less prone to degradation). These snapshot campaigns were combined with continuous measurements during one year (every 12 minutes) of redox potential at several points of the topsoil (1 m) of the infiltration pond, and daily measurements of the infiltration rate. Results show that OM is generated within the MAR system during spring and summer, mainly in the decantation pond and to a lesser extent in the infiltration pond. These endogenous organic matter boosts the microbial activity during warmer seasons, inducing reducing conditions in the topsoil of the infiltration pond and diminishing the infiltration rate due to bioclogging. Therefore, the design and management of surface MAR systems in seasonal climates such as the Mediterranean must consider the seasonal effects of endogenous biological activity on water quality and infiltration capacity of the system. Implications of the findings in the design and the management and planning of surface MAR systems are also discussed.

Highlights

- OM is a key parameter influencing bioclogging and redox potential in infiltration ponds
- Endogenous OM is generated within the MAR facility, mainly in the decantation pond
- Bioclogging and reducing conditions occurred in warmer months due to OM production
- MAR systems may be designed and managed to modify endogenous OM growth

Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Barcelona, April 5th, 2023

Editor.
Journal of Hydrology
Elsevier Publishers.

Dear Professor Corrado,

Enclosed is the paper entitled "A holistic view of Managed Aquifer Recharge surface facilities to understand spatial and temporal changes in the infiltration rate and water quality" by Albert Folch, Carme Barba, Rafael Marcé, Xavier Sanchez-Vila, Alvaro Benito and Paula Rodríguez-Escales.

Managed Aquifer Recharge (MAR) infiltration ponds are engineered systems intended to increase freshwater resources in areas facing water scarcity, also in adaptation to the changing climate and global conditions. Despite its importance these kind of systems are not fully understood. To advance in its management and design we present and interdisciplinary study with a full characterization of a MAR surface infiltration pond system (river, decantation and infiltration ponds, soil and aquifer) to investigate the origin and the fate of organic matter in the facility, in terms of trigger of bioclogging events, as well as driver of the water quality variations.

To do it we have monitored for one year (every 12 minutes) redox potential at several points of the topsoil (1 m) of the infiltration pond, and daily measurements of the infiltration rate. This data has been combined with four sampling surveys in different seasons including the hydrochemical signature and the concentrations of organic matter (OM). This OM has been also characterized by fluorescence, (according to the authors knowledge for the first time in a MAR pond system), which allowed us to differentiate between OM recently generated and non-recently synthetized.

Results show that organic matter is generated within the MAR system during spring and summer, (mainly in the decantation pond) boosting the microbial activity in the topsoil of the infiltration pond, inducing reducing conditions and diminishing the infiltration rate due to bioclogging. The implications of these findings in the design and the management of surface MAR systems are discussed.

