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Modeling of Emerging Organic Contaminants during artificial aquifer recharge, transport, degradation and risk associated

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Abstract

Managed Aquifer Recharge (MAR) is a key strategy to increase freshwater resources in many regions facing water scarcity. The success of a MAR facility implies both technical (water quality and quantity as main examples) and non-technical aspects (legislation, funds, taxes, citizen perception, etc.). Therefore, the aim of this thesis is to improve the management of a MAR facility and to do so, both 1) an assessment of general management of this kind of facilities and 2) the addition of an innovative technical procedure based on numerical modelling to decrease water contaminants in the input water were needed. Specifically, in the case of water contaminants, a reactive barrier was selected as an option and its efficiency was tested in order to see the reduction in nutrients pollutants and emerging organic contaminants (EOCs).

First, a risk assessment was done for a set of MAR facilities across the Mediterranean region. This risk assessment aims for the evaluation of the biggest risks that were perceived by the MAR managers, those risks are related to different technical and non-technical aspects of recharge. Many other works have acknowledged risks of this nature theoretically; however, their quantification and definition has not been developed. In this thesis, the risk definition and quantification has been performed by means of “fault trees” and probabilistic risk assessment (PRA). After that, we have applied this methodology to six different managed aquifer recharge sites located in the Mediterranean Basin. The probabilities of the basic events were defined by expert criteria, based on the knowledge of the different managers of the facilities. From that, we conclude that in all sites, non-technical aspects were as much or even more important than the technical aspects. Regarding the risk results, we observe that the total risk in three of the six sites was equal to or above 0.90. That would mean that the MAR facilities have a risk of failure equal to or higher than 90 % in the period of 2–6 years. The other three sites presented lower risks (75, 29, and 18 % for Malta, Menashe, and Serchio, respectively).

On second place, since water scarcity in the Mediterranean regions is a serious issue, the need for new water sources is high. Managed Aquifer Recharge (MAR) is a key strategy to increase

freshwater resources. In most countries, very high quality of the infiltrating water is required, to limit the impact on the aquifer geochemistry. Usually, this treatment results in expensive procedures, but in this thesis, the possibility of injecting water of lower quality (wastewater) in the aquifer and letting the biogeochemical reactions take place in order to enhance its quality is explored. Here, we present the fate of nutrients (C, N) in the biogeochemical system of a set of laboratory columns to mimic MAR (Modrzyński et al., 2021) that included a reactive barrier formed by mixture of different proportions of sand and compost, supplied with treated wastewater. An integrated conceptual model involving the dynamics of nutrients and biomass (auto and heterotrophic) was developed, and then tested with in the laboratory columns. The model incorporated both saturation and inhibition processes (regarding the nutrients and their byproducts) to provide a comprehensive picture of the nutrient dynamics within the column. The model developed allowed to discriminate the processes that govern the fate of nutrients in relation with the compost enhancing long-term nutrient degradation yet hindering hydraulic parameters that affect infiltration rates.

On third place and following the fate of nutrients, the dynamic of EOCs in the subsurface is studied in this thesis. The processes of sorption and biodegradation for each individual compound are influenced by the overall geochemical signature of water and sediment, and by the reduction-oxidation dynamics. Numerical modeling is a useful tool for process understanding; nevertheless, most of the models existing in the literature for EOC concentration evolution are quite simple, and completely disconnected from the geochemical conditions. In this work, we postulated different conceptual models of EOC fate in the context of Soil Aquifer Treatment activities. The tested models involve the two processes of EOC sorption and biodegradation, and span from them being considered either disconnected to fully connected to the geochemical evolution of major nutrients. The models were then used to interpret the concentrations of five EOC (paracetamol, diuron, benzophenone-3, carbamazepine and sulfamethoxazole) in the experiments of (Modrzyński et al., 2021). The EOC fate models were

coupled with the previous geochemical model focused the carbon and nitrogen cycles validated. Our results demonstrate that the best reproduction of data for paracetamol and sulfamethoxazole is achieved when biodegradation is fully coupled with a geochemical reactive transport model. For benzophenone-3, the best fitting is achieved when a first order degradation is coupled to sorption. Diuron and carbamazepine are best explained assuming a kinetic sorption equation with a slow desorption term. The reduction of all these EOC was observed to be higher with the increasing concentrations of compost the columns had. Therefore, this thesis shows initial promise that reactive column barriers can be a useful tool for EOC reduction in water in a MAR scenario.

With these previously stated aspects, this thesis is articulated in order to offer a big picture of MAR management and its possibilities to increase water resources (using wastewater). This thesis cannot fully develop a strategy for MAR facilities management, nor define a detailed procedure on how to deal with nutrients and EOC. However, it has provided insight on which are the main issues that MAR facilities find themselves during their operation. It has also demonstrated the potentiality of reactive barriers to reduce contaminants in infiltration systems and the main processes in EOC dynamics, therefore implying the possible usage of wastewater as a valuable resource rather than waste.

Resum

La recàrrega gestionada d’aqüífers (MAR) és una estratègia clau per augmentar els recursos d'aigua dolça en moltes regions que s'enfronten a l'escassetat d'aigua. L'èxit d'una instal·lació MAR implica aspectes tant tècnics (qualitat i quantitat de l'aigua com a exemples principals) com no-tècnics (legislació, fons, impostos, percepció ciutadana, etc.). Per tant, l'objectiu d'aquesta tesi és millorar la gestió d'una instal·lació MAR i per fer-ho cal tant 1) una valoració de la gestió general d'aquest tipus d'instal·lacions com 2) la incorporació d'un procediment tècnic innovador per disminuir els contaminants de l'aigua d'entrada (augmentant, per tant, la quantitat d'aigua disponible). Concretament, en el cas dels procediments de contaminació de l'aigua, es va seleccionar una barrera reactiva com a opció i es va provar la seva eficiència per veure la reducció de nutrients (basats en carboni i nitrogen) i contaminants orgànics emergents (EOC).

En primer lloc, per tal de conèixer els principals punts en la gestió general del MAR, es va fer una avaluació de riscos per a un conjunt d'instal·lacions MAR a tota la regió mediterrània. Aquesta avaluació de riscos té com a objectiu l'avaluació dels majors riscos percebuts pels gestors de MAR, aquests riscos estan relacionats amb diferents aspectes tècnics i no tècnics de la recàrrega, com ara disponibilitat d'aigua, qualitat de l'aigua, legislació, qüestions socials, etc. Els estudis han reconegut teòricament riscos d'aquesta naturalesa; tanmateix, la seva quantificació i definició no s'ha desenvolupat. En aquesta tesi, la definició i quantificació del risc s'ha realitzat mitjançant “arbres de falla” i avaluació probabilística del risc (PRA). Hem definit un arbre d'avaria amb 65 esdeveniments bàsics aplicables a la fase d'operació. Després d'això, hem aplicat aquesta metodologia a sis llocs de recàrrega d'aqüífers gestionats diferents situats a la conca del Mediterrani (Portugal, Espanya, Itàlia, Malta i Israel). Les probabilitats dels esdeveniments bàsics es van definir amb criteris experts, a partir del coneixement dels diferents responsables de les instal·lacions. A partir d'això, arribem a la conclusió que en tots els llocs, la percepció dels criteris experts dels aspectes no tècnics va ser tant o fins i tot més important que els aspectes tècnics. Pel que fa als resultats del risc, observem que el risc total en tres dels sis llocs era igual o superior

a 0,90. Això significaria que les instal·lacions MAR tenen un risc de fallada igual o superior al 90% en un període de 2 a 6 anys. Els altres tres llocs presentaven riscos més baixos (75, 29 i 18 % per a Malta, Menashe i Serchio, respectivament).

En segon lloc, atès que l'escassetat d'aigua a les regions mediterrànies és un problema greu, la necessitat de noves fonts d'aigua és alta. En aquesta situació, la recarga artifical d’aqüífers (MAR) és una estratègia clau per augmentar els recursos d'aigua dolça. Tanmateix, els problemes de MAR estan relacionats tant amb la quantitat com amb la qualitat de l'aigua que s'infiltra. A la majoria de països, es requereix una qualitat molt alta de l'aigua infiltrada, per limitar l'impacte en la geoquímica de l'aqüífer. No obstant això, les aigües residuals no es poden utilitzar directament al MAR, per tant la necessitat del seu tractament. Normalment, aquest tractament comporta procediments costosos, però en aquesta tesi s'explora la possibilitat d'injectar aigua de menor qualitat a l'aqüífer i deixar que es produeixin les reaccions biogeoquímiques per tal de millorar-ne la qualitat. Aquí, presentem el destí dels nutrients (C, N) en el sistema biogeoquímic d'un conjunt de columnes de laboratori (Modrzyński et al., 2021) que incloïa una barrera reactiva formada per barreja de diferents proporcions de sorra i compost, subministrades amb aigües residuals per imitar MAR. Es va desenvolupar un model conceptual integrat que implicava els cicles de nutrients i la dinàmica de la biomassa (autòtrofa i heteròtrofa), i després es va provar amb una sèrie d'experiments de transport de soluts en columnes amb diferent fracció de compost en el farciment de la columna. El model incorporava processos de saturació i inhibició (respecte als nutrients i els seus subproductes) per proporcionar una imatge completa de la dinàmica dels nutrients dins de la columna. El model desenvolupat (tres si es consideren les configuracions de 3 columnes) va permetre discriminar els processos que regeixen el destí dels nutrients en relació amb el compost, millorant la degradació dels nutrients a llarg termini però dificultant els paràmetres hidràulics que afecten les taxes d'infiltració.

En tercer lloc i seguint el destí dels nutrients, en aquesta tesi s'estudia la dinàmica dels compostos orgànics emergents (EOC) al subsòl. Els processos d'absorció i biodegradació de cada compost individual estan influenciats per la signatura geoquímica global de l'aigua i el sediment, i per la dinàmica de reducció-oxidació. El modelatge numèric és una eina útil per a la comprensió de processos; no obstant això, la majoria dels models existents a la literatura per a l'evolució de la concentració d'EOCs són força simples i completament desconnectats de les condicions geoquímiques dels sistemes ambientals implicats. En aquest treball, vam postular diferents models conceptuals del destí de l'EOC en el context de les activitats de tractament dels aqüífers del sòl. Els models provats impliquen els dos processos d'absorció i biodegradació d'EOC, i van des que es consideren desconnectats fins a completament connectats a l'evolució geoquímica dels principals nutrients). A continuació, els models es van utilitzar per interpretar les dades informades a la literatura sobre les concentracions de cinc EOC (paracetamol, diuron, benzofenona-3, carbamazepina i sulfametoxazol) en un experiment de columna (Modrzyński et al., 2021); aquestes columnes consistien en una barreja de terra amb diferents fraccions de compost (0%, 10% i 50%), dissenyada per reproduir el destí dels EOC en una bassa d'infiltració amb una barrera reactiva col·locada al damunt. Els models de destí de l'EOC es van combinar amb un model geoquímic anterior centrat en tots els compostos mesurats dels cicles de carboni i nitrogen validats amb els mateixos experiments que el cas dels nutrients. Els nostres resultats demostren que la millor reproducció de les dades de paracetamol i sulfametoxazol s'aconsegueix quan la biodegradació està totalment acoblada amb un model de transport reactiu geoquímic. Per a la benzofenona-3, el millor ajust s'aconsegueix quan una degradació de primer ordre s'acobla a l'absorció. Diuron i carbamazepina s'expliquen millor assumint una equació d'absorció cinètica amb un terme de desorció lenta. Es va observar que la reducció de tots aquests EOC era més gran amb les concentracions creixents de compost que tenien les columnes. Per tant, aquesta tesi mostra la promesa inicial que les barreres de columna reactives poden ser una eina útil per a la reducció d'EOC a l'aigua en un escenari MAR.

Amb aquests tres aspectes esmentats anteriorment, aquesta tesi s'articula amb la finalitat d'oferir una gran imatge de la gestió del MAR i les seves possibilitats per augmentar els recursos hídrics (amb l'ús d'aigües residuals). Aquesta tesi no pot desenvolupar completament una estratègia per a la gestió de les instal·lacions MAR, ni definir un procediment detallat sobre com tractar els nutrients i els EOCs. No obstant això, ha proporcionat una visió sobre quins són els principals problemes que es troben les instal·lacions de MAR durant el seu funcionament. També ha demostrat la potencialitat de les barreres reactives per reduir els contaminants en els sistemes d'infiltració, la qual cosa implica el possible ús de les aigües residuals com un recurs valuós més que com a residu.

Resumen

La recarga gestionada de acuíferos (MAR) es una estrategia clave para aumentar los recursos de agua dulce en muchas regiones que se enfrentan a la escasez de agua. El éxito de una instalación MAR implica aspectos tanto técnicos (calidad y cantidad del agua como ejemplos principales) como no-técnicos (legislación, fondos, impuestos, percepción ciudadana, etc.). Por tanto, el objetivo de esta tesis es mejorar la gestión de una instalación MAR y para ello hace falta tanto 1) una valoración de la gestión general de este tipo de instalaciones como 2) la incorporación de un procedimiento técnico innovador para disminuir los contaminantes del agua de entrada (aumentando, por tanto, la cantidad de agua disponible). Concretamente, en el caso de los procedimientos de contaminación del agua, se seleccionó una barrera reactiva como opción y se probó su eficiencia para ver la reducción de nutrientes (basados en carbono y nitrógeno) y contaminantes orgánicos emergentes (EOC).

En primer lugar, para conocer los principales puntos en la gestión general del MAR, se realizó una evaluación de riesgos para un conjunto de instalaciones MAR en toda la región mediterránea. Esta evaluación de riesgos tiene como objetivo la evaluación de los mayores riesgos percibidos por los gestores de MAR, estos riesgos están relacionados con diferentes aspectos técnicos y no técnicos de la recarga, tales como disponibilidad de agua, calidad del agua, legislación, cuestiones sociales, etc. Los estudios han reconocido teóricamente riesgos de esa naturaleza; sin embargo, su cuantificación y definición no se ha desarrollado. En esta tesis, la definición y cuantificación del riesgo se ha realizado mediante “árboles de falla” y evaluación probabilística del riesgo (PRA). Hemos definido un árbol de averías con 65 eventos básicos aplicables a la fase de operación. Después de esto, hemos aplicado esta metodología a seis lugares de recarga de acuíferos gestionados diferentes situados en la cuenca del Mediterráneo (Portugal, España, Italia, Malta e Israel). Las probabilidades de los eventos básicos se definieron con criterios expertos, a partir del conocimiento de los diferentes responsables de las instalaciones. A partir de esto, llegamos a la conclusión de que en todos los sitios, la percepción

de los criterios expertos de los aspectos no técnicos fue tanto o incluso más importante que los aspectos técnicos. Por lo que respecta a los resultados del riesgo, observamos que el riesgo total en tres de los seis puestos era igual o superior a 0,90. Esto significaría que las instalaciones MAR tienen un riesgo de fallo igual o superior al 90% en un período de 2 a 6 años. Los otros tres sitios presentaban riesgos más bajos (75, 29 y 18 % para Malta, Menashe y Serchio, respectivamente).

En segundo lugar, dado que la escasez de agua en las regiones mediterráneas es un problema grave, la necesidad de nuevas fuentes de agua es alta. En esta situación, la recarga artificial de acuíferos (MAR) es una estrategia clave para aumentar los recursos de agua dulce. Sin embargo, los problemas de MAR están relacionados tanto con la cantidad como con la calidad del agua que se infiltra. En la mayoría de países, se requiere una calidad muy alta del agua infiltrada, para limitar el impacto en la geoquímica del acuífero. Sin embargo, las aguas residuales no se pueden utilizar directamente en el MAR, por tanto la necesidad de su tratamiento. Normalmente, este tratamiento comporta procedimientos costosos, pero en esta tesis se explora la posibilidad de inyectar agua de menor calidad en el acuífero y dejar que se produzcan las reacciones biogeoquímicas para mejorar su calidad. Aquí, presentamos el destino de los nutrientes (C, N) en el sistema biogeoquímico de un conjunto de columnas de laboratorio (Modrzyński et al., 2021) que incluía una barrera reactiva formada por mezcla de diferentes proporciones de arena y compost, suministradas con aguas residuales para imitar MAR. Se desarrolló un modelo conceptual integrado que implicaba los ciclos de nutrientes y la dinámica de la biomasa (autótrofa y heterótrofa), y después se probó con una serie de experimentos de transporte de solutos en columnas con diferente fracción de compost en el relleno de la columna. El modelo incorporaba procesos de saturación e inhibición (respecto a los nutrientes y sus subproductos) para proporcionar una imagen completa de la dinámica de los nutrientes dentro de la columna. El modelo desarrollado (tres si se consideran las configuraciones de 3 columnas) permitió discriminar los procesos que rigen el destino de los nutrientes en relación con el compost, mejorando la degradación de los nutrientes a largo plazo pero dificultando los parámetros hidráulicos que afectan a las tasas de infiltración.

En tercer lugar y siguiendo el destino de los nutrientes, en esta tesis se estudia la dinámica de los compuestos orgánicos emergentes (EOC) en el subsuelo. Los procesos de absorción y biodegradación de cada compuesto individual están influenciados por la firma geoquímica global del agua y el sedimento, y por la dinámica de reducción-oxidación. El modelado numérico es una herramienta útil para la comprensión de procesos; sin embargo, la mayoría de los modelos existentes en la literatura para la evolución de la concentración de EOCs son bastante simples y completamente desconectados de las condiciones geoquímicas de los sistemas ambientales implicados. En este trabajo, postulamos diferentes modelos conceptuales del destino del EOC en el contexto de las actividades de tratamiento de los acuíferos del suelo. Los modelos probados implican los dos procesos de absorción y biodegradación de EOC, y van desde que se consideran desconectados hasta completamente conectados a la evolución geoquímica de los principales nutrientes. A continuación, los modelos se utilizaron para interpretar los datos informados en la literatura sobre las concentraciones de cinco EOC (paracetamol, diuron, benzofenona-3, carbamazepina y sulfametoxazol) en un experimento de columna (Modrzyński et al., 2021); estas columnas consistían en una mezcla de tierra con diferentes fracciones de compost (0%, 10% y 50%), diseñada para reproducir el destino de los EOC en una balsa de infiltración con una barrera reactiva colocada encima. Los modelos de destino del EOC se combinaron con un modelo geoquímico anterior centrado en todos los compuestos medidos de los ciclos de carbono y nitrógeno validados con los mismos experimentos que en el caso de los nutrientes. Nuestros resultados demuestran que la mejor reproducción de los datos de paracetamol y sulfametoxazol se logra cuando la biodegradación está totalmente ensamblada con un modelo de transporte reactivo geoquímico. Para la benzofenona-3, el mejor ajuste se logra cuando una degradación de primer orden se acopla a la absorción. Diuron y carbamazepina se explican mejor asumiendo una ecuación de absorción cinética con un término de desorción lenta. Se observó que la reducción de todos estos EOC era mayor con las crecientes concentraciones de compost que tenían las columnas. Por tanto, esta tesis muestra la promesa inicial de que las barreras de columna reactivas pueden ser una herramienta útil para la reducción de EOC en el agua en un escenario MAR.

Con estos tres aspectos anteriormente mencionados, esta tesis se articula con el fin de ofrecer una gran imagen de la gestión del MAR y sus posibilidades para aumentar los recursos hídricos (con el uso de aguas residuales). Esta tesis no puede desarrollar completamente una estrategia para la gestión de las instalaciones MAR, ni definir un procedimiento detallado sobre cómo tratar los nutrientes y los EOCs. Sin embargo, ha proporcionado una visión sobre cuáles son los principales problemas que se encuentran en las instalaciones de MAR durante su funcionamiento. También ha demostrado la potencialidad de las barreras reactivas para reducir los contaminantes en los sistemas de infiltración, lo que implica el posible uso de las aguas residuales como un valioso recurso más que como residuo.

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Chapter 1

Introduction

1.1 General state of managed aquifer recharge

The lack of water to supply certain regions around many places in the world is a challenge that has caused many adverse effects on their economy and lifestyles. Since the beginning of time, humanity has tried to alleviate this lack of water in certain areas by developing different water storage strategies.

Authors like Bouwer (2002), Dillon (2005), Maliva and Missimer (2012) or Sprenger et al. (2017) have extensively studied different types of water storage systems, from water dams to aquifer recharge. These strategies have different degrees of usage, leaving water dams and river aquifers as the most popular ones worldwide (Dillon et al., 2009). This thesis focuses on the aquifer recharge systems, which are seen as a viable alternative to more common water storage strategies (Dillon, 2005; Dillon et al., 2019). However, a certain degree of management is needed in all water storage systems, which implies both technical and non-technical aspects (Dillon et al., 2009). Most works focus on technical aspects of water recharge (infiltration rate, water quality, fouling, etc.), however, non-technical aspects (water quality legislation, taxes, funding, etc.) are usually oversighted by the scientific community, although they can be as important as the technical ones (Asano and Cotruvo, 2004; Gale et al., 2006; Leviston et al., 2006; Maliva and Missimer, 2012). The interrelation between these two aspects appears in many factors, although it is obvious when considering water quality.

The quality of the recharged water can be analysed in many aspects (turbidity, temperature, nutrients, contaminants, etc.). However, in most cases, the most critical parameters are usually related to nutrients: the primary forms of nitrogen (nitrate and nitrite) and carbon (labile organic matter). This importance is also reflected in the water legislation, usually its key parameters (European Community, 2000). Despite that initial relevance, other compounds are recently finding importance due to the increased concentrations from the increased development and growth of humanity. These compounds are related to cosmetic products and medical drugs and are usually known as Emerging Organic Contaminants (EOCs). Even though some of these EOCs are not included in the legislation for water recharge, their adverse effects and significance are known to the scientific community (Greskowiak et al., 2017). This makes them interesting enough to be considered in any water storage process. Moreover, the main reason they are of interest is that their chemical pathways are not that well known. Many byproducts have similar effects and dynamics, such as unknown degradation, sorption, mineralisation, etc. (Greskowiak et al., 2017).

Water quality implies the legislative aspect for the maximum concentrations of specific chemical species (nutrients, contaminants or pathogens) and the technical part (ways to reduce the concentration of problematic species). In this context, and focusing on the concentrations of nutrients and organic contaminants, the present legislation in the European Union (European Community, 2000) is very restrictive when recharging water into the aquifers. This implies that the quality of the water needed to recharge an aquifer must be more or less equivalent to drinking water standards. From the technical aspect, there was no counterargument to the statement from the legislation; however, in this thesis, the possibility of increasing the infiltrated water quality during its infiltration process is explored. One of the options to improve the water quality during its infiltration process is the usage of reactive barriers, which enhance contaminant removal while water flows through them.

In Sant Vicenç dels Horts (Barcelona, Spain), an example of an experiment that used a reactive barrier can be found (Valhondo et al., 2014). The barrier was created using a mixture of sand and compost, with low proportions of clay and iron. To enhance the presence of reduction-oxidation (redox) processes (ranging from oxygen to sulphate reduction) in the first meters of the aquifer, compost was used as the reactive component of the barrier. However, to guarantee the maximum amount of EOCs degradated, a great variety of redox conditions must be achieved since a wide diversity of bacteria exists in the subsoil (Barba et al., 2019; Rodríguez-Escales et al., 2017). More recently, Valhondo et al. (2020) tested different reactive barriers in a pilot field system in Palamós (Spain). In this case, the wastewater used was from Palamós Waste Water Treatment Plant (WWTP) effluent, which contained its characteristic nutrients (based on carbon and nitrogen) and EOCs. This was done to set the first steps to change the vision of current European legislation in case of recharge.

To cast some light on the mechanics behind nutrient and EOCs dynamics, which are highly uncertain and complex, conceptual and numerical modelisation is needed to test the relative importance of the different redox processes governing the fate of EOCs (Rodríguez-Escales et al., 2020). Nevertheless, these models are very complex, involving the need to couple groundwater flow, conservative solute transport, geochemical models concerning major compounds (cations, anions, and solid interactions), the definition of the redox state and its spatio-temporal evolution, and, finally, the EOC's fate (sorption, transformation, mineralisation, etc.). Despite the complexity of this modelling effort, its necessity remains unshaken because, without the conceptual and numerical models, there is no way to quantify the processes behind nutrients and EOCs dynamics.

Considering all the abovementioned, this thesis focuses on Managed Aquifer Recharge (MAR) via infiltration systems. First in its management via the different MAR stations studied alongside the Mediterranean Basin and considering their technical and non-technical aspects. And secondly, considering both nutrients (carbon and nitrogen) and EOCs in their degradation and sorption dynamics.

1.2 Thesis objectives

With this, the general objective of this thesis is to improve the management of Managed Aquifer Recharge through the development of risk models and to improve the mechanistic knowledge of nutrients and EOCS dynamics (with the relationship between both). Form the general objective; three points can be defined for this thesis direction.

(1) First, the MAR facilities management and its analysis of their main issues. This point sets a management framework for present and future MAR facilities. For this objective, comprehensive knowledge of the main problems/processes for managing these facilities was wanted. Therefore, shading light into the main reasons for success or failure of a MAR facility.

(2) Second, in a MAR facility, water quality is paramount. Therefore, we wanted to test the possibility of adding a reactive barrier in a laboratory pilot recharge facility. Observing its effects on the inlet water (wastewater) chemical properties, specifically in the main nutrients (carbon and nitrogen). Therefore, exploring the possibility of using wastewater as input water in recharge systems.

(3) Third, other chemical compounds may affect the water quality of the recharge systems. The effect of the reactive barrier was tested to see if its presence could significantly affect these contaminants (EOCs) dynamics. Therefore, making reactive barriers a possible treatment for these contaminants.

With these three objectives, a general framework for this thesis can be obtained to improve the knowledge (objective 1), efficiency (objectives 2 and 3) and future possibilities (objectives 2 and 3) of the managed aquifer recharge.

1.3 Thesis outline

The outline of this thesis can be defined in three chapters:

Chapter 2 – A risk assessment methodology to evaluate the risk failure of Managed Aquifer Recharge in Mediterranean basin

This chapter is an introductory chapter, where a general framework and status analysis for MAR is established. In order to create this framework, the first thing that was needed was data from different managed aquifer recharge facilities (in this case, alongside the Mediterranean Basin). This information was obtained via using a digital tool which accounted for the main risks in a MAR facility and calculated the statistical possibilities of MAR failure due to those risks (which could be technical and non-technical). Once the tool was developed and the information compiled, its analysis was undertaken, therefore defining the main aspects to take into consideration in a MAR facility.

From this general framework, a more specific look into managed aquifer recharge was considered (from technical aspects, water quality). This implied taking a look into the usage possibilities of wastewater usage and reactive barriers in MAR.

Chapter 3 - Impact of compost reactive layer on hydraulic transport and C & N cycles: biogeochemical modelling of infiltration column experiments

In order to study the capabilities of reactive barriers and the possibilities of wastewater usage, a pilot infiltration system was designed. This experiment was done by Modrzyński et al., 2021 and served to obtain the data further used in this thesis. This experiment consisted in a set of laboratory columns, infiltrating wastewater with nutrients and EOCs, filled with soil and with different reactive barriers (changing the percentage of compost, which was the reactive compound of the barrier). The experiment showed the changes in the water composition (from inlet to outlet) alongside time (104 days) and space (29 cm). These water changes were related to the different reactive barriers and biogeochemical processes present in the columns. These processes were further modelled in order to further know the mechanics behind them. First a conceptual model was developed (for only carbon and nitrogen nutrients), then a numerical model for the conceptual model and finally the numerical model was computed using IPHT3D (Prommer et al. 2001) in order to see its evolution alongside time and space.

Chapter 4 - A numerical model to evaluate the fate of Emerging Organic Compounds coupled to geochemical conditions in Soil Aquifer Treatment experiments

Following the nutrients dynamics, the EOCs dynamics were taken into account. Again, a conceptual model was developed in order to see the dynamics of these EOCs, considering both sorption and degradation possibilities (including in some cases, the coupling with the nutrients dynamics). After that, a numerical model based on the conceptual one was also developed, which was computed using as well IPHT3D.

Chapter 2

A risk assessment methodology to evaluate the risk failure of Managed Aquifer Recharge in Mediterranean basin

This chapter is an edited version of:

Rodríguez-Escales, P., **Canelles, A.,** Sanchez-Vila, X., Folch, A., Kurtzman, D., Rossetto, R., Fernández-Escalante, E., Lobo-Ferreira, J.-P., Sapiano, M., San-Sebastián, J., and Schüth, C.: A risk assessment methodology to evaluate the risk failure of managed aquifer recharge in the Mediterranean Basin, Hydrol. Earth Syst. Sci., 22, 3213–3227, under a CC BY 4.0 license, https://doi.org/10.5194/hess-22-3213-2018, 2018.

2.1 Introduction

Water scarcity, the chronically lack of sufficient quality water to supply a specific area, is one of the major global challenges. In the Mediterranean Basin, due to low overall precipitation and a pronounced irregularity of rainfall events, it has direct impacts on economic sectors that depend on water, such as agriculture, tourism, and related industries (Fader et al., 2016; Maliva and Missimer, 2012; Navarro-Ortega et al., 2012; Stanhill et al., 2015). Besides this, the population in the Mediterranean Area increased from 81 million in 1960 to 145 million in 2011 (European Environment Agency, 2015), placing additional stress upon existing water resources. Moreover, the Mediterranean Basin is one of the most sensitive regions of the world to climate changes resulting from human activities; according to the latest IPCC projections, average precipitation could decrease by more than 10%, with a larger decrease in summer and in the southern areas (IPCC, 2014).

At the same time, large water quantities are lost to the Mediterranean Sea as surface runoff and discharges from rivers, treated and untreated wastewater, or excess water from various sources during periods of low demand. These alternative water sources potentially can help to increase water availability, both in general terms and in periods of high demand, therefore improving water security. The main factors hindering the effective use of such waters are related to concerns about water quality and the lack of sufficient low cost intermediate storage options. In principal, large storage capacity is available in shallow aquifers, mostly in thick unsaturated zones or in already depleted overexploited aquifers. Managed Aquifer Recharge (MAR) takes advantage of this available storage.

MAR is defined as the intentional infiltration of water into aquifers with the purpose of either later recovering that water for different uses (agricultural, industrial or urban), or obtaining an environmental benefit (Dillon et al., 2009). MAR includes a range of recharge options (surface or subsurface) and water sources (natural, reclaimed or desalinated) (Bouwer, 2002; Dillon, 2005; Maliva and Missimer, 2012; Sprenger et al., 2017). Furthermore, MAR can involve different engineering solutions, among them, infiltration ponds, surface spreading, bank filtration, and wells infiltrating into either the unsaturated or the saturated zones. In addition, water quality can be improved through MAR due to the combination of chemical and biological reactions during transport of the infiltrated water. Water can either be recovered at the point of infiltration (ASR – Aquifer Storage and Recovery), or some distance downgradient (ASTR – Aquifer Storage, Transport and Recovery). The infiltrated water can enable hydraulic control of an aquifer, e.g. to prevent seawater intrusion, aid aquifer quality recovery (amelioration of the groundwater quality), or protect surface water bodies such as wetlands or marshes. Altogether, MAR links water reclamation, water reuse and water resources management.

Due to these beneficial effects, MAR is now widely regarded as a useful tool to ensure a safe and good quality water source for the increasing demand. However, to guarantee the success of any MAR project, some essential elements need to be considered (Dillon et al., 2009), (i) an adequate source of water for recharge, (ii) a suitable aquifer to store and recover water, (iii) available land to construct the facilities, (iv) a sufficient demand for the recovered water, and (v) the capability to efficiently manage such a project. If any of these elements fails, a MAR project is usually not viable. However, the listed factors seem to involve infrastructural and management aspects only, and ignore legal, social, economic, and political constraints that can significantly entangle MAR application, eventually leading to failure of the project as a whole. In addition, the analysis of the potential success of a MAR project should account both for the initial set-up of installation, and also for the potential issues that will arise during its operation (European Community, 2000).

The most common identified technical risks for MAR facilities (e.g. Asano and Cotruvo, 2004; Gale et al., 2006; Leviston et al., 2006; Maliva and Missimer, 2012) are those related to: (i) the operation of the facility (low recovery rates, clogging, mechanical/structural damage, low storage efficiency, high energy consumption); (ii) water quality, either recharged or extracted; (iii) hydraulic engineering impacts, such as rock fracturing, subsidence, or host porous media dissolution; and (iv) environmental impacts, including reduced water outflow to springs and rivers, proliferation of pests and odors, and impact on aquifer dependent ecosystems.

MAR facilities can also be affected by legal, social, economic, and political issues, which increase the risk of failure, meaning that the facility would not begin, or continue operation. Therefore, a full and complete risk assessment must encapsulate all relevant constraints and their confidence level, at a given time and projected into the future. In addition, risk evaluations might include the implementation of measures to control risk, by either diminishing the probability of occurrence of a given hazard, or reducing/correcting its effects if they eventually occur.

The implementation of a MAR facility is therefore subject to a relatively high degree of uncertainty (Bouwer, 2003; Dillon et al., 2009). Uncertainty can be managed using Probabilistic Risk Assessment (PRA), a concept used in various fields of science and engineering. Risk is defined here as the probability of an undesired outcome to happen (evaluated in terms of percentage of occurrence, return period, etc.) and an evaluation of the potential damage that a particular outcome might cause (amount of damage, adverse health effects, impact to ecosystems, etc.). Different definitions for risk in MAR are available in the literature; Maliva and Missimer (2012) defined it as the feasibility (technical and economic) to meet regulatory requirements for aquifer recharge.

Several methods are available for risk evaluation. One such method is the development of Fault Trees, already used in engineered systems (Bedford, 2003; Vesely et al., 1981). Since MAR systems comprise a mixture of natural and engineered components, this approach has received some attention in the hydrological community (e.g. Bolster et al., 2009). The basic idea of PRA based on Fault Trees (PRA-FT) is to take a complex system, difficult to be handled as a whole, and to divide it into a series of quasi-independent simpler events that are manageable individually (i.e. basic events). Once probabilities of occurrence of basic events are computed, they are recombined in a systematic manner to provide the overall risk assessment of the system as a whole. Examples of applications of PRA-FT in hydrogeology include De Barros et al. (2011, 2013), and Jurado et al. (2012).

Although some approaches to evaluate the risk of a MAR system have been developed (Assmuth et al., 2016; Ayuso-Gabella et al., 2011; Dillon et al., 2016; Ji and Lee, 2017, 2016; Juntunen et al., 2017; Page et al., 2010; Toze et al., 2010), comprehensive studies that integrate both non-technical and technical factors are absent (Nandha et al., 2015). In this study, we (i) present precisely an integrated PRA-FT that is applicable for a general MAR facility, and (ii) apply it to six different MAR facilities, that were part of the EU FP7 project MARSOL, located in five different Mediterranean countries: Portugal (1), Spain (2), Italy (1), Malta (1), and Israel (1). To achieve these goals, first, basic events that can lead to MAR failure were compiled based on a literature review of 51 MAR facilities worldwide, and on data from the MARSOL project. The next step was the development of six individual fault trees for the test sites, and assigning probabilities of occurrence for these events. Finally, we used the six sites to compare the different realities, and to test the relative relevance of technical versus non-technical events.

2.2 Literature review: events involved in MAR failure

MAR failure is defined as the need to discontinue operation of the facility due to insufficient potential to infiltrate enough good quality water to recharge the aquifer. Partial failure means that it is possible to mitigate the problem in a short period of time, so that the facility can be put back to operation.

Basic events that can lead to MAR failure were compiled based on a literature review on the problems encountered by different facilities around the world (Aiken and Kuniansky, 2002; Alazard et al., 2016; Assmuth et al., 2016; Bhusari et al., 2016; Chaoka et al., 2006; Flint and Ellett, 2005; Masetti et al., 2016; Murray and Ravenscroft, 2010; Petersen and Glotzbach, 2005; Schneider et al., 1987; Subbasin et al., 2006; Sultana and Ahmed, 2016; Tredoux et al., 2009; Tredoux and Cain, 2010; Tripathi, 2016). We revised 51 MAR facilities at 47 sites (some sites involved more than one facility) located in different countries and climatic conditions worldwide: Australia, Belgium, Botswana, China, Finland, France, Germany, India, Israel, Italy, Jordan, Namibia, South Africa, Spain, Tunisia, and USA. We classified the facilities according to infiltration typology: deep wells (24), surface infiltration (22), and vadose infiltration (5). A summary of the facilities and details can be found in the supporting information.

We then sorted the main causes of MAR failure in terms of frequency of appearance for deep wells and infiltration basins (Figure 2-1). Furthermore, we classified these problems into technical and non-technical problems and sub-classified them into different categories. For the technical ones, we identified four categories: structural damage, quantity issues, quality issues, and failure to achieve specific targets (see Table 2-1). The technical problems with the most occurrence were clogging and the presence of nutrients; they were present in 40-50 % of the reviewed facilities (Figure 2-1) and in all types of MAR facilities. Three types of clogging were reported, being in order of decreasing importance, biological, physical and chemical. On the other hand, the nutrient issues were mainly related to the presence of nitrogen and phosphorus in the recharge water, mostly associated with the use of insufficiently treated reclaimed or surface water, with high nutrients levels, for recharge.

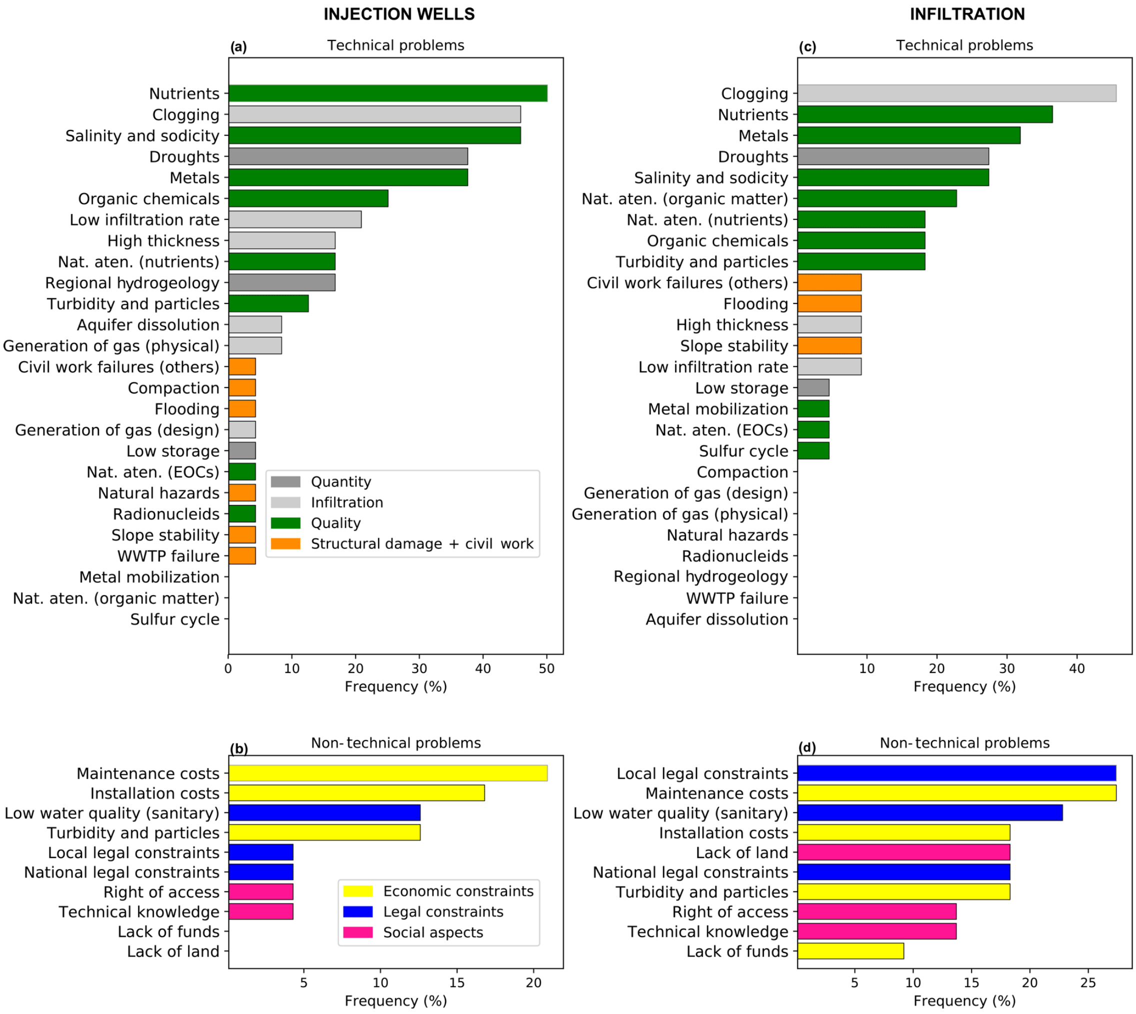


Figure 2-1. *Sorted list in terms of frequency of appearance of the main problems observed in reviewed facilities of deep well injection and infiltration basin. Problems are classified into categories (four for technical, three for non-technical) that are visualized as colors.*

In general terms, quality and infiltration issues were the main aspects that limited the viability of MAR facilities. In fact, the six first technical reasons of MAR failure were the same in all facilities: clogging, nutrients, metals, droughts, low infiltration rate and salinity-sodicity. This can be explained because MAR facilities are often in semi-arid countries were droughts (a main problem from the quantitative point of view) are common. Quantity issues were seldom relevant, and only in infiltration basins. Civil work failures and natural hazards were rarely reported as problems.

Regarding the non-technical aspects, they were classified into four groups: legal constraints, economic constraints, social unacceptance, and governance related problems. The actual issues identified in the MAR facilities revised were thus related to cost (maintenance and installation of the MAR facility), legal aspects (mainly sanitary issues for the infiltrated or the reclaimed waters), and local constraints (land permissions and urban planning issues).

2.3 Methodology. Development of the fault trees and risk evaluation

The methodology used consisted of four steps, modifying the scheme followed by Bedford, (2003): (1) the definition of the concept of system failure and the identification of the key events that would potentially result in such failure; (2) construction of the fault tree depicting the combination of events, seeking the combination of all possible events that may contribute to system failure (where all events should be as independent from each other as possible); (3) developing a probabilistic representation of the fault tree using Boolean algebra and; (4) computing the individual probabilities of event occurrence using conservative approaches and individual event probabilities and upscaling to calculate the global risk of the facility.

2.3.1 Failure definition and identification of key events

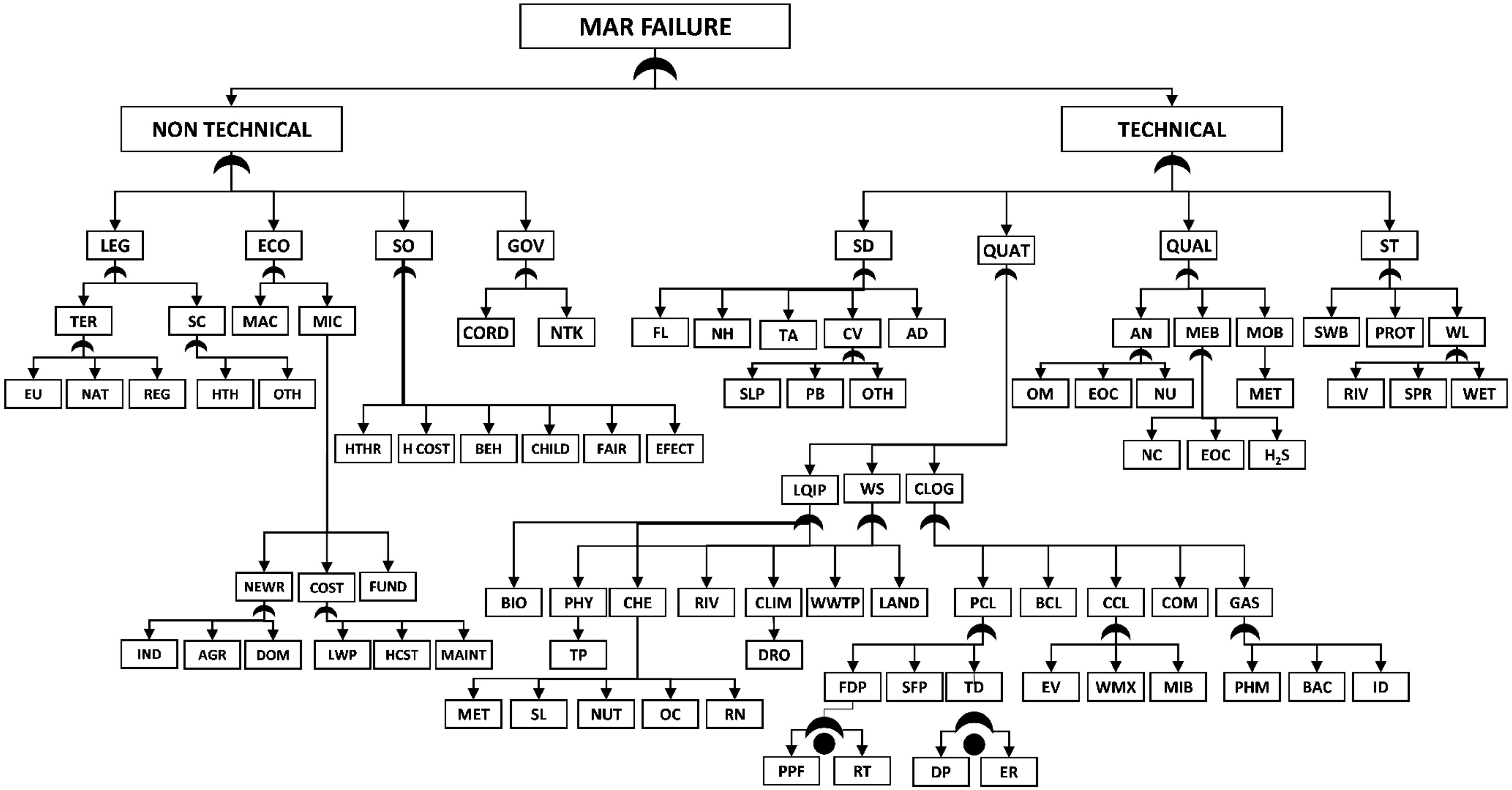
The first step was the identification of the key events that can produce a failure in a general MAR facility by reviewing the literature (supplementary material) and, as a second step, by an extension based on the knowledge and the experience of the facility managers. Failure was based on operation stage, which implies the non-properly functioning of the MAR facility, or the cease of its operation for a prolonged time.

Table 2-1. *Events of the fault tree divided by categories for non-technical and technical issues.*

Non-Technical	Legal constraints (LEG): health, urban, environment, construction permits
	Economic constraints (ECO): lack of funds, maintenance/installation costs, macro and microeconomical problems…
	Social unacceptance (SO): health perception, cost perception, effectiveness perception…
	Governance (GOV): coordination between governmental agencies and technical knowledge about the MAR issues
Technical	Structural damage (SD): damage to the MAR infrastructure due to natural hazards, civil works failure, etc.
	Not enough water or Quantity (QUAT): low water quality (physical, chemical and biological), water scarcity (climate, river regulation, WWTP failure, quantity recharged does not reach some target value that makes it economically feasible) and clogging (physical, biological and chemical) water available does not reach the quality standards needed to allow it to be used in the recharge facility).
	Unacceptable water quality (QUAL): problems with natural attenuation (nutrients, organic matter and emerging organic compounds), metabolites (nitrogen cycle, other nutrients like H2S, etc.) and mobilization of metals. The water finally resulting in the aquifer does not meet some quality standards once it reaches some sensitive location (river, supply well, wetland, …).
	Specific targets (ST): failure to achieve targets related to seawater barriers, protected water bodies and water levels. Seawater intrusion is not sufficiently contained, a protected water body is reached by polluted water or water levels at target surface water bodies (river, spring, wetland) are not reached.