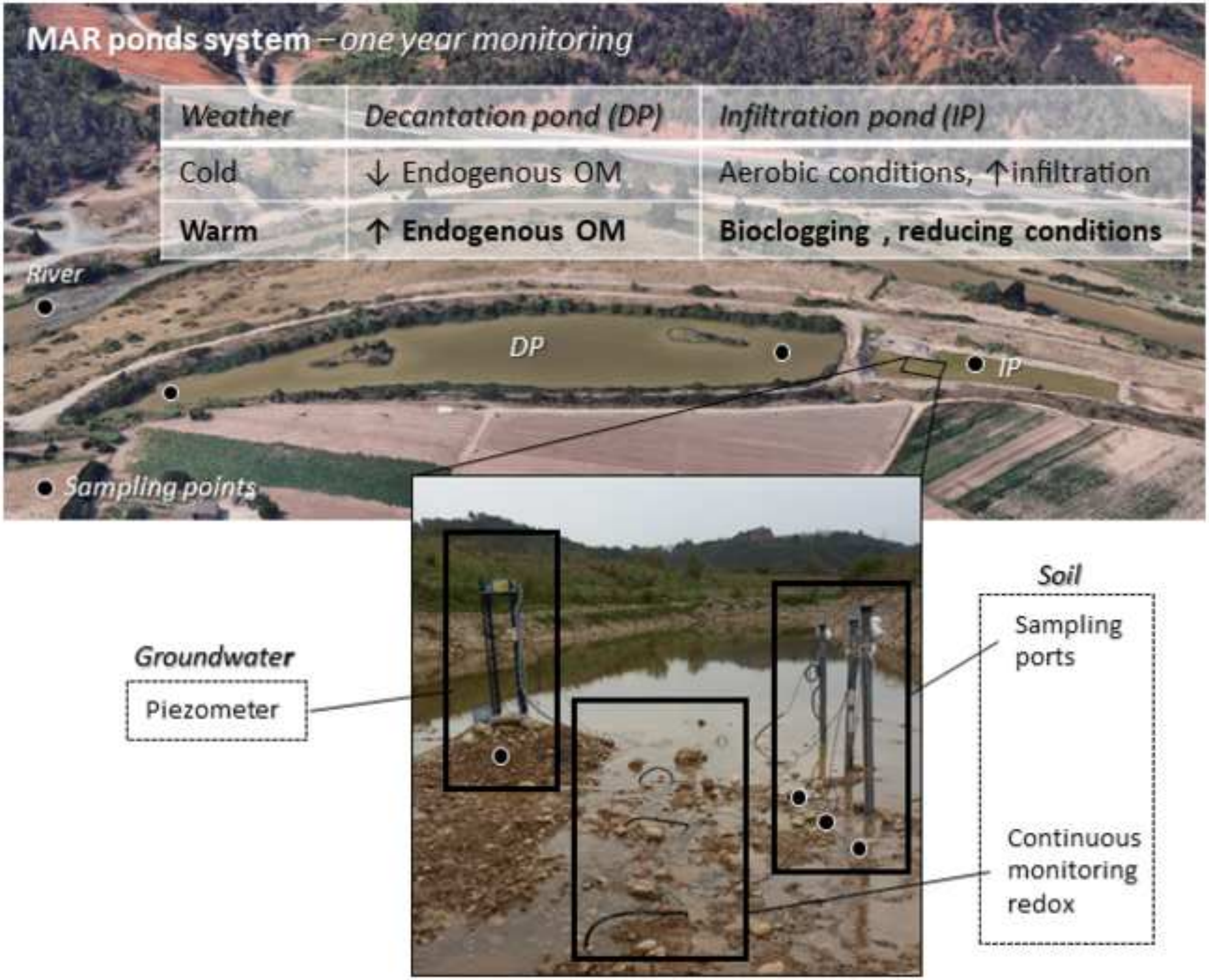
According to the results, we believe that this manuscript is suitable for publication in Journal of Hydrology. This manuscript is an original work; it was not published elsewhere, and it is not under consideration for publication elsewhere. All authors have read the manuscript and have agreed to submit it to Journal of Hydrology

Thank you in advance.

Yours faithfully,

Albert Folch

Graphical Abstract (for review)



MAR ponds system – *one year monitoring*

Weather	*Decantation pond (DP)*	*Infiltration pond (IP)*
Cold	↓ Endogenous OM	Aerobic conditions, ↑infiltration
Warm	**↑ Endogenous OM**	**Bioclogging , reducing conditions**

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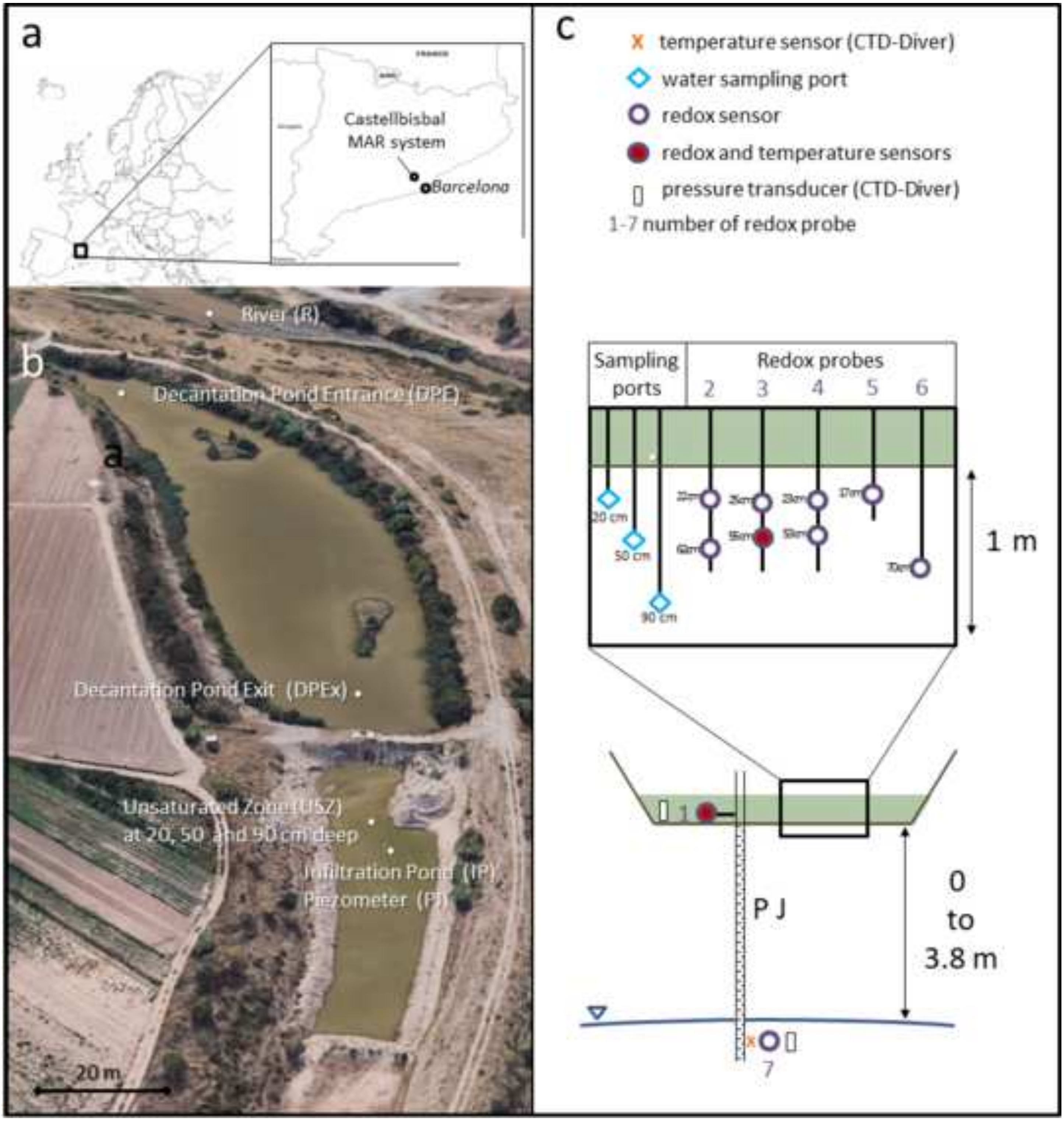