2.3.2 Fault tree construction

The eight categories defined before (technical and non-technical) are described by a few key events, giving a total of 65 (21 Technical and 44 Non-Technical) (see Figure 2-2). A short definition of all the events can be found in Figure 2-2 and in the supporting information.



AD	Aquifer dissolution
AGR	Agricultural use
AN	Inefficient natural attenuation
BAC	Bacterial processes
BCL	Bioclogging
BIO	Sanitary/biological restrictions
BRH	Behavioral requirements
CCL	Chemical clogging
CHE	Chemical restrictions
CHILD	Children surveillance
CLIM	Climate
CLOG	Clogging
COM	Compaction
CORD	Lack of coordination
COST	Cost restriction
CV	Civil work failures
DOM	Domestic use
DP	Deposition
DRO	Droughts
ECO	Economic constraints
EFECT	Perception of effectiveness
EOC	Emerging organic compounds
ER	Erosion
EU	European
EV	Evaporation (excess)
FAIR	Fair distribution of treated wat
FDP	Failure deposition pond
FL	Flooding
FUND	Lack of private/public funding
GAS	Generation of gas
GOV	Governance
H_2S	Other nutrient cycles (H_2S)
HCOST	High cost perception
HCST	High installation cost
HTH	Health legislation
HTHR	Health risk perception
ID	Inappropriate design
IND	Industrial use
LAND	Desalination plant failure
LEG	Legal constraints
LQIP	Low quality water
LWP	Low price of water
MAC	Macroeconomic constraints
MAINT	High maintenance cost/maintenance requirements
MET	Metals (e.g. arsenic, manganese)
MEB	Generation of metabolites
MIC	Microeconomic constraints
MIB	Microbial population catalysis
MOB	Mobilization
NAT	National
NC	Nitrogen cycle (NO_2^-, N_2O…)
NEWR	Not enough wat to recharge due to other econ uses
NH	Natural hazards (e.g. earthquake)
NTK	Non-technical knowledge
NUT	Nutrients (nitrogen, phosphorous)
OC	Organic chemicals (pollutants, EOCs)
OM	Organic matter
OTH	Others
PB	Pipe breakage
PCL	Physical clogging
PHM	Physical Motives
PHY	Physical restrictions
PPF	Pipe filter fails
PROT	Protected water body
QUAL	Unacceptable quality of wat at sensitive location
QUAT	Not enough water recharged
REG	Regional/Local
RIV	River regulation
RN	Radionuclides
RT	Residence time
SC	Scope of legislation
SD	Structural damages
SFP	Source fine particles
SL	Salinity and sodicity
SLP	Slope stability
SO	Social unacceptance
SPR	Spring
ST	Specific targets
SWB	Seawater barriers
TA	Terrorism activities/Vandalism
TD	Transport sedimentation
TER	Territorial constraints
TP	Turbidity/particles
UN	Nutrients
WET	Wetland
WL	Water levels
WMX	Water mixtures
WS	Water scarcity
WWTP	Waste water treatment plant failure
ST	Specific targets

Figure 2-2. *General fault tree for the operational phase.*

2.3.3 Probabilistic representation of the fault tree

The probabilistic analysis is based on two steps: (1) defining a specific probability for each key event to occur, and (2) combining the different events' probabilities, using Boolean algebra, to assign probabilities to the boxes (events) into the one placed immediately above. In this section we illustrate this approach for simplicity and completeness. Additional details about this methodology can be found in Tartakovsky (2007).

For each event, we specify a number of basic subevents following two models: (1) if any basic subevent occurs, then the event will also occur, thus, equivalent to an "OR" operator in Boolean logic; (2) all basic subevents must occur for the event to take place, characteristic of the "AND" operator. So, denoting E as the event, and e_i , $i = 1, \dots, n$ as the basic subevents, the "OR" operators involves:

$$E(or) = \cup_{1,\dots,n}\, e_i, \tag{1}$$

while the "AND" operator results in:

$$E(and) = \cap_{1,\dots,n}\, e_i \tag{2}$$

We illustrate it with a simple example (Figure 2-3), considering that an issue with either social or political implications increase the probability of having a non-technical MAR failure (which in turn would increase the chance of a general MAR failure).

According to the methodology described, we can obtain the probability of the main event (NT), P[NT], as a function of those of the basic events SO and PO

$$P(NT) = P(SO \cup PO) = P(SO) + P(PO) - P(SO \cap PO) \tag{3}$$

Notice that the last term in (4) indicates the product of an intersection; this would be also the case if instead of an "OR" operator we had an "AND" operator, so that in such a case we would have the following formula, $P(NT) = P(SO \cap PO)$. To compute the probability of the intersection of basic events, we rely on the concept of conditional probability (e.g., assuming that politics respond directly to social concern), so that

$$P(SO \cap PO) = P(SO) \cdot P(PO / SO) \tag{4}$$

In the case that SO and PO are independent events, equation (4) simplifies to

$$P(SO \cap PO) = P(SO) \cdot P(PO) \tag{5}$$

This system is transferred to the evaluation of basic events in terms of those placed at a lesser level, and so on.

2.3.4 Computing the individual probabilities of events and the global system failure

The next step is to assign probabilities to all events in the bottom of the tree, and then build up (bottom-up) to assign probabilities using the Boolean rules above, until the top (full system failure) is reached. As a first step, all events were included into four categories depending on probability of occurrence (high, medium, low, or no risk).

A key point in the assessment of risk is assigning probabilities to each individual basic event, this process being quite challenging. One advantage of the fault tree approach is the possibility of assigning them at several stages of involvement, taking into account a combination of simplicity and relevance. The approach consists, first, in assigning a (preliminary) value to all basic events; these values may be based on the experience of the managers of the facility or experts. Such values are combined by the Boolean rules to provide a map of critical paths; i.e., events that are up in the tree and that result in high probability of failure.

The second step would be to devote attention to these significant events and the possibility to correct or reduce their risk in order to reduce the global risk. For those significant events, whose risk contribution is largest, probabilities can be reassigned by using sophisticated approaches, based for example on conceptual or numerical modeling, and also on changing sampling schemes or putting into operation new observation networks. From these new values, the critical events are re-assessed (including total failure). The process can be repeated as many times as needed, to arrive to an improved value of system failure. In addition, corrective and preventive measures could be set to reduce the probability for individual events. The full procedure could go on until either economic resources are exhausted, or else it is considered that further refinement cannot lead to a significant improvement of the final figure.

We provide an example for the purpose of illustration. Let us assume a surface infiltration pond located in a flood plain. We can start by assigning some probability of the MAR facility being affected by flooding (meaning that operation would have to be discontinued for a long time) using a qualitative approach provided by the facility managers (high / intermediate / low / no risk), maybe including the input of local people that would tell us about potential flooding events that took place during their lifetime. It is very relevant to state that these preliminary numbers should always be on the conservative side, meaning that the less technical the evaluation is, the more caution should be included in the actual figures. The second step would use the idea that the facility is located in a 100 year flood plain; if we consider the life of the facility of 30 years, and from simple statistics, we can evaluate the probability that flooding occurs during the lifetime is $1\text{-}0.99^{30}=0.26$. Now, if this number is excessively high and relevant for the evaluation of overall failure, a further step may include a full hydrological analysis through modeling to re-evaluate the probability of flooding.

Additionally, prevention measures for reducing risk by using protection works such as embankments construction may be included. Such a measure could then affect indirectly some events (water quality, social acceptance, …), leading to the need to continuously update all event risks. This step requires a deep knowledge of the system, and must be done under a local perspective and case by case. As the main goal of this paper is to develop a general methodology to evaluate MAR failure and to compare six sites, this type of analysis is out of scope, and we did not perform any detailed analysis of the risk reduction of any event.

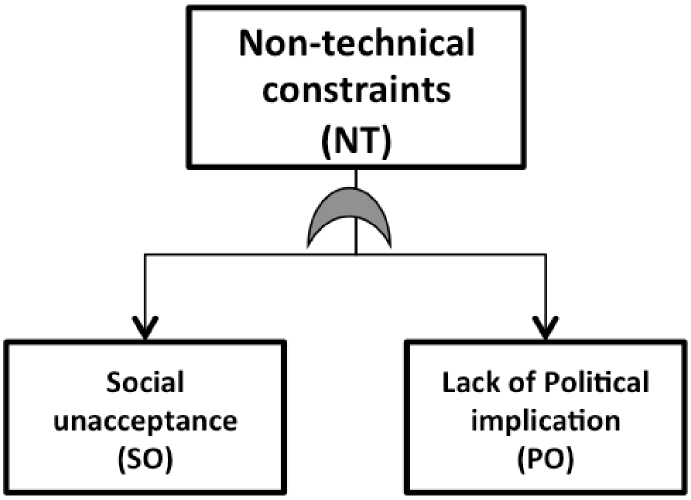


Figure 2-3. *Simplified illustrative case for non-technical constraints involving only sociopolitical constraints. The symbol below the upper event represents an "OR" operator.*

2.4 Description of the field sites

The PTA-FT analysis was performed in six MAR facilities, located in different parts of the Mediterranean basin, offering a broad view of risk perception in the whole area. A summary of the characteristics and context of these sites can be found in Table 2-2.

Table 2-2. *Events of the fault tree divided by categories for non-technical and technical issues.*

	ALGARVE	**LOS ARENALES**	**LLOBREGAT**	**SERCHIO**	**MENASHE**	**MALTA**
Location	Algarve (Portugal)	Los Arenales (Spain)	Sant Vicenç dels Horts (Spain)	Serchio (Italy)	Menashe (Israel)	South Malta (Malta)
Type of recharge	Surface infiltration basins and large wells	Surface infiltration (channels, ditches, ponds) & wells	Surface infiltration (infiltration basins)	Riverbank filtration	Infiltration basin	Deep wells
Source of recharge water	River water and WWTP water	River water	River water	River water	Storm-water Desalinated seawater	WWTP water
Use of the recharged water	Improving aquifer water quality and aquifer storage to prevent seawater intrusion	Agriculture	Improve aquifer quantity and quality	Improve aquifer water quantity and investigation	Store excess of storm water and desalinated water	Coastal barrier for seawater intrusion, increase water quantity and quality
Surrounding	Farmlands	Farmlands	Farmlands and industrial park	Coastal zone and urban areas	Industrial Residential Agriculture	Coastal zone, agricultural region
Aquifer Geology	Alluvial	Aeolian sandy	Alluvial	Sand and gravel alluvial	Interlayered sands calcareous-sandstone and clays	Coastal "floating-lens" aquifer
Political support	Águas do Algarve	Spanish Ministry of Agriculture, Fishing, Food Environment	Catalan Water Agency	Provincia di Lucca administration	Mekorot National Water Company Water Authority	Malta Resources Authority (MRA) and Water Services Corporation (WSC)
Social setup	Framers irrigation associations willing to contribute to financing MAR	Farmers, small industry presence and local public administrations	Water Users Community (Farmers and industry presence)	NA	Pressure on land-use from Industrial sector vs water sector	NA

The first site is located in the Algarve region (south of Portugal). It is based on an infiltration basin constructed in the Rio Seco river bed (Campina de Faro Aquifer system). This MAR facility is aimed at improving the water quality of the Campina de Faro aquifer. It was constructed in 2006 (Lobo-Ferreira and Leitão, 2014). The surroundings of the MAR facility are mainly agricultural and one of its main problems is related to water quality due to agriculture diffuse water pollution, mainly by nitrate (Lobo-Ferreira et al., 2017). This site includes other MAR facilities in the Querença-Silves aquifer and Melides watershed, not included in this evaluation.

The second site, Los Arenales, is located in the center of Spain (Castilla y León). The MAR facility is aimed at providing enough water for the development of rural activities in the zone. Besides this, MAR is also aimed at improving the groundwater quality (reducing nitrate concentrations). In this case, the site is an ensemble of different small facilities (infiltration ponds, river bank filtration and infiltration wells) located in the same aquifer (Los Arenales alluvial aquifer). It started its activity in 2002 and it was expanded in 2003, 2004 and in 2012.

The MAR Llobregat site is located in Catalonia (NorthEast Spain), in an alluvial aquifer placed some 10 km SW of Barcelona City. It is composed of one settling pond and one for infiltration. The recharge water comes from the Llobregat River and the main goal of the facility is to increase the water storage in the aquifer, as well as to improve the quality of the recharged water. A reactive layer was placed at the bottom of the infiltration pond to improve the degradation of both traditional pollutants and emerging organic compounds (e.g. pharmaceuticals) (Valhondo et al., 2015). The area surrounding the facility involves agricultural, industrial and urban uses. It started its activity in 2009.

The induced riverbank filtration scheme along the Serchio River in Sant'Alessio is located in Lucca (Italy). The main goal of this MAR facility is to provide continuous availability of water with good chemical quality for drinking uses to the people of the coastal Tuscany (Rossetto et al., 2015). The surroundings of the zone are mainly peri-urban/rural. This facility provides 15 Mm^3/year and started its activity in the ’60s; it was further improved by building a river weir to increase storage at the beginning of 2000.

The Menashe site is located in Israel. Constructed in 1967, the site includes a settling pond and 3 infiltration ponds and a canal in which storm water flowing in ephemeral streams are diverted for infiltration in sand dunes overlaying the northern part of the Israeli Coastal Aquifer. Since 2013, the facility is used also for infiltration of desalinated-seawater (1-3% of production) from the nearby Hadera desalination plant on the Mediterranean coast (Ganot et al., 2017; Ronen-Eliraz et al., 2017). Freshwater is recovered from wells surrounding the infiltration ponds mainly for residential and industrial consumers.

The Malta site is located in the South Malta Coastal Aquifer. The main objective of this site is the implementation of a MAR facility to act as a seawater intrusion barrier and to minimize the salinization risk of the aquifer using a series of infiltration boreholes. The site is located on the coastal margin of a predominantly agricultural region in a limestone aquifer. The activity started in 2016, and is considered as a pilot site to guide the future implementation of MAR in the Maltese islands.

2.5 Probability assignment and global risk computation

2.5.1 Risk probability assignment

The probabilities for the basic events were defined by the personal in charge of each MAR facility, according to their own experience (expert criteria). These experts had to fill a simple questionnaire providing the four categories in terms of frequency of events (high, medium, low and no risk) for the sixty-five base risk events. These questionnaires followed the same schemes as the fault trees. The values provided by the experts reflected the probability that the MAR facility failed due to one of these basic events during a period of 2-6 years. The qualitative answer was then translated to absolute values of probabilities, in coherence with the importance of the event in a potential failure of the facility.

2.5.2 Global risk computation: MAR-RISK APP

Once the probability values for each basic event were defined, and the questionnaires filled, global risk values for each facility were computed using a visual tool application, the MAR-RISKAPP. This tool was carried out in a friendly interface, aimed at being used by the managers of MAR facilities worldwide. The tool allows the user to assign one of the four risk categories to each basic event. A value of probability is then assigned by default to each event and category. The user can then manually modify each one of the probability values to keep updating the values of the full tree. The global probability of system failure is then computed internally.

The MAR-RISKAPP is an open application which can be downloaded from the website (http://marsol.eu/35-0-Results.html). The main flowchart of the APP is summarized in Figure 2-4 and the manual of the app is summarized in the supplementary material.

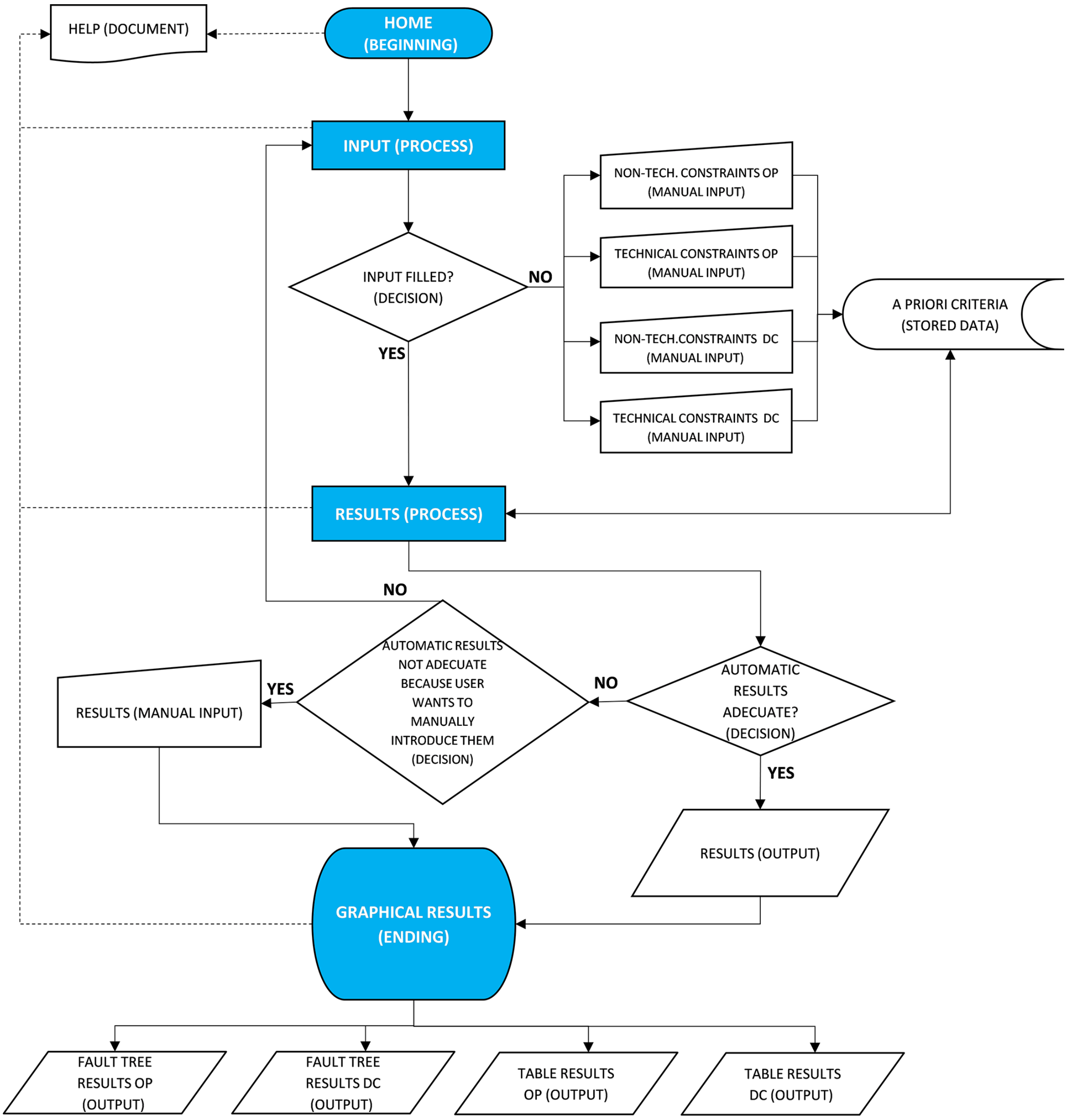


Figure 2-4. *Flowchart for the main program of the MAR-RISKAPP.*

2.6 Results and Discussion

2.6.1 Comparison of risk probabilities defined by expert criteria

As a first step, we have compared the differences between the values provided by the facility managers, internally incorporating personal knowledge and technical expertise, in the six sites. Notice that this way we compare “perception of risk” rather than actual risk. The results, presented as a box plot of all the values reported by categories, showed that the larger values of risk perceived corresponded to events classified as non-technical (Figure 2-5). The risk values (in probability terms) in decreasing order were: Legal constraints, Social aspects, and Economic constraints. On the other hand, for the technical part, the order was (also in decreasing order): Water quantity, Structural damage, and Water quality. Therefore, the perception of risk of the managers of each MAR facility, based on their knowledge and experience, indicates that non-technical aspects are critical and can eventually lead to the facility failing to operate; it might imply that during operation and when the facility has been located in a technically appropriate site, much more uncertainty is expected to non-technical issues than to technical ones.

Legislation was the category with highest risk perception. In general terms, this is explained by lack or extremely new (such in Italy with DM 100/2016) pieces of specific legislation about managed aquifer recharge at the European level. The existing European water directives only provide little guidance for authorizing aquifer recharge schemes (Hochstrat et al., 2010). Consequently, MAR regulation is covered by different institutions and authorities dealing with water, environmental and health legislation. For example, in Menashe, the water recharged is to be used as drinking water, therefore the health legislation risk exceeds other associated legal risks. On the other hand, in Algarve, the infiltration zone is inside a nitrate vulnerable zone and a coastal nature reserve, leading to highest environmental regulations risks. In the Malta case, highest legal risks are associated to the potential for saline intrusion.

The following category in terms of risk perception was social aspects, related to the unacceptance of recharge technology by the society. We believe that this could be related, again, to the lack of a concise legislation, which creates social uncertainty. We observed that social issues were mostly present in those sites with strong political implications, where the public administrations or the agricultural users participate in the management (and even in the construction) of the MAR facility, such as Llobregat, Los Arenales, or Malta.

Regarding the water quantity aspects, their relatively high importance could be explained because the sites are located in a Mediterranean climate (floods and droughts are typical in such environments). Besides this, it is related to the infiltration capacity of the system (especially in infiltration basin like Los Arenales and Llobregat) and this is traditionally one of the main technical issues in MAR (Figure 2-1). Nevertheless, in general terms, infiltration capacity of the system was not an important category in risk perception, probably because the sites were located in high permeable zones, suitable for recharge, and most of the sites included in their maintenance tasks actions to minimize its importance.

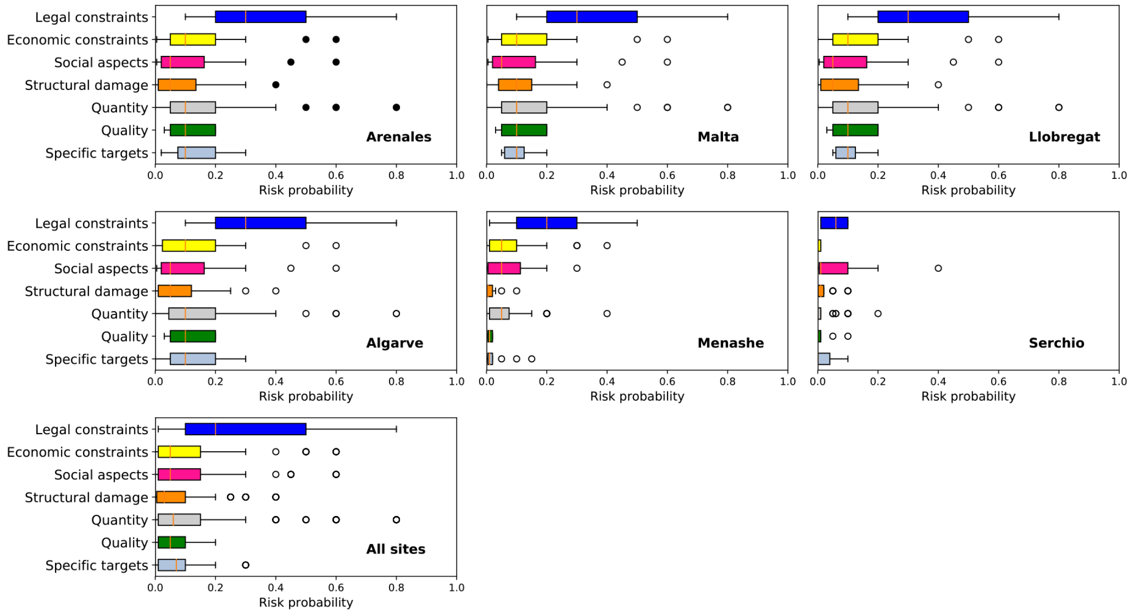


Figure 2-5. *Distribution of the expert criteria by category and for the three levels (low, medium, high) grouped by categories.*

The risk perception on the quality issues included three main topics: recovered-water use, water source and legislation. For example, Serchio recharged water is used as a drinking water, consequently, quality plays a higher role than, for example, in Malta, where water is used as a water barrier to salt intrusion. On the other hand, quality is also important in sites where quality aspects existed independently of recharge, like Arenales (high presence of nitrate in groundwater due to farming activity in the zone, see San Sebastián et al., 2017) and Llobregat (quality problems related to industrial and urban activities, see Valhondo et al., 2015).