Figure 2

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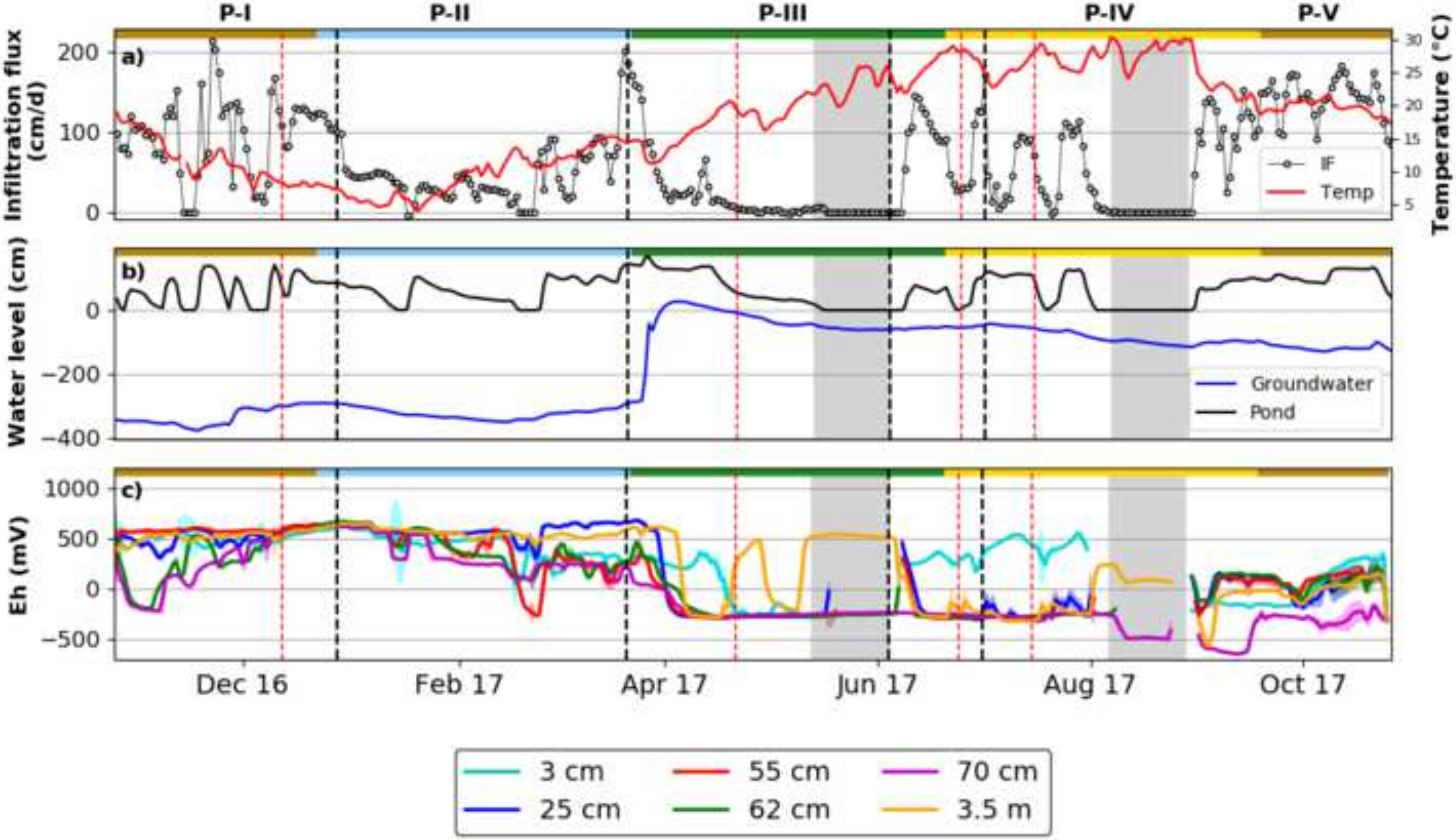

Figure 3

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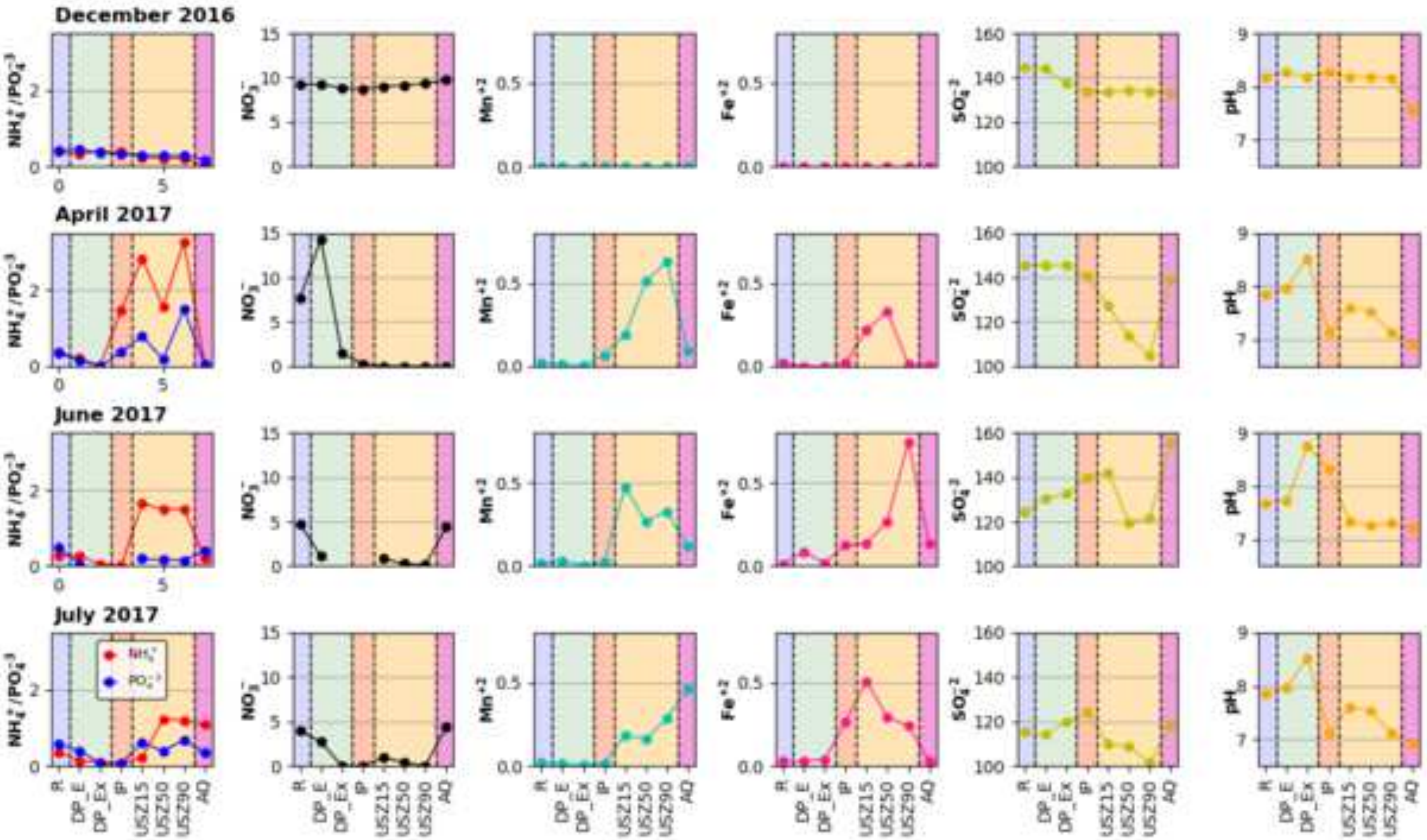