Structural Damages category is non-negligible, but in general it is not perceived as critical, probably because we are considering sites already in operation. This issue could be more significant in the design process of a facility, and also during construction.

2.6.2 Comparing risk in the different sites

The risk values for the six sites studied are summarized in Figure 2-6. We can observe that the total risk of three of the six sites (Los Arenales, Algarve and Llobregat) is very large (equal or above 0.9), indicating that facility failure is almost certain during a 2-6 year period. This indicates that the system will most probably have to discontinue operation; however, this does not imply that the system cannot be put back to operation again. Lack of specific legislation, economic constraints, social issues, and quantitative aspects are the most probable cause for failure of these three facilities. Regarding water quantity being a potential cause of failure, the fact that all three sites involve surface infiltration with river water promote that quantity and clogging aspects are important, as Mediterranean rivers display low flows and high solid content. Besides this, these three sites are quite young (around 10 years old), which could imply that are not completely optimized.

On the other hand, Serchio, Menashe, and Malta have lower risk values (0.18, 0.29, and 0.75 respectively). The cases of Serchio and Menashe can be explained because they are the oldest sites, with large experience in the operation of the facilities (therefore lowering the Technical risks to below 0.1). Furthermore, river bank filtration in Serchio is done with water with less suspended solids, so that the risk of clogging is low. The case of Menashe is justified by the use of desalinated and storm water for recharge. The presence of solids in these two recharge waters is very low. In the case of Malta, the low risk value could be just perception based on the site just recently started operation.

From all technical constrains, the one with the highest risk is related with water quantity. Half of the sites showed significant risk in terms of quantity, somewhat correlated with the sources of water for infiltration (so, being largest for those relying on surface water, Algarve, Llobregat, and Arenales). In the case of Malta, quantitative problems are related to the need to produce good quality water from wastewater. Algarve site is a particular case as its aim is to improve groundwater quality with recharging water from a non-perennial stream (surface water flows only 60-70 days per year). So, the lack of water is already considered in the MAR scheme. In terms of quality, again, the three sites supplied with river water are those showing the highest risks. That could respond to the variability of river water quality along the year. The geological/hydrogeological context does not seem to have any effect in the technical risk values despite it is very significant to define the site were to construct the MAR facilities.

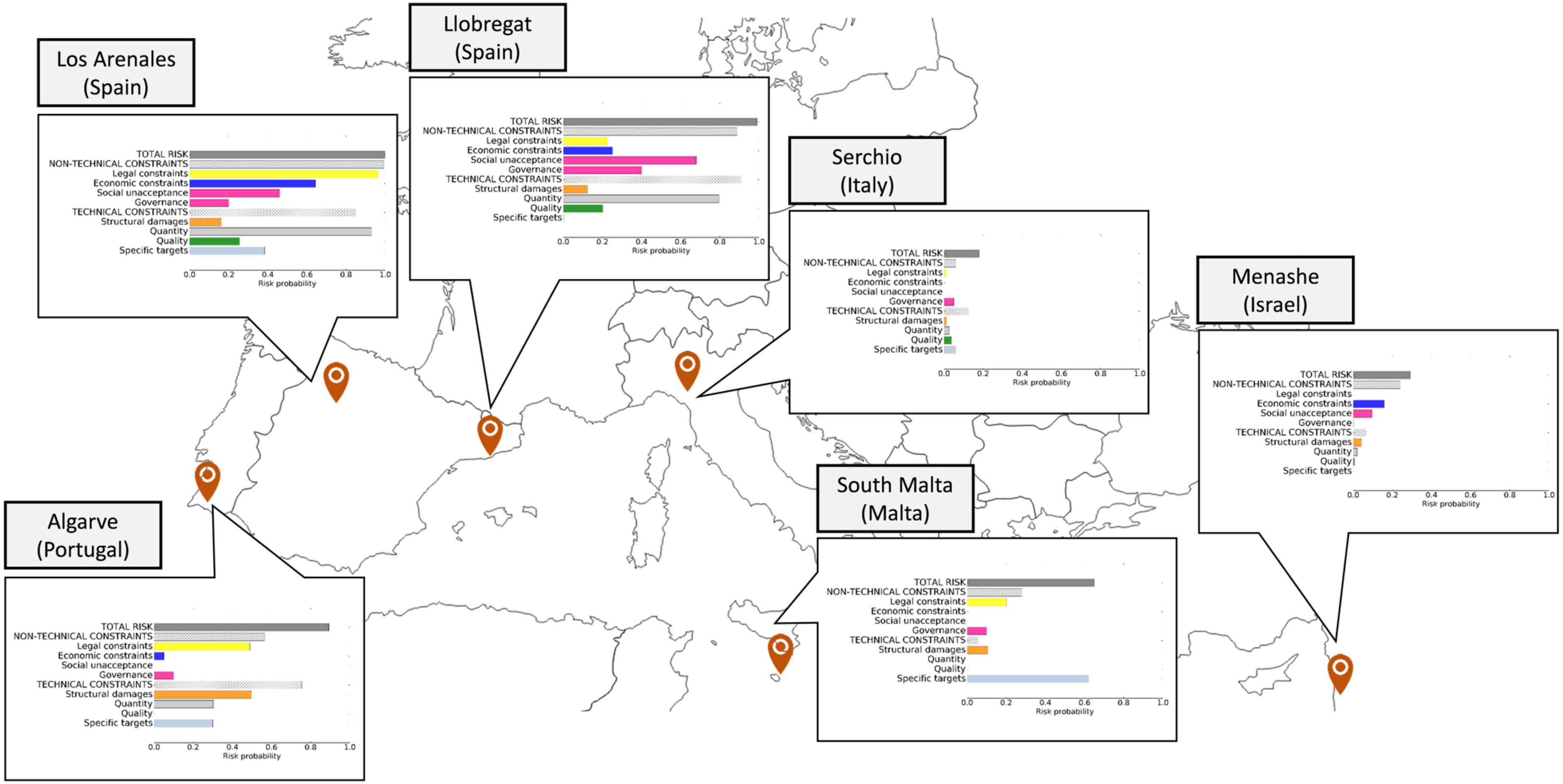


Figure 2-6. *Risk in the different MAR sites.*

Individually, the main risk issues for the technical issues in the Llobregat site were quantitative aspects, mainly clogging due to fine particles (probability = 0.4) and recharge water turbidity (0.4). The non-technical issues, were mostly related to social aspects: lack of coordination amongst stake holders (0.4), children surveillance (0.3), and fair distribution of water (0.3). These three social aspects are aligned with the indicators of acceptance of Mankad and Walton (2015). For the Algarve site, the technical issues were mostly potential flooding (0.3), droughts (0.3), vandalism/terrorism (0.2) and clogging (0.2). Non-technical issues were mainly related to regional/local legislation (0.3). Non-technical issues for the Menashe site include domestic water use (0.15), perception of effectiveness (0.05) and high cost perception (0.05); for the technical ones, terrorism activities (0.02) and clogging due to compaction (0.02) were the most significant.

Serchio site had for the non-technical main risks the lack of knowledge on MAR activities (0.05) and health legislation (0.01). About the Technical aspects, quality aspects related to organic compounds were the largest (0.01). Los Arenales site had very large risk values associated with national (0.6), regional/local (0.8) and other legislation (0.5), agricultural water use (0.6), and fair distribution of water (0.45); the most significant technical issues were flooding (0.1), nutrients in the recharge water (0.5), droughts (0.8), generation of gas - physical clogging (0.2), nitrogen metabolites (0.2), river (0.1) and wetland water levels (0.2). Malta site identified the European legislation (0.2) and lack of coordination (0.1) as the main non-technical risk drivers. About the technical aspects largest risks included pipe breakage (0.05), and different specific targets: seawater barriers (0.4), protected water body (0.1) and groundwater levels (0.3).

The risk values obtained are mostly correlated to the expert criteria values. This correlation was evaluated by applying a Pearson product-moment correlation between the Expert criteria basic events (considered the Medium Risk values) and the Results basic events for each site. There were in total 65 basic events, leaving a total of 63 degrees of freedom and considering a p-value of 0.05 as the confidence limit of acceptance. It was observed that, in general terms, a correlation between the perception of risk (Expert criteria) and actual risk (Results) existed. This mainly means that the facility managers know the main problems of the sites and thus define the Expert criteria values accordingly. This indicates the relevance of using such a simplified method for preliminary risk assessment.

The actual results of the analyses showed correlation (in terms of p-value) in the cases of Llobregat ($p=0.026$), Los Arenales (7.38×10^{-13}), Malta (3.2×10^{-7}), Algarve (0.048) and Serchio (2.12×10^{-8}), while for Menashe site (0.6), that correlation could not be observed. Looking at the data, Menashe Expert criteria values lack absolute zero values (0 from 65), however the result values obtained show a high proportion of NO RISK (risk = 0) values (52 from the total of 65). Then the difference between both Expert criteria and Results become apparent, probably related to the knowledge of the personnel in charge of the Menashe site and their confidence in the lack of risk of their operations.

2.7 Conclusions

In this paper, we have developed a methodology to evaluate the risk of failure of Managed Aquifer Recharge (MAR) facilities, and we have applied it to six different facilities located in the Mediterranean Basin. The methodology was based on the development of a Probabilistic Risk Assessment based on Fault Trees. The PRA-FT methodology considered different categories affecting the operation of the facility. We further defined 65 basic events that individually or properly combined can produce global failure of the MAR facility. These events were compiled from a literature review of 51 MAR facilities and, then, extended with the results of the European Project MARSOL (“Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought”).

The methodology consists of providing probability values to all basic events to take place in a window of time. Then, event at an upper level are computed from Boolean Algebra until the top of the tree (total failure) is quantified. The initial step is to provide values based on Expert Criteria, assigned from the four risk categories: low, medium, high, and no risk. All values can be updated sequentially and probabilities are recalculated, until the values converge. The basic events include both technical and non-technical events.

A full preliminary (without updating) assessment of risk was developed for 6 sites located in the Mediterranean Basin. It was found that the non-technical aspects can be the most significant ones, contributing more than the technical issues to the overall assessment of risk. This is despite we are considering only facilities under operation, so that some issues are supposed to be already resolved. In short, the combination of legal and economic factors can be really a strong contribution to global risk.

All events considered, we found that in the facilities analyzed, the major contributors to overall risk were, in decreasing order of importance: Legal constraints, Social aspects, Economic constraints, Quantity issues, Structural damages, Specific targets and Quality issues. In particular, when the recharge water is supplied by a river, quantity aspects increase their relevance, due to the uncertainty in the future potential capacity for supplying in a dry and variable climate such as the Mediterranean Area.

The site-specific results were obtained from a questionnaire, and so they provide “perception of risk” rather than “actual risk”, and thus could and should be amended. The PRA-FT methodology allows now to concentrate on the specific issues that individually, or combined, lead to the largest probability of failure, and concentrate the efforts in updating such values by means of detailed evaluations or specific projects of rehabilitation. The system can go on using any number of reevaluations until an acceptable value or either until no further improvement can be obtained.

Regarding the results on perception of risk for the individual sites, it was surprising to get three of them (Los Arenales, Algarve, and Llobregat) above 0.90 in a 2-6 y period. The main contributors to failure were related to non-technical reasons and to quantity aspects. Actually, in recent years all three facilities had to discontinue operations at least one, indicating that the evaluations provide reasonable estimations. The Malta site is a very recent one, with little history behind, and this it is not possible to evaluate whether the perception of risk of 75% is high or low.

On the other hand, the risks perceived for the other two sites, Serchio and Menashe, can be considered low (18% and 29%, respectively). A potential reason is that they are the oldest facilities, so that experience has been accumulated for decades. Also, the facilities have been able to adapt to evolving regulations (both local and at the European levels). In both cases, low risk values correlated also with low perception of quantitative risk (mainly related to clogging), due to the sources of recharge water in both cases (river bank filtration in Serchio and desalinated and storm water in Menashe.

Chapter 3

Impact of compost reactive layer on hydraulic transport and C & N cycles: biogeochemical modelling of infiltration column experiments

This chapter is an edited version of:

Canelles, A., Rodríguez-Escales, P., Modrzyński, J.J., Albers, C. and Sanchez-Vila, X. 2021. Impact of compost reactive layer on hydraulic transport and C & N cycles: Biogeochemical modeling of infiltration column experiments. Science of The Total Environment 770, 145490. © 2021 Published by Elsevier B.V. https://doi.org/10.1016/j.scitotenv.2021.145490

3.1 Introduction

Managed aquifer recharge (MAR) is a well-established technology capable of increasing the water resources storage with the purpose of either later being recovered for different uses (agricultural, industrial or urban). It can also be used for obtaining environmental benefits, such as: reducing the physical impacts in rivers and lakes (mainly geological natural formations) due to water storage structures (dams mainly) for drinking purposes; reducing saline intrusion due to well over-exploitation; protection of local wildlife due to ecosystem preservation (without the anthropic modification of lakes and rivers, wildlife can maintain their original ecosystems), among other (Dillon et al., 2019). Consequently, MAR emerges as an efficient tool to minimize water scarcity, especially in arid and semi-arid regions, such as the Mediterranean basin (Rodríguez-Escales et al., 2018). Water scarcity, to be exacerbated in the future due to climate change, combined with high population density, draw an alarming scenario for water security in the Mediterranean region and worldwide in the coming decades (IPCC, 2007; Giorgi and Lionello, 2007; Pedretti et al., 2012).

The two main controversial topics that are limiting the widespread implementation of MAR facilities are the infiltration rate capacity losses over time and the quality of the infiltrating water (e.g. Rodríguez-Escales et al., 2018). The infiltration rate capacity decreases with time driven by the physical and chemical characteristics of the water supplied to the MAR facility and to the actual technology used for recharge (Dillon et al., 2018). Physical and biological clogging are two main reasons of infiltration rate loss (Carles Brangarí et al., 2017; Rodríguez-Escales et al., 2018). Whereas physical clogging depends on the size and amount of particles in suspension in the input water (Pedretti et al., 2012), bioclogging is mostly controlled by biofilm growth on soil grains that conform the porous media, reducing the effective size of the pores. Biofilm growth is mainly governed by the concentration of supplied nutrients and by temperature.

The quality of the infiltrating water mainly depends on the biochemical signature of the input water and the reactions that take place within the system (mainly the top few cm). Due to the combination of environmental and human health protection laws, in some cases the biogeochemical signature of the water that can legally be infiltrated are restrictive, in some cases allowing only the infiltration of water of drinking quality (Dillon et al., 2019) or even osmotized water (Ganot et al., 2018). On the contrary, two most common sources of water supplied to MAR facilities are excess river water in flood episodes, and effluents from wastewater treatment plants (WWTPs, after either secondary or tertiary treatment). In the latter case, MAR actions can be considered as a solution to re-naturalize wastewater, within the context of circular economy (Dillon et al., 2010), where treated wastewater should be seen as a resource rather than a waste (Van Der Hoek et al., 2016).

However, due to the abovementioned concerns about water quality, the usage of wastewater outflow has been limited and dependend on the type of MAR technology (Maliva and Missimer, 2012). Nevertheless, we contend that using water with drinking standard quality for aquifer recharge is a very narrow vision, as looking exclusively to the quality of the supplied water overlooks and ignores the purifying capacity of the subsoil, which can considerably improve water quality (Silver et al., 2018). Rather, we focused in the quality of water once it reaches the aquifer, or even the discharge point, being either a well, a spring or a body of surface water. Consequently, MAR facilities implementation must track the evolution of water quality along the infiltration path and with time. This implies tracking the fate of different target compounds, and, to enhance attenuation processes during recharge within the context of soil-aquifer remediation technologies. In the case of nitrogen compounds present in the recharged water ($\mathrm{NH_4^+}$, $\mathrm{NO_3^-}$, $\mathrm{NO_2^-}$), limitations in the accepted concentrations for water to be used in MAR facilities is linked to the risk for humans to develop methahemoglobine or stomach cancer, or else to promote water eutrophication (Grau-Martínez et al., 2018, 2017; Maeng et al., 2011; Miller et al., 2006). Therefore, the goal would be to create an environment capable of completely reducing the N-compounds and promoting the formation of dinitrogen gas, being a harmless compound. That means promoting a reductive environment, which normally is conditioned by the presence of labile organic carbon (OC, acting as an electron donor in a reduction-oxidation system). Since the concentration of labile OC in the aquifer is low, a potential solution to enhance the metabolism of nitrogen compounds is the addition of an external pool into the system. In the context of a MAR facility involving an infiltration pond, this can be achieved by the installation of a reactive layer partially composed of organic carbon into the bottom of a pond (Alazard et al., 2016; Dillon et al., 2009; NRMMC, 2006; Valhondo et al., 2014).

A successful experience in this regard was the installation of a permeable reactive layer at the MAR system placed at the Llobregat Lower Valley (Valhondo et al., 2014) near Barcelona (Spain); this layer enhanced not only the degradation of nutrients and emerging organic compounds, but also the biological activity of the subsoil (Barba et al., 2019). Different materials for organic layers have been tested and reported in the literature, several of them sharing similar concentration values in labile organic carbon. For example, organic substrates such as compost (Grau-Martínez et al., 2017; Schaffer et al., 2015; Valhondo et al., 2014), softwood (Gibert et al., 2008) and palm leaves (Grau-Martínez et al., 2017) were tested with positive results in terms of the reduction of nitrogen compounds in experiments under batch conditions.

The Nitrogen cycle is complex, as processes depend on the redox state of the system and the presence of biomass (quantity, diversity, density, etc.). The most common nitrogen-compound present in a WWTP outflow is ammonium, NH_4^+, which can be oxidized to nitrate, NO_3^-, in the presence of oxygen, catalyzed by autotrophic biomass (nitrification). Nitrate can then be reduced to dinitrogen gas, N_2, in the presence of an electron donor by either autotrophic or heterotrophic biomass (denitrification). Both nitrification and denitrification processes are sequential, forming a suite of intermediate nitrogen compounds (e.g., NO_2^-, NO, or N_2O). Their formation should be avoided; first, NO_2^-, is quite a harmful compound that can be accumulated during either nitrification or denitrification; second, NO_x are greenhouse gases. Finally, the processes of dissimilatory nitrogen reduction to ammonia (DNRA), using organic carbon as electron donor and potentially accumulating nitrite (Grau-Martínez et al., 2017; van den Berg et al., 2016), is quite common in the nitrogen dynamics, thus introducing more complexity to the system.

In this way, it is quite important to improve the knowledge about the impact of a reactive barrier in the processes governing the fate of nitrogen compounds, especially concerning the accumulation of hazardous products (ammonia, nitrite or NO_x). Geochemical modelling is particularly useful to improve this understanding. In the literature, there are different conceptual models for the N-cycle in the subsoil, incorporating only a subset of the processes described, such as nitrification (Koper et al., 2010; Urakawa et al., 2016), denitrification (Green et al., 2008; Mastrocicco et al., 2011; Rodríguez-Escales et al., 2016) or DNRA (Rubol et al., 2013). Nevertheless, most of them do not include the interrelation between processes and reactions (Schmidt et al., 2012), or do not account for changes in input dynamics that define the evolution of the biological community in the system (Akhavan et al., 2013).

Besides, the enhancement of degradation enforced by the presence of a reactive layer would imply an increase in biomass production, and, consequently, a significant biofilm growth leading to partial pore network clogging. In this way, the evaluation of the risk of clogging as a function of time and distributed in space due to the installation of an organic reactive layer is not yet available in the literature.

Considering all of these, the main aim of this work is to develop a comprehensive geochemical model of carbon and nitrogen dynamics in porous media, aimed at determining the impact of a reactive layer in the context of managed aquifer recharge. As a side objective, we want also to evaluate changes in transport parameters due to biofilm growth induced by the presence of such reactive layer. To this end, we present the conceptual model describing interrelation between biogeochemistry and hydraulic parameters. Subsequently, the model is validated with data from a set of column experiments (Modrzyński et al, 2021) developed with different proportions of compost (being the source of labile organic carbon) and sand. To further see in detail these experiments, see in this thesis the supplementary material for chapter 2 (based on Modrzyński et al, 2021), in addition see Modrzyński et al, 2021 for further details about the column experiments. Finally, we present the results of the model allowing for a thorough discussion of biogeochemical and hydraulic processes and calibrated parameters.

3.2 Methodology

In this work, three sequential steps were considered: (1) conservative transport analysis and modelling, setting the baseline for the evaluation of the potential effect of biofilm growth upon transport; (2) building the conceptual model for the biologically catalysed geochemical reactions; and (3) construction of the numerical model and its implementation. Finally, the numerical model is verified with flow through experimental data in columns from (Modrzyński et al., 2021).

3.2.1 Flow and conservative transport model: evaluation of the impact of biofilm growth upon transport parameters

The first step was to create the flow and the conservative transport models. We assumed transport in bioclogged porous media to be well described by a dual porosity model (e.g., Haggerty and Gorelick, 1995; Lawrence et al., 2002), already used frequently in the literature to model a number of tracer tests in column experiments (Delay et al., 2013; Rodríguez-Escales and Sanchez-Vila, 2016; Seifert and Engesgaard, 2007). A dual porosity domain model represents the porous medium as composed of a mobile and one (or alternatively a suite of) immobile fluid porosity regions that coexist. In the former, representing the volume occupied by the aqueous phase, advection and dispersion are the main driving processes; in the latter, being the region where biofilm dynamics derived from the growth of heterotrophic and autotrophic biomass take place attached to the sediment, only diffusion is considered. Both regions exchange mass proportionally to the difference in their concentrations at any given time. The equation describing the concentration of species *i* in the mobile zone, $c_{m,i}$, here assuming a simple one-dimensional domain as it will be later applied to column experiments, is:

$$\phi_m \frac{\partial C_{m,i}}{\partial t} = -q \frac{\partial C_{m,i}}{\partial x} + \phi_m \frac{D \partial^2 C_{m,i}}{\partial x^2} - \Gamma_i \tag{1}$$

where D is the dispersion coefficient, q is specific discharge, ϕ_m the porosity corresponding to the mobile zone, and Γ_i the source-sink term controlling the mass transfer of species *i*, between the mobile (m) and the immobile regions (im), given by:

$$\Gamma_i = \alpha \phi_{im} \left(C_{m,i} - C_{im,i} \right) \tag{2}$$

with α the mass transfer rate coefficient [T^{-1}], ϕ_{im} [-] the porosity corresponding to the immobile region (volume fraction occupied by the biofilm), and $C_{im,i}$ the concentration of species *i* in the immobile region. The actual total porosity is then $\phi_t = \phi_m + \phi_{im}$. The reason behind this porosity change is that the formation of biofilm colonizes pores that were initially occupied by water in sediments (bioclogging), so that the pores occupy the same volume at the beginning and end of the experiment. Therefore, a key parameter in characterizing the shape of the breakthrough curve in the dual porosity model is the ratio of porosities (Fernàndez-Garcia and Sanchez-Vila, 2015) given by $\beta = \phi_{im}/\phi_m$. In the limiting case of $\beta = 0$, equivalent to $\Gamma_i = 0$, equation (1) converges to the classical advection-dispersion equation (ADE).

3.2.2 Reactive transport model: processes and governing equations

Biogeochemical processes: nitrogen and carbon cycle

The biogeochemical conceptual model for the nitrogen and the carbon biochemical cycles is depicted in Figure 3-1, showing the main processes involved. Under aerobic conditions, two processes are considered: oxidation of organic matter (process 1 in Figure 3-1) and oxidation of ammonia (process 2.1 and 2.2). The former is triggered by heterotrophic biomass (indicated by

6.3 in the figure 3-1), and the latter by autotrophic one (5.1 and 5.2 in the Figure 3-1). In both cases, we considered a growth of biomass which could eventually decay and form inorganic carbon. In the case of nitrification, the oxidation of ammonia to nitrate (nitritation, process 2.1) leaves nitrite as an intermediate product which is then transformed into nitrate (nitratation, process 2.2). We did not distinguish between microbial populations (only distinguished between aerobic and anaerobic) in order to simplify the model.

Concerning anaerobic conditions, we considered oxidation of organic carbon due to denitrification, i.e., the reduction of nitrate to dinitrogen gas (process 3.1 and 3.2). This process is mainly driven by heterotrophic denitrifying biomass (6.1 and 6.2). In this case, we also considered two steps in the reduction of nitrate, as well as the transient accumulation of nitrite. The accumulation of other intermediate nitrogen compounds, NO and N_2O, was neglected. Besides, we also considered Dissimilatory Nitrate Reduction (DNRA, process 4), a process that implies a consumption of nitrate and organic carbon in order to generate ammonia by DNRA-specific biomass (heterotroph, number 6.4 in the Figure 3-1).

The model also describes the release of labile dissolved organic carbon (DOC) and ammonia from compost, a process independent from Eh conditions (process 7). Organic matter was considered in two fractions, easily degradable and recalcitrant, and it was considered that only the former could be degraded and therefore the latter was unaccounted for in the biogeochemical reactions.

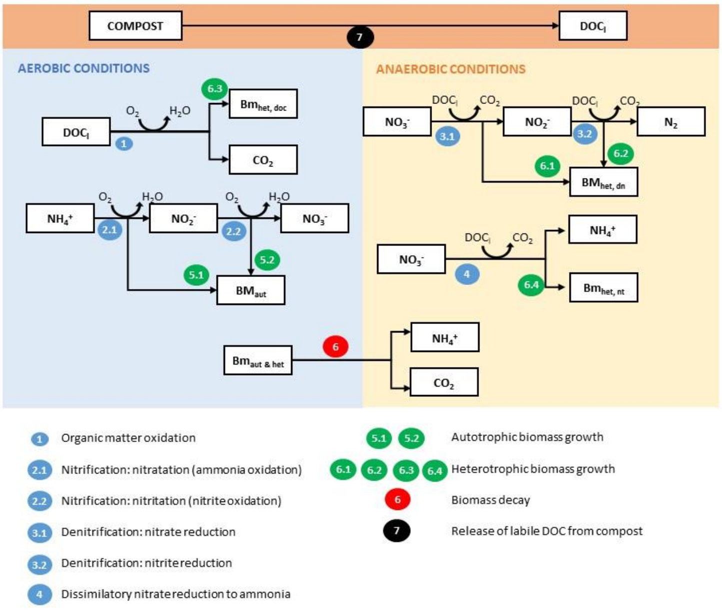


Figure 3-1. *Conceptual model of biogeochemical processes occurring during column experiments. In aerobic conditions, the reactions included are nitrification (two steps, from ammonium to nitrite and then to nitrate) and labile organic matter oxidation. For the anaerobic reactions, denitrification (two steps, from nitrate to nitrite and then to nitrogen gas) and DNRA (which implies the conversion of nitrate into ammonium). Finally, the biomass (auto and hetero) decay is included (which generates carbon dioxide and ammonium).*

Geochemical models: processes and reaction rates

The next step was the construction of the geochemical numerical model. Table 3-1 compiles all the reactions considered in the modeling process and sketched in Figure 3-1, including the stoichiometric coefficients and the expressions for the individual reaction rates. As a general rule, we included double Monod Kinetic terms in the main redox reactions: oxidation of organic matter, nitrification, denitrification and DNRA. Reactions were assumed kinetically controlled, characterized by a set of parameters: $K'_{max,j}$ [T^{-1}] being the consumption rates of electron donor per unit value of biomass of the "j" process; $K_{s,i}$ [ML^{-3}] the saturation constants of the "i" compounds; b [T^{-1}] a decay constant for autotrophic biomass (b_{aut}) and heterotrophic biomass (b_{het}); and $K_{I,j}$, [ML^{-3}] the inhibition constants for the "j" compounds. Both autotrophic and heterotrophic biomass were introduced into the model as two different immobile species; they were conceptualized as having an average chemical composition of $C_5H_7O_2N$ (Porges, N., Jasewicz, L. and Hoover, 1956). We did not distinguish between different autotrophic biomass, e.g. ammonia-oxidizing bacteria or nitrite-oxidizing bacteria since it would increase complexity and uncertainty in the model. Nevertheless, we distinguish between total heterotrophic biomass and denitrifying and DNRA biomass by adding a ratio into the model ($\alpha_1 = 0.1$ and $\alpha_2 = 0.05$, respectively). The release of organic carbon from compost was modeled as first order kinetics. Here, compost was defined as an immobile species, with a stoichiometric of compost release calibrated to fit the experimental data of organic matter and ammonia.

Table 3-1. *Stoichiometric relationships between the components of the biogeochemical reactions and processes rates, where K_max^'= /Y_h. Here, we only shown the main compounds of the reaction. In DNRA we had no information in regard to the biomass yield between DNRA specific biomass and the stoichiometric reaction, therefore the stoichiometric reaction does not include that yield effect, however it does include the effect of biomass concentration (10% of total heterotrophic biomass for denitrification and 5% for DNRA, which are represented as alfa in the equations below). *Note that in the reaction rates, oxygen is considered O instead of O2. This is intended, because the ipht3d model had oxygen in that notation, it is correctly converted in the reaction rates and onwards.*

Process and reaction	DOC	CO_2	NH_4^+	NO_3^-	NO_2^-	N_2	H^+	O_2	HCO_3^-	$Compost$	BM_{het}	BM_{aut}	$Reaction\ rates^*$
Nitrification (nitritation)	$0.1722\ NH_4^+ + 0.2223\ O_2 + 0.022CO_2 + 0.0055\ HCO_3^- \rightarrow 0.1666\ NO_2^- + 0.60582\ H_2O + 0.333H^+ + 0.0055\ C_5H_7O_2N$												$K'_{max,nit_1} \cdot \frac{[NH_4^+]}{[NH_4^+] + K_{s\,NH_4^+}} \cdot \frac{[O\ \ ]}{[O\ \ ] + K_{s\,O}} \cdot \frac{K_{i\,NO_2^-}}{[NO_2^-] + K_{i\,NO_2^-}} \cdot [BM_{aut}]$ (6)
	-	-0.0055	-0.1722	-	$+0.1666$	-	$+0.333$	-0.2223	-0.0055	$-$	$-$	$+0.0055$	
Nitrification (nitratation)	$0.503\ NO_2^- + 0.018\ CO_2 + 0.2271\ O_2 + 0.003\ H^+ + 0.010\ H_2O \rightarrow 0.5\ NO_3^- + 0.0035\ C_5H_7O_2N$												$K'_{max,nit_2} \cdot \frac{[NO_2^-]}{[NO_2^-] + K_{s\,NO_2^-}} \cdot \frac{[O_2]}{[O_2] + K'_{s\,O}} \cdot \frac{K_{i\,NO_3^-}}{[NO_3^-] + K_{i\,NO_3^-}} \cdot [BM_{aut}]$ (7)
	-	-0.018	$-$	$+0.5$	-0.018	$-$	-0.003	-0.2271	$-$	$-$	$-$	$+0.0035$	
Aerobic oxidation of org. matter	$0.25\ CH_2O + 0.1\ O_2 + 0.03\ HCO_3^- + 0.03\ NH_4^+ \rightarrow 0.22\ H_2O + 0.13\ CO_2 + 0.03\ C_5H_7O_2N$												$K'_{max,DOC} \cdot \frac{[DOC]}{[DOC] + K_{s\,Doc}} \cdot \frac{[O\ \ ]}{[O\ \ ] + K''_{s\,O}} \cdot [BM_{het}]$ (8)
	-0.25	$+0.13$	$+0.03$	$-$	$-$	$-$	$-$	-0.1	-0.03	$-$	$-$	$+0.03$	
Compost release (fitted)	$+0.9$	$-$	$+0.1$	$-$	$-$	$-$	$-$	$-$	$-$	-1	$-$	$-$	$r'_{max} \cdot [Compost]$ (9)
Denitrification (nitrate reduction)	$0.2679\ NO_3^- + 0.0179\ H^+ + 0.25\ CH_2O \rightarrow 0.1607\ CO_2 + 0.1964286\ H_2O + 025\ NO_2^- + 0.01786\ C_5H_7O_2N$												$K'_{max,denit_1} \cdot \frac{[DOC]}{[DOC] + K'_{s\,DOC}} \cdot \frac{[NO_3^-]}{[NO_3^-] + K_{s\,NO3-}} \cdot \frac{K'_{i\_O}}{[O\ \ ] + K'_{i\_O}} \cdot \alpha_1 [BM_{het}]$ (11)
	-0.25	$+0.161$	$-$	-0.2679	$+0.25$	$-$	-0.018	$-$	$-$	$-$	$+0.01786$	$-$	
Denitrification (nitrite reduction)	$0.1859\ NO_2^- + 0.1859\ H^+ + 0.25\ CH_2O \rightarrow 0.15385\ CO_2 + 0.01923\ C_5H_7O_2N + 0.27564\ H_2O + 0.16667\ N_2$												$K'_{max,denit_2} \cdot \frac{[DOC]}{[DOC] + K''_{s\,DOC}} \cdot \frac{[NO_2^-]}{[NO_2^-] + K'_{s\,NO2-}} \cdot \frac{K'_{i\,NO_3^-}}{[NO_3^-] + K'_{i\,NO_3^-}} \cdot \frac{K'_{i\_O}}{[O\ \ ] + K'_{i\_O}} \alpha_1 [BM_{het}]$ (12)
	-0.25	$+0.154$	$-$	$-$	-0.186	$+0.167$	-0.186	$-$	$-$	$-$	$+0.16667$	$-$	
Dissimilatory Nitrate Reduction to ammonia (DNRA)	$2\ CH_2O + 1\ NO_3^- \rightarrow 1\ NH_4^+ + 2\ CO_2$												$K'_{max,DNRA} \cdot \frac{[DOC]}{[DOC] + K'''_{s\,DOC}} \cdot \frac{[NO_3^-]}{[NO_3^-] + K'_{s\,NO3-}} \cdot \frac{K'_{i\_O}}{[O\ \ ] + K'_{i\,O}} \alpha_2 [BM_{het}]$ (13)
	-2	$+2$	$+1$	-1	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	
Autotrophic biomass decay	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	-1	$b_{aut}[BM_{aut}]$ (14)
Heterotrophic biomass decay	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	$-$	-1	$-$	$b_{het}[BM_{het}]$ (15)

Description of the experiment and data set

The conceptual model described was then applied to interpret a number of column experiments available in the literature (Modrzyński et al., 2021), aiming at finding the impact of the addition of different proportions of compost within soil material (sand) in the different compounds involved in the nitrogen cycle. These infiltration experiments consisted of five treatments with two replicates each (a total of 10 columns) that ran for a total time of 116 days. The water flow in the column was vertical (top to bottom) fixed at 0.5 mL/min. The columns were 6.6 cm of interior diameter, and composed of a top layer of field sand (2-2.5 cm) underlain by the 29 cm-long reactive layer (for the different proportions of field sand and vegetal compost, see Table 3-2), with a coarse silica sand layer at the bottom (3 cm). For the compost molar composition, we considered a chemical formula of $C_{204} H_{325} O_{85} N_{77} S$, and an average density of 550 Kg/m^3. For further details on the column setup and reactive barrier composition, see Modrzyński et al., 2021 and Valhondo et al., 2020. In addition, selected columns were inoculated with real wastewater (activated sludge) for a short period of time (see Table 3-2), in order to test the effect of the addition of real wastewater biomass (further details in Modrzyński et al., 2021). The packing of the columns was done under fully water saturated conditions to minimize the amount of trapped air during filling. A total of 6 sampling points were installed at each column: one at the inflow water headspace, four along the column (at 4, 8, 13 and 20 cm depth), and one at the outflow (30 cm depth), allowing the delineation of aqueous concentrations of ammonium, nitrate, nitrite, O_2, and dissolved organic carbon (DOC) at selected times at all six sampling ports.

At the end of the experiments of Modrzyński et al., 2021, the columns were dismantled and the sediment was characterized in terms of biofilm development from samples taken in all 10 columns at four different depths: in the reactive barrier, at zones around the first (depth A, 4cm), second (depth B, 8 cm), and third sampling point (depth C, 13 cm), as well as at the interface between the reactive barrier and the silica coarse sand (depth O, 29 cm). For depths A, C and O, two samples per depth were taken, these integrating both the external and the internal parts of the column. For depth B, 3 samples were taken for the outer part of the column and 3 for the inner part of the column, in order to test if there were differences between them and if some kind of preferential heterogeneity could be observed. In each sediment sample, we measured the amount of glucose in the Extracellular Polymeric Substances (EPS), the non-soluble Organic Matter (associated to sedimentary organic matter and biological material), bacteria density in the sediment, and presence of algae (in the form of chlorophyll-a). Sediment samples of 3ml (approximately 7g) of sediments were stored frozen in plastic vials.

The sampling for bacterial analysis was also performed in drained sediment samples of 1 ml (2.3 g) from the columns, stored in glass vials with 10 ml of inlet water and 100 µl of a Formaldehyde solution at 37%, and stored in the fridge (unfrozen). For depths A, C and O, two samples integrating both the external and internal parts of the column were taken. No samples from depth B were taken in this case. Specific details of sampling and conservation procedures were identical as those in Perujo et al. (2019), based on the works of (Amalfitano et al., 2009; Amalfitano and Fazi, 2008).

Table 3-2. *Composition of the reactive layer in terms of percentages (in volume) of vegetal compost and sand. Each column was run in duplicate and inoculated. Column 1 and 2 were also run without inoculum in order to evaluate its effect.*

Column Notation	**Proportion (%) compost / sand**
1	0 / 100 (Pure sand)
2	10 - 90
3	50 - 50
4	0 / 100 (Pure sand)
5	10 - 90

Biogeochemical model set up

We constructed a numerical biogeochemical model using PHT3D v 2.17 (Prommer et al., 2001). This code couples the transport simulator MT3DMS (Zheng and Wang, 1999) and the geochemical code PHREEQC-2 (Parkhurst and Appelo, 2013), based on a sequential split-operator technique. The column experiments were modelled considering a 1D model with a total length of 29 cm (average of reactive barrier length for all the columns) divided in 100 cells of 0.29 cm with a width of 0.3419 m (in order to simulate the total surface of the column experiments assumed rectangular in the code). The model ran for 104 days (0.005 days for delta t), corresponding to the sampling period. The time discretization was selected to satisfy the Peclet and Courant numbers criteria. Dispersive transport was computed according to the third-order total variation diminishing scheme.

The conservative transport model with dual domain in PHT3D incorporated the parameters determined in the tracer test (see the next section). For the reactive part we incorporated the rates described in Table 3-1. For the reactions in equilibrium, they were taken directly from the general PHREEQC database. Kinetic processes (see Table 3-1) were incorporated into the module in the form of BASIC routines, as explained in Rodríguez-Escales et al., 2016 and Carrey et al., 2018.

The experiment had four distinctive sub-periods in terms of signature of the inlet water. The chemical signature of the water in these sub-periods is described in Table 3-3. These values were used as input concentrations for the numerical model.

Table 3-3. *Chemical signature of the injected water (in mol/L) for the four sub-periods. (*) DIC - Dissolved Inorganic Carbon; (**) DOC - Dissolved Organic Carbon; (***) these values are 15% higher than the experimental concentration in Modrzynski et al. (2020), in order to correctly fit the experimental data with the numerical model. Compost and the two elements representing biomass are considered solid species and their concentrations are related to the porosity of the media.*

Compounds	Sub-period – I days 0 to 5	Sub-period – II days 5 to 19	Sub-period – III days 19 to 29	Sub-period – IV days 29 to 116
NH_4^+ (M)	6.43 x 10^{-4}	6.43 x 10^{-4}	1.60 x 10^{-4} ***	1.60 x 10^{-4}***
DIC* (M)	3.00 x 10^{-3}	3.00 x 10^{-3}	3.00 x 10^{-3}	3.00 x 10^{-3}
Ca (M)	2.00 x 10^{-3}	2.00 x 10^{-3}	2.00 x 10^{-3}	2.00 x 10^{-3}
Cl (M)	1.30 x 10^{-2}	1.30 x 10^{-2}	1.30 x 10^{-2}	1.30 x 10^{-2}
DOC** (M)	2.34 x 10^{-3}	8.83 x 10^{-4}	2.79 x 10^{-4}	3.92 x 10^{-4}
K (M)	6.00 x 10^{-4}	6.00 x 10^{-4}	6.00 x 10^{-4}	6.00 x 10^{-4}
Mg (M)	1.50 x 10^{-3}	1.50 x 10^{-3}	1.50 x 10^{-3}	1.50 x 10^{-3}
Na (M)	1.00 x 10^{-2}	1.00 x 10^{-2}	1.00 x 10^{-2}	1.00 x 10^{-2}
O_2 (M)	3.15 x 10^{-4}	3.15 x 10^{-4}	3.15 x 10^{-4}	3.15 x 10^{-4}
SO_4^{-2} (M)	1.5 x 10^{-3}	1.5 x 10^{-3}	1.5 x 10^{-3}	1.5 x 10^{-3}
pH	6.4	6.4	6.4	6.4
Pe	14.265	14.265	14.265	14.265
Biomass (het) (M)	8.00 x 10^{-6}			
Biomass (auto) (M)	1.00 x 10^{-6}			
Compost (M)	100% sand	-		
	10% comp	0.010		
	50% comp	0.053		

The calibration process of the biogeochemical model was performed manually (first considering data from the literature, then focusing on one biogeochemical process at a time and then going for another process until the iterative process yielded global good results), using the experimental concentration data for ammonium, nitrite, nitrate and DOCat the outflow of the columns and in the experimental profiles performed. For the calibration we considered the duplicates of the experiments.

3.3 Results and discussion

3.3.1 Conservative transport and biofilm growth: evaluating the evolution of hydrological parameters.

At the beginning and at the end of the column experiments a conservative tracer test was performed in order to characterize the apparent transport properties of the columns, and in particular to test the impact of biofilm growth in the columns upon transport of conservative species. The tracer selected was tritium; it was instantaneously injected using a laboratory syringe in the stagnant zone of each column, and monitored continuously at the outflow of the column, thus being able to reconstruct the breakthrough curves (BTCs). For more details about the experimental procedure and analysis of the tracer test, see Modrzyński et al., 2021.

While the tests performed prior to the experiments could mostly be interpreted using the traditional Advection Dispersion Equation (ADE), we preferred to interpret all tests using a common model, being the dual domain, to allow comparison of hydraulic parameters between …. The experimental BTC data was fitted using the CXTFIT code (Toride et al., 1995); the parameters fitted were: dispersivity; total, mobile and immobile porosities; and mass transfer coefficient (Table 3-4, showing the mean value and the standard deviation of the calibrated parameters).

Table 3-4. *Apparent transport parameters determined from the tracer tests including their standard error.*

		COLUMN 1: 100% sand		COLUMN 2: 10% compost		COLUMN 3: 50% compost	
	Units	Initial	End	Initial	End	Initial	End
Flow rate	mL/min	0.5	0.5	0.5	0.5	0.5	0.5
Water velocity	cm/min	0.0344	0.039	0.031	0.035	0.028	0.029
Dispersivity	cm	0.040 ± 0.009	0.037 ± 0.016	0.219 ± 0.103	0.194 ± 0.075	0.762 ± 0.099	0.724 ± 0.724
$\boldsymbol{\phi_T}$	[-]	0.424	0.366	0.471	0.424	0.518	0.504
$\boldsymbol{\phi_{im}}$	[-]	0.028 ± 0.011	0.037 ± 0.046	0.021 ± 0.228	0.030 ± 0.190	0.031 ± 0.159	0.146 ± 0.151
$\boldsymbol{\beta}$	[-]	0.071 ± 0.030	0.111 ± 0.148	0.047 ± 0.529	0.076 ± 0.510	0.064 ± 0.349	0.408 ± 0.596
α	$\boldsymbol{min^{-1}}$	0.125 ± 0.025	0.1597 ± 7.4 x 10^{-3}	0.0492 ± 0.013	0.068 ± 0.0255	0.0081 ± 1.28 x 10^{-5}	0.1403 ± 1.96 x 10^{-4}

Regardless the initial values, after the four months of the experiment, the fitted immobile porosity changed significantly (Figure 3-2 and Table 3-4), mostly in the columns containing compost. On the contrary, no significant influence of inoculation on hydraulic parameters was observed (results not shown). For this reason, data corresponding to non-inoculated columns were included as additional replicates of columns 1 and 2, respectively (see Table 3-2).

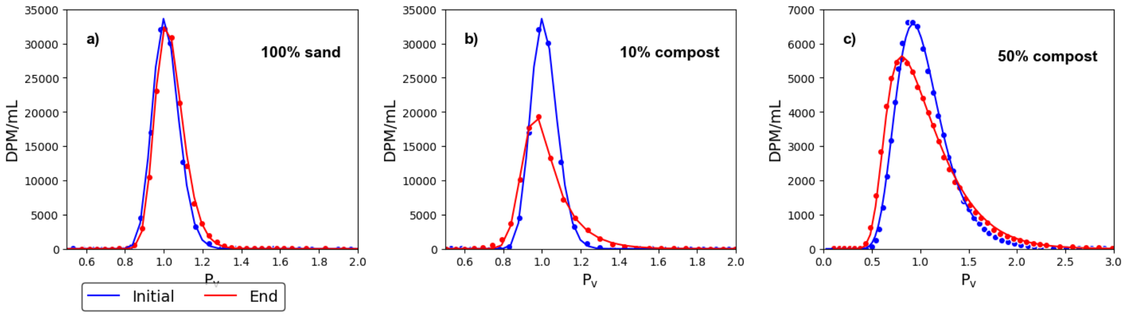


Figure 3-2. *Breakthrough curves of the tracer tests performed at the beginning (day 0) and the end of the experiments (day 116). The points represent the experimental concentration of tritium recorded whereas the lines are the model results. Column notation is displayed in Table 2.*

Non-Fickianity in the curves increases with β ($\beta = 0$ corresponding to pure Fickian behaviour). For all three experiments we observed a significant increase of the fraction of immobile porosity from the initial tracer experiments (displaying very low β values), to those performed once the experiments were completed. The effect is most significant in the column containing 50% proportion of compost. Enhanced tailing in all columns after day 104 is also modelled by (relatively similar for all columns) values of the mass-transfer rates (α). Tailing is associated with the changes in the ecosystem of the microorganisms (quantitatively and qualitatively) colonizing the columns as observed in other works (Rodríguez-Escales et al., 2016; Rubol et al., 2014). The α values in the colonized columns reported in Table 3-4 indicate residence times of the tracer within the biofilm on the order of 6-15 min, consistent with the value reported by Sanchez-Vila and Rodriguez-Escales (submitted) of 5 min as overall representative of similar experiments performed worldwide.

Data corresponding to bacterial density in the sediment correlates significantly with the percentage of compost and β (Figure 3-3a). Bacterial density was correlated with the compost content, with 20 - 25 x 10^7, 5 - 10 x 10^7, and 2 - 3 x 10^7 cells per g_{DW} for 50%, 10% and 0% compost, respectively. This suggests the compost enhances bacterial growth in the system leading to the variation in the hydrological transport parameters.