Figure 4

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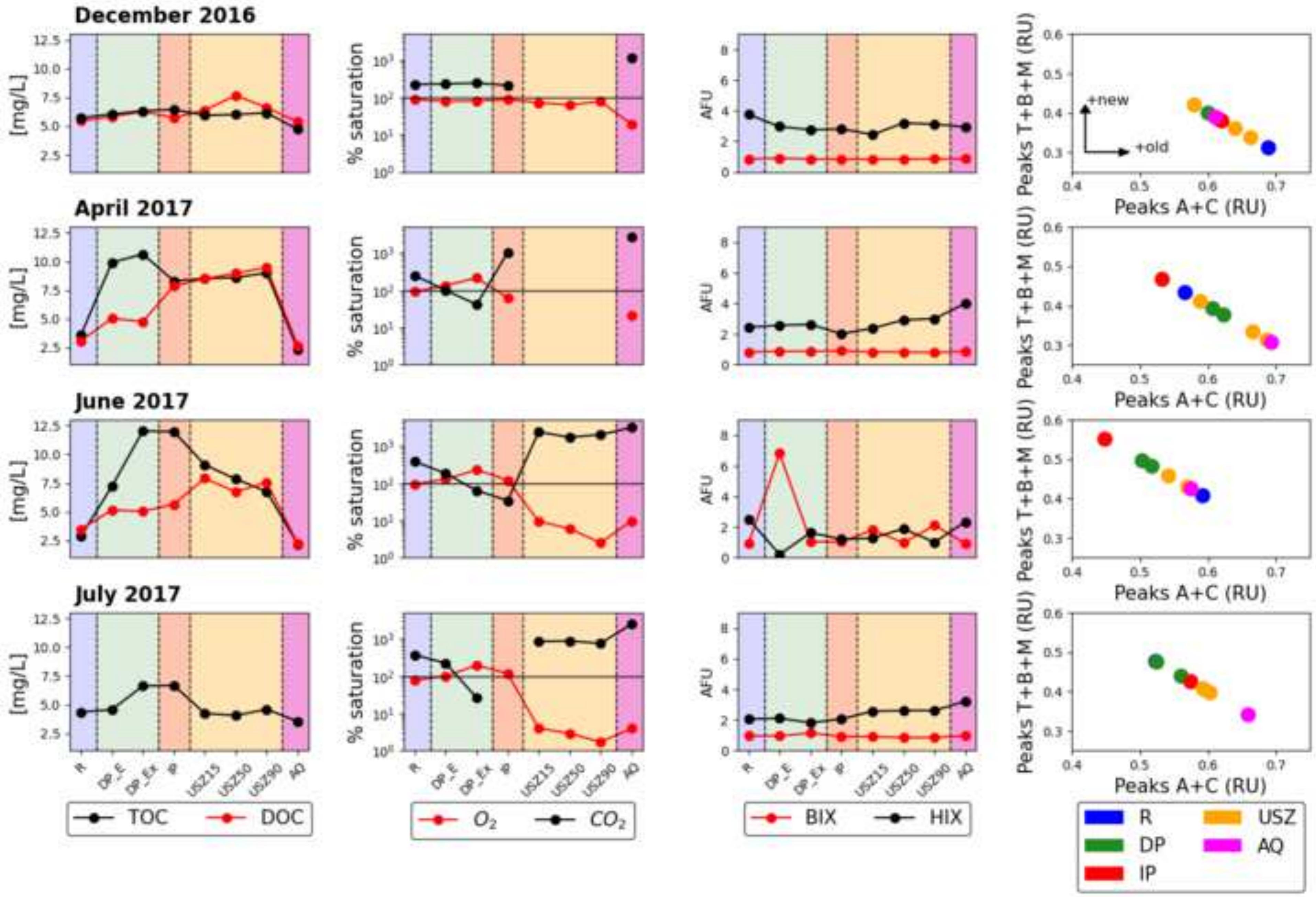

Figure capitations

Figure 1. Castellbisbal MAR site description. a) General location of the site; b) Close-up of the facility and location of the sampling points; and c) Detail of the location of the different monitoring points and sensors in cross section.

Figure 2. Temporal evolution of the different continuous measurements. a) Infiltration flux in cm/d (black) and temperature within the infiltration pond (red solid line); b) Water level at piezometer PJ (blue) and the infiltration pond (black); c) Redox potential (from sensor redox probes) at different depths. Grey zones are periods where infiltration was discontinued, either due to scrapping operations (June), or for summer holidays (August).

Figure 3. Hydrochemical results of the four sampling campaigns. All units (except pH) are in mg/L. The color pattern relates to the different places within the recharge facility: blue, river (sample denoted by R); green, decantation pond (samples DP-E at the entrance, and DP-EX at the exit); orange, infiltration pond (IP); light orange, unsaturated zone-soil (samples USZ 15, 50 and 0, with numbers indicating depth in cm); and magenta, aquifer (AQ, measured in PJ).

Figure 4. Evolution of TOC, oxygen, CO2 content, BIX, and HIX indices at the different sampling campaigns. See the notation for sampling points in the caption of Figure 3. The last column displays the proportion of fresh-like components (vertical) to humic-like ones (horizontal) corresponding to each sampling point and survey.

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