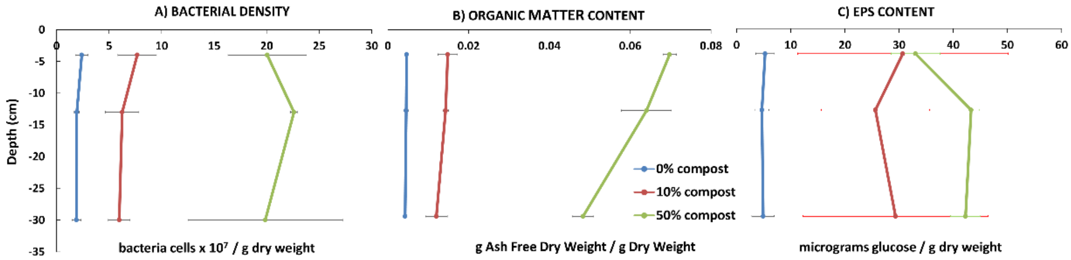


Figure 3-3. *Bacterial density, solid organic matter and EPS content in different depths, the error bars denote the standard deviation between the samples from each column setup.*

Noteworthy, the peaks of bacterial density correspond to the first centimetres of the column. We associate this observation to differences in bacterial growth, known to be much higher in aerobic conditions as compared to anaerobic since oxygen, being the electron acceptor, provides much better energy yield than most electron acceptors (in addition to having a biomass growth yield higher than anaerobic bacteria). Only to be followed closely by nitrate energy yield, which is the reason why this compound is used in those environments where oxygen availability is low (Rittmann and McCarty, 2012). On the other hand, as the content of chlorophyll-a was negligible, the growth of biomass was not associated to photosynthetic metabolism (in addition the columns were covered in aluminium foil to prevent light penetration).

The change in transport properties during the experiments is also reflected in the biological variables measured at day 104 for different depths (4, 8 and 25 cm) (see Figure 3-3). The content of non-soluble organic matter (0.5% in 100% sand columns, 1.0-1.5% in 10% compost columns, 5-7% in 50% compost columns, Figure 3-3) increased with the percentage of compost mixed with sand. Note that in compost columns a decrease of non-soluble organic matter in depth was observed in Figure 3-4, whereas it remained constant in full sand columns. This was arguably associated to a potential release of soluble organic matter in columns that decreased over time and confirms the necessity of adding this process to the conceptual model displayed in Figure 3-1. Furthermore, it would indicate limitation of the use of compost as a material in a reactive barrier has a limited lifetime, especially in terms of providing an extra source of dissolved organic carbon.

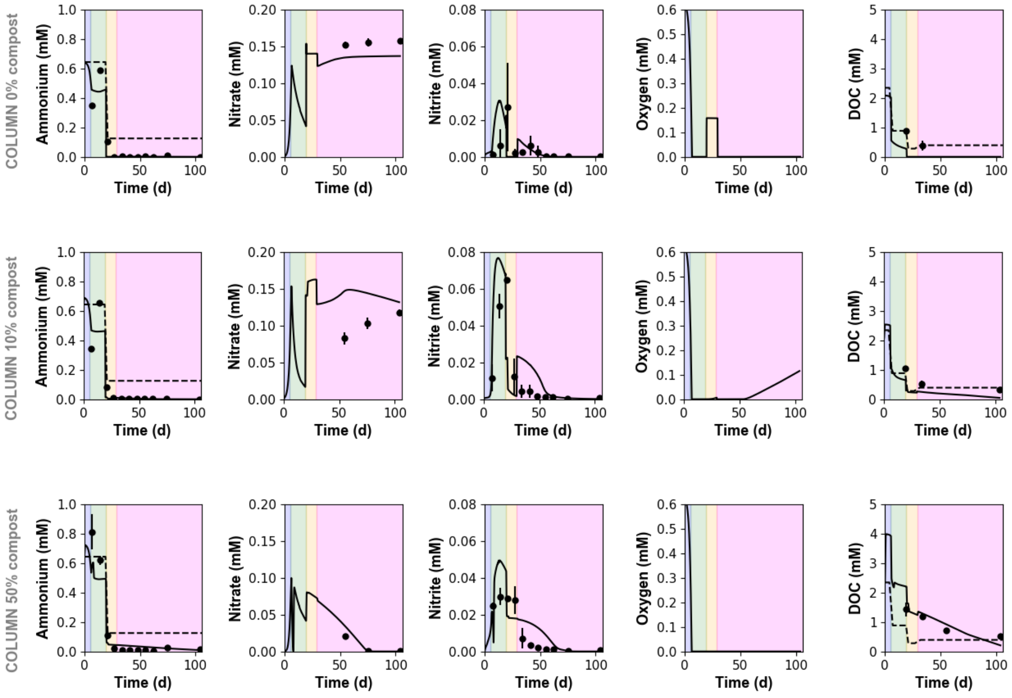


Figure 3-4. *Results of the biogeochemical modeling at the outflow of the different columns. Black points indicate experimental data whereas black solid lines are the model results. Dashed black lines represent the respective concentrations at the inlet. Background colors of the plots refer to the different Inflow sub-periods (Table 3) in the experiment: blue – I, green – II, yellow – III, red – IV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)*

Finally, EPS quantity (measured as glucose) also correlated (for both cases p-value significantly low) positively with the proportion of compost (coefficient of determination r^2= 0.81) and β (r^2=0.46) in Figure 3-3c. However, the correlation due to β is subject to variation because the value of this parameter has a lot of variability in the data obtained (specially for the case of 0% compost). We associate this effect to the growth of biofilm favoured by the nutrients supplied by the compost and the addition of microorganisms already present in the compost, again consistent with the reported changes in transport parameters.

Therefore, after combining the data from tritium BTCs and biological analysis, the question that arises is whether the addition of compost on the top soil of an aquifer forming a reactive barrier is overall beneficial when combining quantitative and qualitative aspects. So far, the impact on infiltration dynamics, reducing total infiltration capacity and enhancing non-Fickian transport caused by biofilm expansion in the pore network is clear, increasing with compost content and time. However, the indirect impact of biofilm growth is quite complex. The presence of compost enhances biological activity. This agrees with surface infiltration experimental information in field scale studies, where biofilm needs to be scraped, treated or dried repeatedly to sustain the infiltration yields over time (Dillon et al., 2019, 2009). Such enhanced biological activity affects geochemical reactions catalysed by microorganisms, resulting in a significant transformation of the water quality. In the following section, we will evaluate the impact of such transformation upon the N and C cycles.

3.3.2 Biogeochemical modelling: evaluating the impact of a reactive layer in the carbon and nitrogen cycles

The biogeochemical model described in Figure 3-1 is used to simulate the breakthrough curves (BTCs) at the outflow of the column (Figure 3-4) and the depth profiles alongside the columns (supporting information Figures S1, S2 and S3). Figure 3-4 presents both the experimental data and the best fitted model using the parameters listed in Table 3-5. Profile data at selected times are presented in the Supporting Information (Figures S1, S2 and S3). In general, the model is well adjusted to the experimental data. In order to understand relative importance of the different processes, we studied the evolution of rates presented in Figure 3-5.

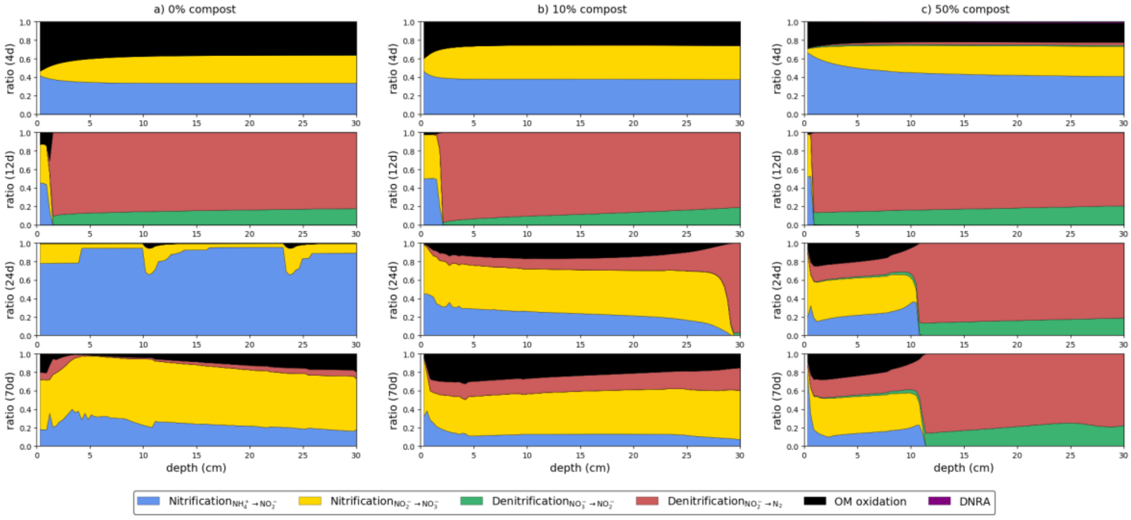


Figure 3-5. *Kinetic rates profiles for the three column setups, including data from the four sub-periods modeled (days 4, 12, 24 and 70 respectively for sub-periods I to IV). The days selected in the graphs were approximately at the middle of each sub-period (Table 3).*

Table 3-5. *Fitted parameters from biogeochemical modeling. Literature data obtained from Gao et al., 2010; Dinçer and Kargi, 2000; MacQuarrie and Sudicky, 2001; Lee et al., 2006.*

	Units	COLUMN 100% sand	COLUMN 10% compost	COLUMN 50% compost	LITERATURE
Nitrification (Oxidation of ammonium)					
K'_{max,nit_1}	d^{-1}	4.234	3.715	4.579	1 - 100
$K_{s,O}$	M	1.3×10^{-5}	5×10^{-6}	1×10^{-6}	6.25×10^{-6} - 4.812×10^{-5}
K_{s,NH_4^+}	M	1×10^{-5}	1×10^{-5}	1×10^{-5}	7.143×10^{-6} - 3.571×10^{-4}
K_{I,NO_2^-}	M	4×10^{-5}	8×10^{-5}	4×10^{-5}	NF
Nitrification (Oxidation of nitrite)					
K'_{max,nit_2}	$S^{-1}(d^{-1})$	10.368	8.64	8.64	1 - 100
$K'_{s,O}$	M	1×10^{-6}	1×10^{-6}	1×10^{-5}	6.25×10^{-6} - 4.812×10^{-5}
K_{s,NO_2^-}	M	4×10^{-6}	1×10^{-6}	1×10^{-5}	7.143×10^{-6} - 3.571×10^{-4}
K_{I,NO_3^-}	M	2×10^{-4}	1×10^{-4}	1.7×10^{-4}	NF
Aerobic oxidation of organic matter					
$K'_{max,DOC}$	$S^{-1}(d^{-1})$	0.9504	0.864	0.8208	1 - 100
$K''_{s,O}$	M	1×10^{-6}	1×10^{-5}	2×10^{-5}	6.25×10^{-6} - 4.812×10^{-5}
$K_{s,DOC}$	M	9×10^{-5}	4×10^{-4}	2.8×10^{-4}	8.33×10^{-6} - 3.33×10^{-3}
Denitrification (reduction of nitrate)					
$K'_{max,denit_1}$	$S^{-1}(d^{-1})$	2.592	9.936	3.9744	0.2 - 40
K_{s,NO_3^-}	M	1×10^{-4}	5×10^{-5}	1×10^{-6}	7.143×10^{-6} - 3.571×10^{-4}
$K'_{s,DOC}$	M	1×10^{-5}	7×10^{-5}	5×10^{-6}	8.3167×10^{-4}
$K_{I,O}$	M	5×10^{-6}	2×10^{-5}	1×10^{-4}	NF
Denitrification (reduction of nitrite)					
$K'_{max,denit_2}$	$S^{-1}(d^{-1})$	0.39744	2.16	2.2464	0.2 - 40
K'_{s,NO_2^-}	M	1×10^{-6}	2×10^{-5}	1×10^{-6}	NF
$K''_{s,DOC}$c	M	6×10^{-5}	2×10^{-4}	1×10^{-5}	8.3167×10^{-4}
$K'_{I,O}$	M	9×10^{-5}	7×10^{-5}	9×10^{-5}	NF
K'_{I,NO_3^-}	M	2×10^{-4}	1.5×10^{-4}	6×10^{-5}	NF
DNRA					
$K'_{max,DNRA}$	$S^{-1}(d^{-1})$	-	-	82.08	NF
K'_{s,NO_3^-}	M	-	-	2×10^{-5}	NF
$K'''_{s,DOC}$	M	-	-	2.8×10^{-4}	NF
$K''_{I,O}$	M	-	-	6×10^{-6}	NF

GROWTH AND DECAY OF AUTOTROPHIC BIOMASS					
$Y_{ox\ amm}$	M_{auto}/M	0.16	0.16	0.16	0.2– 0.3
$Y_{ox\ nitit}$	M_{auto}/M	0.035	0.035	0.035	NF
b_{aut}	d^{-1}	1 x 10^{-8}	1 x 10^{-8}	1 x 10^{-8}	0.02–0.06
GROWTH AND DECAY OF HETEROTROPHIC BIOMASS					
$Y_{ox\ DOC}$	M_{hetero}/M	0.6	0.6	0.6	NF
$Y_{denitit}$	M_{hetero}/M	0.035	0.035	0.035	NF
$Y_{denitat}$	M_{hetero}/M	0.038	0.038	0.038	NF
b_{het}	d^{-1}	1 x 10^{-8}	1 x 10^{-8}	1 x 10^{-8}	NF
Y_{DNRA}	M_{hetero}/M	-	-	0.01	NF
RELEASE COMPOST					
K	$S^{-1}(d^{-1})$	-	8.64 x 10^{-5}	2.6784 x 10^{-4}	NF

In sub-period I (days 0 to 5), nitrification was the dominating process, indicated by the high concentrations of ammonia and oxygen in all the column systems (Figure 3-4 and 3-5). However, there was not enough oxygen to exhaust ammonia and organic carbon. Columns with 10% compost and even more that with 50% compost, showed the activation of DNRA activity, due to the increase of organic carbon release from the compost. Focusing on the relative importance of different process rates (Figure 3-5), we found that nitrification, organic carbon oxidation and compost release (in columns 2 and 3) showed the highest rates. Besides, due to the short time and high concentrations of oxygen, organic carbon and ammonia, inhibition and saturation terms embedded in the expressions for rates were not significant, so that data could be fitted as well using simple first-order degradation rates, governed by $K'_{\max}$. For this same reason, the estimated inhibition or saturation constants are highly uncertain.

Sub-period II (days 5 to 19) was characterized by the increasing effect of denitrification due to the previous consumption of oxygen and the presence of generation of nitrate from nitrification. This was especially true in the profiles corresponding to day 7 (bottom half) and day 14 (all the column) that show the lack of oxygen (Figures S1, S2 and S3 from the supporting information). In this sub-period the inlet concentration of organic carbon was significantly reduced (from 2.3 to 0.88 mM), which could explain the nitrite accumulation associated to denitrification (Betlach and Tiedje, 1981) in addition to the accumulation due to incomplete nitrification. This accumulation, present in all columns, was most significant in those including a fraction of compost. Indeed, in the column with 10% compost, the concentration of nitrite had a peak exceeding the drinking water standard (WHO, 2011). Thus, it would seem that the presence of a reactive layer in infiltration facilities could lead to transient accumulations of nitrite. Besides denitrification, a significant process in this sub-period was the presence of DNRA (mostly in the column with 50% compost, see Figure 3-5) due to the higher effect of organic carbon in compost release. Note that DNRA processes are short lived, not only because they require a high concentration of organic carbon, but because they need nitrate as their input, competing directly with denitrification (see Figure 3-5). The kinetics of DNRA are required to take as much nitrate as possible but only until a certain amount of organic matter ($1x10^{-3}$ mM approximately due to the Ks of organic matter with a value of 2.8×10^{-4} M), guaranteeing that DNRA only occurred at the beginning of the column experiment in agreement with the experimental data.

Sub-period III (days 19 to 29) was defined by a sharp decrease in the inlet concentrations of both ammonia (reducing from 0.64 to 0.16 mM) and organic carbon (from 0.88 to 0.28 mM). Under these conditions of limited electron donor concentrations, oxidation of organic carbon, denitrification and DNRA were significantly hindered. In the 100% sand column, the concentration of organic carbon was below the K_S and therefore the reactions barely took place (Figure 3-5), and consequently the concentration of oxygen eventually increased enough to generate aerobic conditions. On the other hand, columns with a fraction of compost still had a significant release of organic matter and therefore the organic carbon concentrations were not below the K_S level and denitrification was still present. Overall, nitrification regained more importance, reducing nitrite and increasing nitrate concentrations.

Sub-period IV (days 29 to 116) maintained the same ammonia concentration as sub-period III, but with a slight raise in the organic matter concentration (from 0.28 to 0.39 mM). This had relatively no effect on the 100% sand column because the main process was still nitrification (accumulating nitrate). This was fully observed in the profiles for all columns, displaying an increase in nitrate concentration with depth, indicating that there was not enough organic matter to have a significant effect of denitrification at these final sub-periods. However, in columns with compost, denitrification was more significant, causing an accumulation of nitrite, consistent with both experimental data and the fitted K_S value of organic carbon (see Table 3-4). In the 50% compost column, nitrite accumulation indicated incomplete denitrification. This observation was also confirmed in the profiles, where at the top half of the column nitrification was quite present (high nitrate concentrations), while at the bottom half complete denitrification occurred (fully consuming both nitrate and nitrite, see Figures 3-4 and 3-5).

The kinetic of nitrification and aerobic oxidation of organic carbon are in general similar (within the same order of magnitude) for all the columns (Table 3-5). Denitrification, on the other hand, implied significant differences in the calibrated K_S values, indicating that the larger the fraction of compost, the higher the tendency to consume respective substrates. Inhibition, can be fitted with similar values for all reactions (except for denitrification reduction of nitrate in the nitrate inhibition), probably because this process was hardly activated during the relatively short duration of the experiment.

Generally, the evolution of the biogeochemical signature of the infiltrating water was affected by the inclusion of a source of labile organic carbon at the top surface of an aquifer in the form of a reactive barrier, significantly affects the fate of the different compounds involved in the nutrient (C, N) cycles, both short and long term. When the barrier contains compost, transient accumulations of nitrite can be observed together with an overall increase in nitrate concentrations, probably due to the oxidation of leached ammonia. This could pose a risk for aquifer nitrate pollution; yet, this is counteracted by the DOC leaching, favoring denitrification and nitrate reduction. Besides, adding a reactive layer increases the number and the intensity of bacterial processes occurring in the top layer of the barrier, increasing the variability of processes coexisting within a very thin layer (e.g. there is a clear transition from an oxic to an anoxic zone). In terms of purification capacity of MAR, this variability would increase the potential for degradation of some recalcitrant compounds (e.g., Emerging Organic Compounds) mostly occurring by co-metabolism (Dalton and Stirling, 1982; Rodríguez-Escales et al., 2017).

3.4 Conclusions

The presence of a compost reactive barrier placed on top of an infiltration pond used as a MAR facility has both pros and cons. In this work, we studied how addition of compost might influence both the infiltration rates (i.e. quantitative issues and sustainability), and the evolution in space and time of the quality of the infiltrating water. This was done by analyzing flow through column experiments, combined with biological analysis of the sediments once the columns were dismantled. Emphasis is placed in formulating a complex conceptual model of the fate of the different compounds that constitute the nutrient (C and N) cycles involved, and using this model to interpret the observations in the experiments reported by Modrzyński et al., 2021.

Overall, the potential of compost is to release labile organic carbon, enhancing biomass development and biofilm formation, and subsequently stimulate processes catalysed by the microorganisms. Therefore, the reactive barrier acts by reducing significantly the infiltration capacity of the system; the higher the compost percentage, the faster the growth of microorganisms and the reduced porosity, reducing overall saturated hydraulic conductivity, and enhancing dispersivity as observed in breakthrough curves of tracer tests. The combination of compost with sand implies that this infiltration capacity reduction can be managed adequately by analysing in the future optimal proportions of compost and sand, and including other materials, like wood chips or other more permeable materials. This analysis could be assessed by means of full integrated biogeochemical models once a few batch and column experiments are performed (to obtain the values specific of the local parameters) with local soil and compost in the study areas of interest to install future MAR facilities.

This reduction in infiltration is potentially compensated by the benefits in water treatment resulting in improved water quality. The larger the volume colonized by biofilm, usually means the larger the increase in bacterial activity, although and overgrowth of biofilm may be also harmful for these bacteria if nutrients are blocked from deeper parts of the biofilm. Such activity results in a pronounced enhancement of geochemical reactions, in particular those catalysed by microorganisms, such as nitrification, denitrification and organic matter oxidation. The addition of compost in the reactive barriers will have a significant impact on the nutrient dynamics: In the short run, the addition of compost caused leaching of nutrients (both carbon and nitrogen) and the occurrence of DNRA, while in the long run, the overall concentrations of nutrients (especially nitrogen) were the lowest of the three column setups. Finally, in terms of purification capacity of MAR systems, this variability would also increase the possibility of the degradation of recalcitrant compounds by co-metabolism.

To conclude, there is a need to look at MAR from an integrated point of view, balancing the quantitative with the qualitative aspects. This will allow to maximize the overall benefits of recharging aquifers with treated wastewater, rather than having to rely on excessively high-quality water for recharge. Eventually, this can expand the potential of MAR in providing water security in the changing climate.

Chapter 4

A numerical model to evaluate the fate of Emerging Organic Compounds coupled to geochemical conditions in Soil Aquifer Treatment experiments

This chapter is an edited version of:

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4.1 Introduction

Water scarcity is a worldwide hazard, expected to worsen in the coming years as an effect of climate change. One way to reduce the risk associated with prolonged droughts is by relying on unconventional water resources. Amongst the methods for indirect reuse, Managed Aquifer Recharge (MAR) is used worldwide, being a tool both to increase water resources in the subsurface (Dillon et al., 2018; San-Sebastián-Sauto et al., 2018) and to enhance the quality of the infiltrating water, leading also to significant environmental benefits (Dillon et al., 2018). MAR implies the increase of aquifer storage by supplying opportunity (most often, reclaimed) water for infiltration. This recharged water can then be used for all productive sectors (agriculture, industry, and domestic). Thus, MAR is a useful technology in both arid or semi-arid regions presenting high risk of water shortage due to the combination of decrease in resources by climate change and increase in groundwater demand from the increase in population or in agricultural needs (UN, 2015). Examples can be found worldwide, including the Mediterranean (Rodríguez-Escales et al., 2018), Western USA (Alam et al., 2020), Australia (Arshad et al., 2014), among many others.

In the context of circular economy, the source of water for recharge often come from the effluent of wastewater treatment plants (WWTP) after secondary treatment, infiltrated by means of infiltration ponds. This is one of the many methods for MAR, being classified as one subgroup of Soil Aquifer Treatment (SAT) tertiary treatment methods. As such, there is a need to monitor water quality, mostly to avoid the potential of MAR-SAT to become a source of diffuse pollution (Song et al., 2019).

Amongst the many pollutants present in the recharging waters, here we focus on the fate of Emerging Organic Compounds (EOCs) in the subsurface. All waters carry a mixture of compounds with different origins and chemical properties. This chemical signature changes during the residence time within the porous media driven by several biogeochemical processes. One such process is sorption, that for organic compounds depends, among other issues, on the molecules ionization. For the neutral ones, sorption is mainly affected by the octanol-water partition coefficient (K_{ow}) and, at the same time, by the organic carbon partition one (K_{oc}). For ionic compounds, interactions are related to the pK_a of the compound and the pH of the media (Franco et al., 2009). A second common process, biodegradation, is also highly compound dependent (Greskowiak et al., 2017). Degradation is mainly related to the reduction-oxidation (redox) conditions; if the system is biologically active and shows more than one redox condition, the probability of degradation of an individual EOC increases, since co-metabolism degradation is favoured (Rodríguez-Escales et al., 2017). All of this implies that predicting EOCs fate in the environment is hard and it cannot be done assuming a unique behaviour; rather, sometimes a compound by compound analysis is needed (Rodríguez-Escales and Sanchez-Vila, 2016).

To increase the number of EOCs that are degraded in a MAR-SAT system and their removal rate, some authors suggest the addition of a permeable reactive layer (PRL) at the bottom of the infiltration ponds (Grau-Martínez et al., 2017; Schaffer et al., 2015; Valhondo et al., 2020). The PRL promotes a number of biomediated geochemical reactions, so that the removal rates of EOCs occurring within the soil is increased. An early example of PRL was installed in the Sant Vicenç dels Horts (Barcelona) infiltration pond (Valhondo et al., 2014). This reactive layer was composed by a mixture of sand and compost, with low proportions of clay and iron. Compost produced a pool of labile organic carbon that slowly released to the aquifer, which enhanced the presence of reduction-oxidation (redox) processes, ranging from oxygen to sulphate reduction, within the first meters of the aquifer. A great variety of redox conditions implied an increase of the probability of EOCs being degraded, since a wide diversity of bacteria were found in the subsoil (Barba et al., 2019; Rodríguez-Escales et al., 2017). On the other hand, iron and clay provided positively and negatively charged surfaces, respectively, which promoted the ionic interaction between these and ionic EOCs (Kutzner et al., 2016; Silver et al., 2018).

Due to the high uncertainty and complexity in the processes that take place in the subsurface, conceptual and numerical modeling are integrative indispensable tool to test the relative importance of the different redox processes governing the fate of EOCs (Rodríguez-Escales et al., 2020). Nevertheless, these models are very complex, involving the need to couple groundwater flow, conservative solute transport, geochemical models concerning major compounds (cations, anions, and solid interactions), definition of the redox state and its spatio-temporal evolution, and, finally, the EOC's fate. Yet, most of the numerical models existing in the literature are disconnected from the geochemistry of the aquifer (Henzler et al., 2014; Nham et al., 2015; Schaffer et al., 2015). These approximations would be only good for compounds that are degraded without any interaction with the soil or with other solutes that are presented in major concentrations. Nevertheless, it has been widely proven that degradation of most of EOCs depends on geochemical conditions and often degraded under co-metabolism (Banjac et al., 2015; Banzhaf et al., 2012; Henzler et al., 2014; Lapworth et al., 2012). The use of a simple decay constant implies that all the complexity of the system is transferred to a single lumped parameter, lacking any physical meaning.

Similar is the case for modeling sorption processes. Sorption is also related to groundwater geochemistry; for example, ionization of the organic compound is governed by the pH of the system. In redox processes, pH can oscillate naturally from 6 to 8. Both oxygen and nitrate reduction imply a little acidification of the system, whereas iron and manganese reduction a little basification. At the same time, a generation of secondary minerals coexist, depending on both redox conditions and pH, like iron and manganese oxides and hydroxides or calcite (Rodríguez-Escales et al., 2020). All of these greatly impact EOCs sorption; first, pH condition the ionization degree of organic compounds displaying a pK_a value close to the pH (e.g., most of the compounds belonging to the group of benzophenones). On the other hand, mineral precipitation generates new surfaces to act as sorbents. Similar to the case of degradation, most EOCs sorption models in the literature oversimplify the real processes occurring, and consider a very simplistic equilibrium model, thus only governed by the lumped parameter K_d (Schwarzenbach et al., 1993).

Considering all of this, in this paper we have developed a numerical model that couples sorption and biodegradation processes for a mixture of EOCs to the global geochemistry of a soil-water system. The model is tested with experimental information regarding the fate of five EOCs (carbamazepine, sulfamethoxazole, diuron, paracetamol and benzophenone-3) in experimental columns simulating a process of SAT coupled with a PRL including different proportions of a sand-compost mixture (Modrzyński et al., 2021). The starting point is a complex geochemical model focused on different compounds from the carbon and nitrogen cycles already presented by Canelles et al. (2021) in the same experiments. To explore and test the significance of including the coupling of major compounds with EOCs fate, we tested in parallel different simplified models, ranging from the simplest one -both sorption and biodegradation fully disconnected from geochemistry- to the most complex one – processes fully connected.

4.2 Methodology: Development of the full conceptual model

4.2.1 Geochemical model: processes involving compounds from C- and N-cycles

The geochemical model was centred in the governing processes that occur typically in a MAR-SAT facility. The most important are those related to the carbon and the nitrogen cycles, being: 1) oxidation of organic carbon under aerobic conditions; 2) nitrification, with two steps (ammonia to nitrite, and nitrite to nitrate); 3) denitrification, with two steps (nitrate to nitrite, and nitrite to nitrogen gas); and 4) Dissimilatory Nitrate Reduction (DNRA) (Canelles et al., 2021; Modrzyński et al., 2021). In Canelles et al. (2021), the resulting geochemical model is extensively detailed.

4.2.2 General model conceptualization: EOCs sorption

Sorption removes EOCs from the liquid phase by their retention into the solid surfaces. Different mechanisms explain such interactions: ion bonding or ligand exchange, chemiosorption (formation of a covalent bond with the soil molecular structure), ion-dipole and dipole-dipole interaction, charger transfer, hydrogen bonding, and hydrophobic bonding by Van der Waals forces (von Oepen et al., 1991). The most important sorbents present in the soil are the sedimentary organic matter (SOM) and the inorganic clay minerals, both displaying a negative electrical charge at the surface (Appelo and Postma, 2005). Consequently, depending on the charge of the organic compound, a different potential for sorption would be expected, with positive charges showing the highest values. Although lipophilic interactions are weaker than the ionic ones, they are the most important for the majority of organic chemicals (Franco et al., 2009). In general terms, equilibrium sorption is reached when the activity of the organic compound in the two phases (water and solid) are kept constant. This is conceptualized as:

$$EOC_{aq} + SOM \leftrightarrow EOC - SOM \,, \tag{1}$$

where EOC refers to the Emerging Organic Compound, the subindex aq indicating that it is present in the aqueous phase, SOM is the sedimentary organic matter, and $EOC - SOM$ is the complex formed by the sorbed EOC to the SOM surface. This equilibrium of the sorption reaction is governed by the constant equilibrium K_d:

$$K_d = \frac{C_{i,s}}{C_{i,aq}} \,, \tag{2}$$

where $C_{i,s}$ and $C_{i,aq}$ are the equilibrium concentration of species i sorbed to the soil and to water, respectively, assuming an activity coefficient equal to one. K_d is defined as a partition coefficient, but actually, due to the complexity and heterogeneity of real soils, in reality it is a lumped parameter that encompasses multiple processes and multiple equilibria occurring simultaneously in the soil. For organic compounds, K_d is usually related to the amount of sedimentary organic matter (f_{om} if it is referred to organic matter, or f_{oc} if it is organic carbon) and the K_{OC} (organic carbon-water partition coefficient) by $K_d = f_{OC}K_{OC}$. K_{OC} correlates linearly with the octanol-water partition coefficient, K_{ow} by (Franco et al., 2009; Schaffer et al., 2012):

$$logK_{oc} = a + b\ logK_{ow}\ , \tag{3}$$

where a and b are empirical parameters for non-hydrophic compounds with values of 0.52 and 1.02, respectively (Sabljić et al., 1995). As stated, the word sorption includes many physico-chemical mechanisms; in general, there is a distinction between adsorption and absorption. The former refers to a surface interaction of the organic compound, whereas the latter is related to the penetration of the organic compound into the solid structure (Schwarzenbach et al., 1993). Consequently, adsorption is assumed to cause weaker bonds than absorption and, coherently, it is a more reversible process. When sorption occurs in an environmental system, it is almost impossible to distinguish between the different sorption mechanisms; contrarily, desorption allows to distinguish between adsorption and absorption. It has been widely described that sorption is not always fully reversible, as some fraction of organic compounds is strongly bonded to the solid phase (Durán-Álvarez et al., 2012; Martínez-Hernández et al., 2014; Schübl et al., 2021). Although in general terms, sorption is typically assumed in equilibrium (Barret et al., 2011; Joss et al., 2006; Rodriguez-Escales et al., 2012), when slower desorption occurs due to stronger interactions or because of heterogeneous media, it is possible to disregard equilibrium and to use a kinetic formulation (Berhane et al., 2017; Martínez-Hernández et al., 2014), as:

$$\frac{dC_{i,aq}}{dt} = -k_m\left(C_{i,aq} - \frac{C_{i,soil}}{k'_d}\right), \tag{4}$$

where k_m $[T^{-1}]$ would be the sorption-desorption kinetic rate, and k_d' $[L^3/M]$ the distribution coefficient. Another point to consider is that organic compounds are not necessarily neutral.

They can be hydrolysed, either by themselves or by their functional groups, becoming weak acids or bases. Ionization is an equilibrium reaction,

$$EOC_{aq} \leftrightarrow EOC^{-} + H^{+} \tag{5}$$

characterized by the pK_a ($pK_a = -logK_a$) and pH values. Depending on these two values, the fraction of neutral (α_n) compound is given by:

$$\alpha_{EOC_n} = \frac{1}{1+10^{pH-pK_a}} \; . \tag{6}$$

From (6), if the organic compound is ionized, K_{OW} should be redefined, due to the coexistence of two compounds in the water phase. For that, D_{OW} is defined as the distribution between the neutral form of the organic compound in the two liquid phases (Scherrer and Howard, 1977):

$$logD_{OW} = logK_{OW} + \log(\alpha_{EOC_n}) \; . \tag{7}$$

Note that when the compound is neutral, $\alpha_{EOC_n} = 0$, and D_{OW} and K_{OW} are equal. The expression (1), in case of ionisable compound, should be readapted to D_{OW} instead of K_{OW} as described in (Schaffer et al., 2012). Consequently, both reversible and non-reversible sorption will be affected by the presence of ionisable compounds.

4.2.3 General model conceptualization: EOC's biodegradation

Besides sorption, biodegradation also affects the EOC's fate in a MAR-SAT facility. Biodegradation implies the breakage of the organic molecule, which is mediated or facilitated by microorganisms, and in general aimed at transforming the organic compounds in smaller and more polar ones. During Phase I of metabolism, reactive groups such as $-COOH$, $-OH$, $-NH_2$, or $-SH$ are added or made available, either by redox reactions or by hydrolysis. Afterwards, the products of Phase I reactions are either eliminated or enter into Phase II reactions. In the latter, conjugates are formed, which inactivate and enhance the elimination of the compound. All these reactions need energy, which is available from the reduction oxidation reactions using electron acceptors present in the solution (e.g. oxygen). The metabolic pathway, the degradation rate, and also the produced transformation products, depend on the electron acceptor availability in the media and, consequently, on the redox potential. Degradation of EOCs is enhanced when labile organic compounds are being degraded at the same time (co-metabolism) (Henn et al., 2020; Xiong et al., 2020; Zhou et al., 2019). Thus, coupling EOCs biodegradation to labile organic carbon oxidation is crucial to properly understanding and modeling the full decay process.

Besides the existence of a labile organic oxidation, degradation of a given individual EOC is either favoured or not depending on the geochemical conditions of the soil-water system; in particular reduction-oxidation potential. Some EOCs are best degraded under aerobic conditions (Burke et al., 2017; Xu et al., 2009), whereas others under anaerobic ones (Barbieri et al., 2011; Hoppe-Jones et al., 2012). The EOCs biodegradation rate is usually modelled using a first-order rate,

$$\frac{dC_{i,aq}}{dt} = -k_i C_{i,aq} \, , \tag{8}$$

where $C_{i,aq}$ is the concentration of EOC in the aqueous phase $[M/L^3]$, k_i is the first order degradation constant $[T^{-1}]$, in most cases used as a lumped parameter that just describes the overall reported concentrations in given lab or field experiments (Burke et al., 2014; Joss et al., 2006; Martínez-Hernández et al., 2016; Nham et al., 2015). It is then possible to incorporate additional parameters to couple the expression of the degradation rate with the geochemical conditions:

$$\frac{dC_{i,aq}}{dt} = -k_i C_{i,aq} F_i L_i \, , \tag{9}$$

where now F_i $[-]$ is a factor that couples the EOCs degradation rate to a certain geochemical process, and L_i $[-]$ is a parameter related to the existence of a lag phase adaptation period that microorganisms may need to start to metabolize the more recalcitrant compounds. The first term (F_i) is defined as an activation term to a certain reduction-oxidation condition:

$$F_i = \frac{r_m}{r_m + q_{i,m}} \, , \tag{10}$$

where r_m is the rate of “m” reduction-oxidation process $[\mathrm{ML^{-3}T^{-1}}]$ and $q_{i,m}$ is the activation parameter $[\mathrm{ML^{-3}T^{-1}}]$ for a certain reduction-oxidation term of a “i” EOC. The lag phase, L_m $[-]$ value at a certain time T_m $[\mathrm{T^{-1}}]$, was computed as:

$$L_m = \frac{T_m}{T_f} \tag{11}$$

T_f $[\mathrm{T^{-1}}]$ being the total time of the column experiment.

Considering all of this, we have conceptualized different combinations for modeling the EOCs sorption and degradation (Table 4-1). Note that the individual EOC’s fate is always computed after 1) flow and transport model, and 2) geochemical model (Figure 4-1). All the conceptual models, reactions and equations assumed in the different scenarios are summarized in Figure 4-1.

Table 4-1. *Different models considered*

		SORPTION	**BIODEGRADATION**
Sorption only	MODEL 1A	Equilibrium sorption/desorption coupled to EOCs ionization	No biodegradation
	MODEL 1B	Kinetic sorption/desorption coupled to EOCs ionization	No biodegradation
Sorption + biodegradation	MODEL 2A	Best fitted model of sorption (kinetic)	Uncoupled first order kinetic degradation
	MODEL 2B	Best fitted model of sorption (kinetic)	Coupled first order kinetic degradation to geochemistry

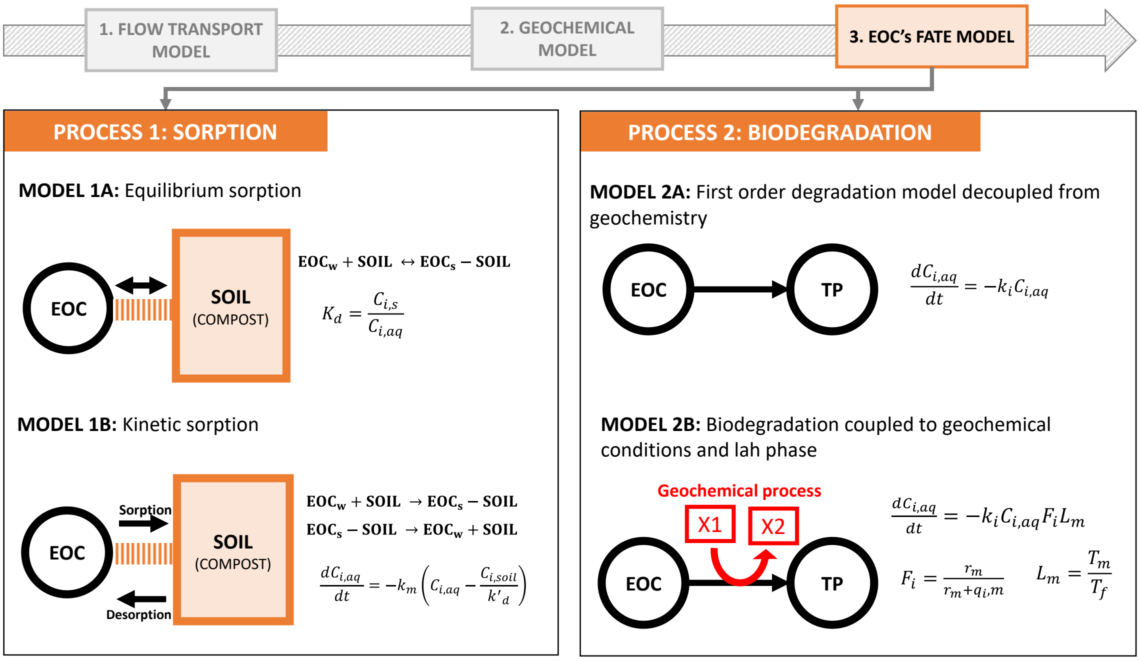

Figure 4-1. *Summary of the different conceptual models evaluated for sorption and degradation.*

4.2.4 Validation of the numerical model: column experiments

In order to validate the different modeling scenarios, we used the experimental data obtained from column experiments (Modrzyński et al., 2021) aimed at reproducing a MAR-SAT pilot field system located in Palamós (Spain) (Valhondo et al., 2020). The experiments consisted of three columns in duplicate that all ran for a total time of 116 days: Column 1 (C1), filled with 100% of pure sand; Column 2 (C2), filled with a mixture of 10% compost and 90% sand; and Column 3 (C3), mixing 50-50% of compost and sand. The water flow in the column was vertical (top to bottom) fixed at a constant rate of 0.5 mL/min. The columns were 6.6 cm of inner diameter and composed of a top sand layer (2-2.5 cm) underlain by the 29 cm-long reactive layer (C1 to C3), with a coarse silica sand layer at the bottom (3 cm). Six sampling points were installed at each column: one at the inflow water headspace, four along the column (at 4, 8, 13 and 20 cm depth), and one at the outflow (30 cm depth). For further details on the column setup, reactive barrier composition and sampling, see Modrzyński et al., 2021. The column was filled with synthetic water simulating the effluent of the Palamós WWTP and spiked with a cocktail of EOCs: carbamazepine (CBP), diuron (DIU), paracetamol (PML), benzophenone-3 (BP3) and sulfamethoxazole (SMX) (see Table 4-2 for their characteristics).

Table 4-2. *Properties of the Emerging Organics Compounds evaluated.*

	CAS Number	pK_a	$logK_{ow}$
Carbamazepine	298-46-4	15.96	2.45
Diuron	330-54-1	13.18	2.68
Paracetamol	103-90-2	7.84	0.46
Benzophenone-3	1013-88-3	7.07	3.79
Sulfamethoxazole	723-46-6	4.54	0.89

The EOCs inflow concentration varied along the 116 days of the experiment. Initially, for CBP, SMX and DIU inflow concentration was kept close to 1 ppb during 67 d; then, it was decreased to around 0.3 ppb until the end of the experiment. PML concentration was 1.5 ppb the first 67 days and then decreased to 0.67 until day 99 and to 0.16 ppb until the end of the experiment. Finally, BP3 inflow concentration varied from 1 ppb to 0.16 along the experiment.

4.2.5 Model set-up and calibration

A flow and a conservative transport model of the column experiments was already available in the literature (Canelles et al., 2021), aimed at characterizing the main hydrological parameters as well as the relative importance of the transport processes. The computed characteristic time for advection (t_a) was 0.6 d, whereas for dispersion (t_D) was in the range between 20 and 70 d for the C3 and C2 and around 500 d for C1. The biogeochemical model is also described in Canelles et al. (2021). It is composed by the kinetic processes previously enumerated, the most important chemical water equilibriums (see Phreeqc database), and the biomass growth and decay – both in autotrophic (nitrification) and heterotrophic (rest of processes) forms. The model also describes the release of labile dissolved organic carbon (DOC) and ammonia from the compost solid phase.

The biodegradation and sorption model of EOCs was constructed using PHT3D v2.17 (Prommer et al., 2001) and coupled to the bio-geochemical model described in (Canelles et al. 2021). PHT3D couples the transport simulator MT3DMS (Zheng and Wang, 1999) and the geochemical code PHREEQC-2 (Parkhurst and Appelo, 2013), based on a sequential split-operator technique. The 29 cm (average of reactive barrier length for all the columns) columns were modelled in 1D, with 100 cells of 0.29 cm with a width of 0.3419 m to represent the transverse area of the column. The model ran for 104 days (with time steps of 0.005 d), corresponding to the experimental full sampling period. The time discretization was selected to satisfy the Peclet and Courant numbers criteria. The dispersive transport term was computed according to the third-order total variation diminishing scheme. The model included all the geochemical processes described previously as well as the different EOCs models summarized in Figure 4-1. The calibration process was centered in the experimental EOCs concentrations both at the outflow of the column and in the different column profiles performed at selected times. The calibration was performed manually. The fitted parameters were obtained by comparing the model results with the average of the two replicates for each experiment.

4.3 Results and discussion

4.3.1 Sorption models

First, we evaluated the impact of sorption in the fate of the five EOCs, fully disregarding degradation. Figure 4-2 shows the experimental data of the five EOCs evaluated at the inlet (black dots) and outlet of the column (red dots). The lines represent the output of the numerical models assuming: 1) conservative advective transport (blue line, equivalent to the values used for input to the model); 2) equilibrium sorption (dashed red line) and 3) kinetic sorption/desorption (solid red line). Table 4-3 displays the best fitted parameters for all numerical models. The top row in Figure 4-2 corresponds to the column with no compost, so that sorption is not accounted for (all EOCs behaved as conservative tracers).

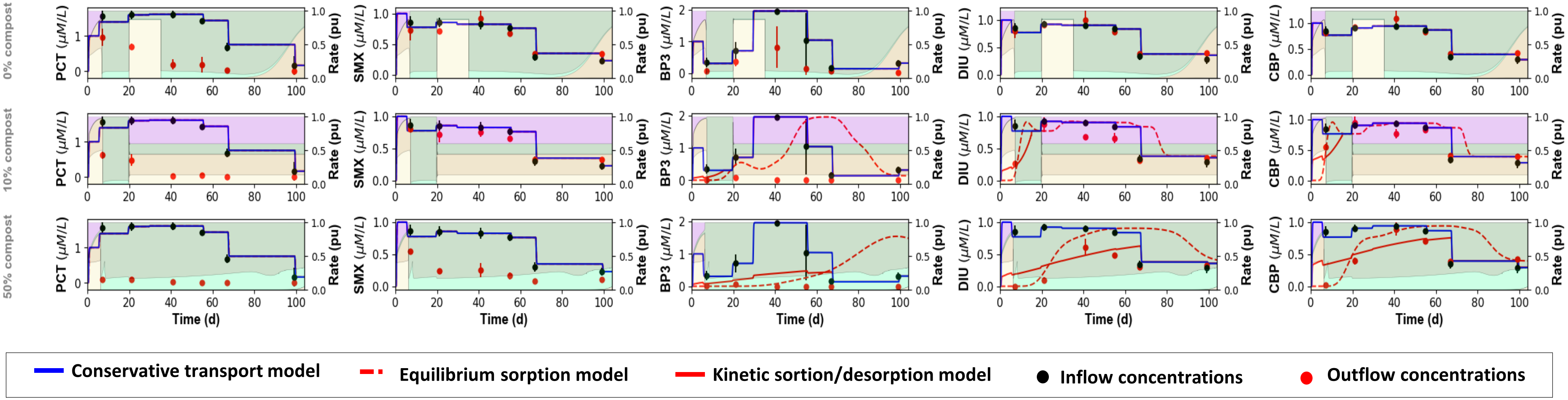

Figure 4-2. *Preliminar sorption results (model) with experimental results in the different column experiments for the different EOCs. Background colors indicate in percentage to unity, the rate for the different geochemical processes (purple, oxidation of organic matter; yellow palete, nitrification, ranging from light – oxidation of ammonia – to dark – oxidation of nitrite-; green, denitrification, light – reduction of nitrate- and dark – reduction of nitrite, respectively.*

Neither PCT nor SMX were sensitive to sorption processes in any of the three columns, as expected from the low $\log K_{ow}$ values, in both cases below 1 (see Table 4-1). This indicates that under equilibrium conditions most of the molecule remained in the aqueous phase. Ionic interactions of PCT and SMX were also discarded since both compounds remained in the neutral and anionic forms (low pK_a values, see Table 4-2) at working pH values (around 7). But, as both silica sand and compost (Bakatula et al., 2018; Stumm and Morgan, 1996) show negatively charged surfaces at neutral pH values, no interaction of any type was expected, and thus the observed decrease in concentrations was not related to sorption. Such results are coherent with observations in the literature (Lorphensri et al., 2007; Löffler et al., 2005; Yamamoto et al., 2009). Also, (Ranieri et al., 2011) observed similar results in a constructed wetland for PCT, while sorption of SMX has only been reported in positively charged soils (Kočárek et al., 2016). Nevertheless, both compounds responded to the presence of compost, by reducing the experimental concentration values at the outlet as the fraction of compost increased, but in no case this could be associated to sorption mechanisms. Regarding the fate of BP3, DIU, and CBP, sorption could not be discarded for columns displaying a fraction of compost (Figure 4-2). The equilibrium sorption model (dashed line) could fit adequately the initial experimental points but failed for the late time ones, where the models overestimated the observations, also corresponding to the input values being lower than the top inlet concentrations that took place within days 40-60, and especially after the suddenly decrease of inlet concentration (day 67). For late times, experimental concentration values at the column outlet were virtually identical to those at the inlet, indicating that desorption was not occurring.

The assumption of kinetic sorption-desorption improved the overall fitting (solid red line in Figure 4-2), in particular for CBP and DIU, and except for very early times. Characteristic time for sorption/desorption can be characterized by the inverse of K_m values (Table 4-3), ranging between 1.7 and 4.3 days. This would mean that relevant changes due to sorption/desorption mechanisms would occur around these times. Since the average residence time of the columns was 1.2 d (Modrzyński et al., 2021), sorption/desorption was not under equilibrium conditions.

Table 4-3. *Best fitted parameters in the two tested sorption models. (*) Recalculated from logD_ow values*

	Equilibrium sorption model	**Kinetic sorption / desorption**	
	$logK_{OC}$*	$K_m(s^{-1})$	$k'_d(L/Kg)$
PCT	0.98	[-]	[-]
SMX	1.42	[-]	[-]
BP3	4.38	5×10^{-5}	75
DIU	3.02	3.5×10^{-5}	75.31
CBP	3.25	2.0×10^{-5}	45.31

The effect of sorption increased with the percentage of compost present in the mixture. Indeed, we observed that retardation became relevant in columns C2 and C3. In porous media, the main sorption mechanism for neutral compounds, like CBP and DIU, is partitioning into organic phases (e.g., compost). Other intermolecular interactions – van de Waals, dipole-dipole, dipole-induced dipole and hydrogen bonding- are less relevant (Pignatello and Xing, 1996). The presence of compost further introduced heterogeneity in the pore network distribution, increasing with time associated to the development of biofilm (Canelles et al. 2021). This implied that some parts of the columns were not well connected and water reached those zones mostly by diffusion, resulting in different arrival times to parts of the columns. Consequently, reaching equilibrium conditions in the whole column took several days. Given the different characteristic times, after 67 days of experiment and with a relatively constant inflow concentration, equilibrium could be assumed. But, when the inflow concentration suddenly decreased (day 67), at short times, desorption would only occur preferentially from the macropores, where advection was the main transport process. Note that the characteristic times of dispersion in C2 and C3 were, respectively, 20 and 500 days, whereas that of advection was 0.6 d. During this period, the system was far from equilibrium conditions, and the kinetic model improved concentrations fitting significantly. During that period, delayed desorption could then be expected from the micropores, but this effect was not observed in the experiments, probably because of their duration. Delayed desorption has been previously described for CBP in natural soils in the presence of high ionic strength wastewater (Durán-Álvarez et al., 2012), and for that of DIU in soils amended with charcoal (Yu et al., 2006) or in primary size fractions of soil (Wang and Keller, 2009). Nevertheless, at our spatial and temporal scale, the sorption-desorption kinetic model is sufficient to reproduce the fate of CBP and DIU driven by sorption.

On top of the previous information, another variable was added to the sorption modeling of CBP and DIU. This was the columns "drainage effect", which consisted on the drainage of all the water present inside the columns during the soil sampling period. This effect was reported in (Modrzyński et al., 2021), where the authors considered that it increased temporally the sorption capabilities of the column. This could be linked to the fact that MAR-SAT processes usually use dry-wet periods to enhance infiltration and create new flow paths (Dillon et al., 2018). These new paths could imply also new sorption binding sites for the EOCs. This effect was simulated in the numerical model as a two-week increased period, beginning at the day of the sampling (days 8 and 42). The drainage effect is mostly visible in the curves of DIU and CBP (Figure 4-3), where the steep changes in concentrations between days 8 – 22 and 42 – 56 represent this effect of the temporal increase of sorption binding sites.

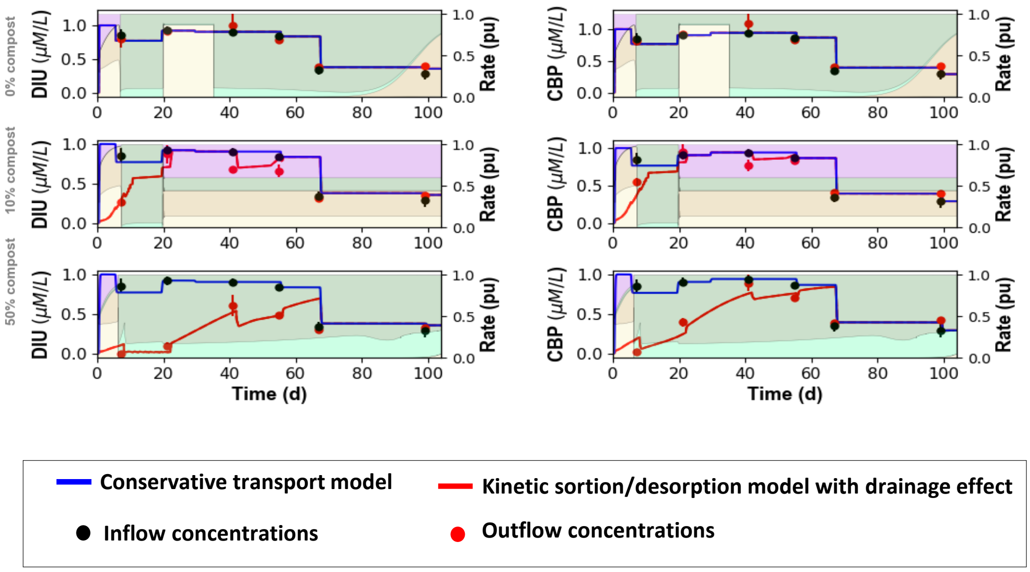

Figure 4-3. *Final model results (model) and experimental results in the different column experiments for DIU and CBP. Background colors indicate in percentage to unity, the rate for the different geochemical processes (purple, oxidation of organic matter; yellow, nitrification, ranging from light -first step – to dark – second one-; green, denitrification (light and dark for first and second steps, respectively).*

In summary, sorption can be fully disregarded as a relevant mechanism to study the fate of PCT and SMX (also with small relevance for BP3), while it seems a very significant process to study CBP and DIU in soils with the presence of compost. More, the model that better reproduced the observations was the kinetic equilibrium model. For this reason, we decided to test only the sorption kinetic model combined with biodegradation, to try to get a good fit of the actual data.

4.3.2 Biodegradation models

The next step in the modeling process was then focusing on biodegradation (on top of kinetic sorption-desorption in some cases). As specified in Figure 4-4, we tested two alternative models, one considering first-order degradation (Model 2A, Equation (8)), and a second one that couples the EOCs degradation rate to a certain reduction-oxidation process (PCT and SMX), incorporating as well the presence of a lag period (only for PCT) (Model 2B, equation (9)). Table 4-4 shows the best fitted parameters for each model. Note that although this fitting was done independently from the previous one (Table 4-3), estimated sorption parameters were quite similar (in the same order of magnitude). For CBP and DIU, adding a first order degradation did not improve (data not shown).

The net result is that for CBP and DIU, incorporating biodegradation could capture their fate with a very good reproduction of observed data; yet, kinetic sorption was still the main removal mechanism for these two compounds. In both cases, the degradation constant was 10^{-6} s, implying a half-life of 8 days, well above the resident time of water within the column. Thus, biodegradation was not the primary process in the fate of CBP and DIU. On the other hand, the fitted values for k'_d indicate that sorption was a real relevant process, and furthermore, the K_M values in the order of $7-8\,\mathrm{x}\,10^{-5}$ indicate representative times of around 4h, therefore relevant at the time scales of the experiment.

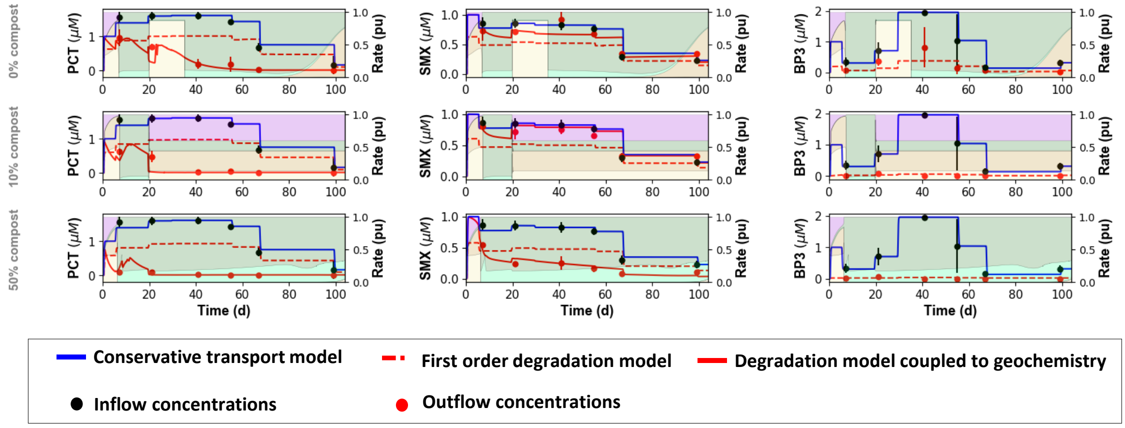

Figure 4-4. *Final model results (model) and experimental results in the different column experiments for PCT, SMX and BP3. Background colors indicate in percentage to unity, the rate for the different geochemical processes (purple, oxidation of organic matter; yellow, nitrification, ranging from light -first step – to dark – second one-; green, denitrification (light and dark for first and second steps, respectively).*

Table 4-4. *Best fitted parameters for the two model scenarios of biodegradation coupled to sorption-desorption kinetic model.*

	M2A. SIMPLE BIO DEGRADATION			M 2B. BIODEGRADATION COUPLED TO GEOCHEMISTRY				KINETIC SORPTION /DESORPTION	
	$k\,(s^{-1})$			$k\,(s^{-1})$			$q_{i,m}\,(M)$	$k'_d(L/Kg)$	$k_M(s^{-1})$
	C1	C2	C3	C1	C2	C3			
PCT		1×10^{-5}		2×10^{-4}	4×10^{-4}	8.5×10^{-4}	5×10^{-13}	[-]	[-]
SMX		1×10^{-5}		8.5×10^{-5}	1.3×10^{-4}	2.4×10^{-4}	1×10^{-8}	[-]	[-]
BP3	3.5×10^{-5}	5×10^{-5}	6.5×10^{-5}	3.5×10^{-5}	5×10^{-5}	6.5×10^{-5}	[-]	75	5×10^{-5}

On the other hand, biodegradation played an important role in understanding the fate of the other three compounds: PCT, SMX and BP3 (Figure 4-4). Adding a first order degradation made the models sensitive, allowing a first approximation to the experimental points. Nevertheless, it was not enough to fit the experimental data. The exception is BP3, where the first-order degradation model fitted well the experimental data, indicating that its biodegradation was ubiquitous in the column and was independent on geochemistry. Different authors have observed that BP3 was degraded under different redox conditions (Li et al., 2007; Liu et al., 2012; 2013; Rodríguez-Escales and Sanchez-Vila, 2020), which would indicate that, apparently, BP3 was independent on that conditions. This is not exactly true, because it is better degraded under co-metabolism, and degradation rate depends on the redox conditions (Liu et al., 2012; 2013). But, if any degradation of organic carbon is occurring, BP3 is removed.

For PCT and SMX, it was necessary to couple the degradation model to the presence of biogeochemical processes (Figure 4-4, solid red lines) acting at the same time (aerobic for PCT and denitrification for SMX). The fitting of PCT was specially improved by coupling PCT degradation to the aerobic biodegradation rates of the column system. PCT is better degraded under aerobic conditions (Li et al., 2014; Yamamoto et al., 2009). Incorporating aerobic respiration into the rate of PCT was especially sensitive (Figure 4-4). The aerobic respiration included the degradation of organic carbon and nitrification (see Canelles et al. 2021). Note that this coupling was made with a function encompassing the total rate of aerobic processes instead of oxygen concentration by itself, F_i factor (equation 10). We believe this had more sense since PCT degradation occurs because oxygen reduction was occurring, not because of the presence of oxygen itself. Best fitting for PCT experimental data evolution needed the inclusion of a lag phase. This is common in all types of biodegradation (Rodríguez-Escales et al., 2014; Van Breukelen et al., 2017) and it is related to the adaptation time that bacteria needs to remove some recalcitrant compounds.

Regarding SMX degradation, similarly to PCT, it was needed to couple it to a geochemical process. In this case, the process was denitrification. The relationship between SMX degradation and denitrification have been proved in previous works (Barbieri et al., 2012; Nödler et al., 2012; Rodríguez-Escales and Sanchez-Vila, 2016; Xiong et al., 2020). Nitrite – as an intermediate product of denitrification- interacts with amine radical of SMX promoting its transformation

(Ceresa et al., 2021; Rodríguez-Escales and Sanchez-Vila, 2016). As in our columns, nitrite was mainly accumulated during denitrification (Canelles et al. 2021), and relating SMX degradation to nitrite temporal evolution improving its fittings. Contrarily to PCT, no lag phase was needed. This is coherent because SMX degradation in the presence of nitrite is mediated by abiotic mechanisms, which do not need an extra adaption time as in the case of biodegradation.

Note that in any case, it was possible to fit a unique degradation parameter for the three columns, although they are quite similar and on the same order of magnitude (Table 4-3). Indeed, all the values increased as a function of the compost fraction, indicating that some additional process could be contemplated. In the case of BP3, a possible explanation could be the potential sorption of this compound into the biofilm (Rodríguez-Escales and Sanchez-Vila, 2020; Torresi et al., 2017), which would be highest in the column with the largest fraction of compost. Regarding PCT and SMX, sorption into an organic phase (like biofilm) is not expected, as discussed above. Nevertheless, we still believe that the presence of biofilm, highest in the column with most compost, enhanced degradation.

Finally, it is important to highlight that the presence of organic compost enhanced through different mechanisms the removing of the five evaluated EOCs. This is clearly represented in Figure 4-5, where we computed the relative removing rates for all the compounds.

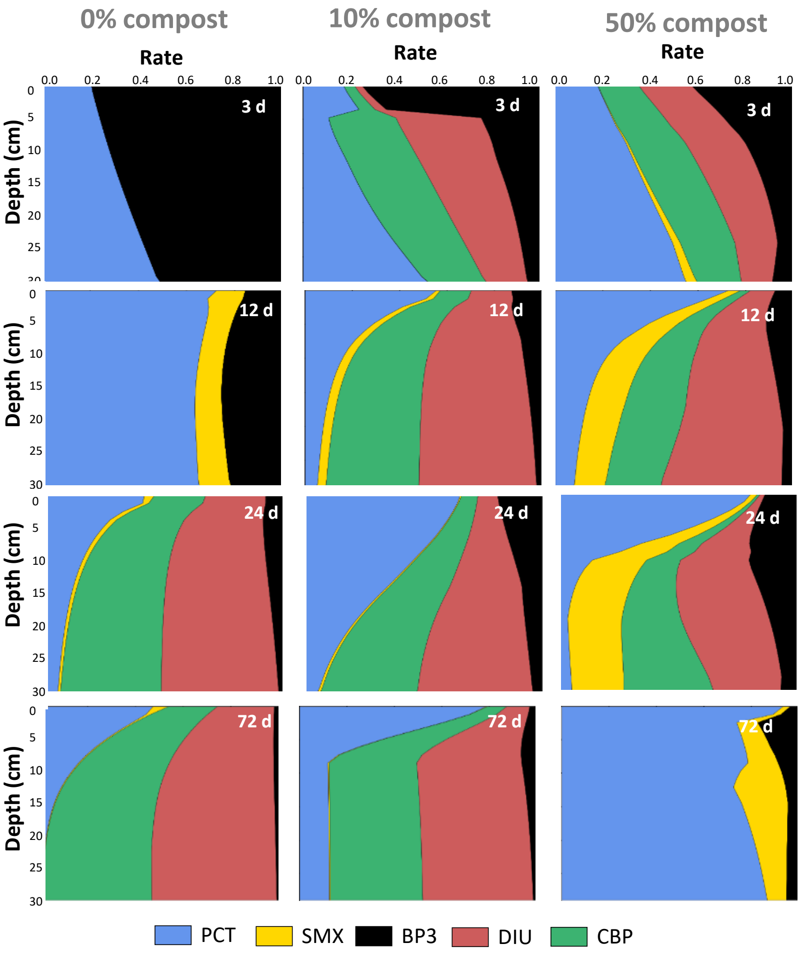

Figure 4-5. *Relative removal rate of each EOC along the column. The relative removal rate was respect the total removal rate for all EOCs.*

It is observed that the largest the percentage of compost in the reactive barrier composition, the highest the overall EOCs removal. Going into more detail in this Figure 4-5, the information shown represents the relative ratio of transformation of EOCs processes (including degradation and sorption for their respective cases). Therefore, the data shown simply represents the comparison between the different EOCs processes, this however does not show any information about the absolute values of the rates. This implies that even though a percentage of a certain reaction is high (relative data), it does not mean that the amount of reaction is high (absolute data).

4.4 Conclusions

In this work a numerical model that couples the Emerging Organic Compounds fate with the main geochemical processes in a Soil Aquifer Treatment environment was developed. Our model was verified in column experiments involving the fate of five EOCs for different proportions of compost mixed with soil. To reproduce the EOCs fate, we focused on both sorption and biodegradation processes, including the dynamics changing alongside time and column depth, and either coupled or uncoupled to the geochemical evolution within the columns.

In the case of sorption, the best model was the sorption/desorption kinetic one. From the EOCs tested, CBP and DIU were the most affected by sorption mechanisms; BP3 was also affected by sorption, but not as much. Finally, paracetamol and sulfamethoxazole were not significantly affected by sorption processes in this case.

For biodegradation, two models were first conceptualized and then tested: first-order degradation and degradation coupled to geochemistry. The former was only significant for BP3, were combined with the kinetic sorption model was enough to provide a good fitting to the experimental data. On the other hand, SMX and PCT could be only reproduced if degradation was coupled to geochemical processes. In the case of SMX to relevant geochemical process was denitrification and in the case of PCT it was oxygen reduction. On the other hand, DIU and CBP were not significantly affected by degradation.

Finally, it can be stated that overall EOCs concentration reduction as compared to the input values was enhanced with increasing compost fraction in an infiltration column experiment. Therefore, permeable reactive barriers placed at the bottom of infiltration ponds are suggested as a new tool for efficient EOC removal in managed aquifer recharge operations.

Chapter 5

Conclusions

In this thesis a general assessment of the Managed Aquifer Recharge facilities and their main risks was done. This served not only to provide a tool to evaluate those risks, but also to determine the importance of the technical and non-technical aspects of a MAR facility, therefore helping future management situations. After this general review, a more in depth analysis was done in the technical aspects of the recharge systems. This was done in order to see if wastewater and reactive barrier could be used in an aquifer recharge system. To see this, a model (conceptual, numerical and computational) was developed for both nutrients and emerging organic contaminants. This was done in order to know the dynamics behind the transformation of the wastewater and the dynamics of nutrients and EOCs. In order to summarise this, down below are presented the main conclusions for each chapter.

In Chapter 2, it was found that the non-technical aspects can be more significant than the technical ones, contributing more than the technical issues to the overall assessment of risk. In summary, the combination of legal, social, and economic factors can provide a really strong contribution to global risk in a MAR facility. Therefore, future risk works based in managed aquifer recharge should aim for non-technical factors as well as technical ones.

From Chapter 3, compost has the potential to release labile organic carbon, enhancing biomass development and biofilm formation, therefore stimulating processes catalysed by the microorganisms. Because of this, the reactive barrier acts by significantly reducing the infiltration capacity of the system; the higher the compost percentage, the faster the growth of microorganisms and the reduced porosity, reducing overall saturated hydraulic conductivity, and enhancing dispersivity as observed in breakthrough curves of tracer tests. However, defining different percentages of compost (to be better adapted to the local characteristics of the MAR system) can be a solution to offset some of this infiltration reduction. Despite these issues, there are also benefits in water treatment resulting in improved water quality. The larger the volume colonised by biofilm, usually means the larger the increase in bacterial activity and geochemical reactions, in particular those catalysed by microorganisms, such as nitrification, denitrification and organic matter oxidation (specially in the cases with higher compost percentage).

Finally, in Chapter 4, the relationship between nutrients and emerging organic contaminants in a Soil Aquifer Treatment environment was studied and developed using a model. This was focused on both sorption and biodegradation processes, including the changes of these dynamics alongside time and column depth, and either coupled or uncoupled to the geochemical evolution within the columns (depending on the EOC type). Overall EOCs concentration reduction as compared to the input values was enhanced with increasing compost fraction in an infiltration column experiment.

Final thoughts and future research

Due to this thesis dual objective of increasing the knowledge in both MAR management and reactive barrier usage, the general implications that this work have, are diverse.

On one hand, this work has proven that managed aquifer recharge is susceptible to risks outside the classic technical considerations that are most known. Therefore, this thesis shows that in the future facilities that intend to recharge water into aquifers have to take into consideration multiple aspects that transcend what can be considered in a technical manual. Social acceptance, politics, legal constraints, are some of the examples that are usually overshadowed by conventional aspects, even though in some cases these can be far more damaging for a MAR success than the later ones. These results therefore, can change the way that MAR facilities are designed and evaluated in the near future, if they want to have some degree of real success.

On the other hand, this thesis has also proven that wastewater (which contains high amounts of nutrients and EOCs) can be treated using reactive barriers. This statement confirms a tendency in the scientific community about the possible usage of wastewater as recharge water and the usefulness of reactive barriers. In this work, the usage of reactive barriers (with compost) clearly reduced the contaminants concentration in the outlet. However, the question still remains on which type of reactive barriers to use, how to design them and if their reduction is enough to comply with drinking water standards when the water is collected from the aquifer. This thesis does not aim to respond specifically these questions, however what this thesis does is to set a path for future investigations about reactive barriers and managed aquifer recharge, which could lead to more resources (wastewater) being used for recharge systems. This is especially important for the case of EOCs since they are ubiquitous in the water around the world, and new ways to eliminate them are being searched, specially using natural conditions. The fact that the EOCs dynamics and pathways are usually unknown or too complicated, makes the possibilities of this thesis even bigger. Since the definition of conceptual and numerical models for these EOCs dynamics can help find someday ways to eliminate these EOCs from the water systems around the world, significantly increasing the health of the world population when consuming water.

Appendix for Chapter 2

Summary of the facilities and details

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
WATER FACTORY 21, COASTAL BARRIER SEAWATER INTRUSION	DEEP WELLS	ORANGE COUNTY (USA), 1977	4 YEARS	PROBLEMS - MICROBIOLOGICAL, METEOROLOGYCAL (EXCESS OF RAIN DIMINISHES THE AMOUNT OF WATER INJECTED), DESIGN AND CONSTRUCTION COSTS (16 MILLION $), OPERATION COSTS (2 MILION $ A YEAR), CLOGGING, WASTEWATER TREATMENT PLANT FAILURE, SALINITY/SODICITY (WATER INTRUSION), GEOLOGIGAL HETEROGENEICITY (DIFFERENT GEOLOGICAL MATERIAL LAYERS PRESENT), NOT SHALLOW AQUIFER OR HIGH THICKNESS (THE WELLS ARE REALLY DEEP 850 - 1150 FEET)	(ASANO, 1985)
OPERATIONS AT THE CEDAR CREEK WASTEWATER RECLAMATION-RECHARGE FACILITIES	DEEP WELLS	NASSAU COUNTY, NEW YORK, (1979)	3 YEARS (4 INCLUDING CONSTRUCTION)	PROBLEMS - DESIGN AND CONSTRUCTION COSTS (22 MILLION DOLLARS), CIVIL WORK FAILURES “VERY LIKELY” (OTHERS - UNDERDRAIN SYSTEMS, DUAL-MEDIA FILTER SYSTEM, CARBON ADSORVERS, MECHANICAL/ELECTRONIC PROBLEMS), OPERATIONAL COSTS (8 MILLION DOLARS), WASTEWATER TREATMENT PLANT FAILURE	(ASANO, 1985)
PROPOSED GROUNDWATER RECHARGE	DEEP WELLS	EL PASO, TEXAS (1985)	UNKNOWN	PROBLEMS - CONSTRUCTION COST (OVER 22 MILLION DOLLARS), NUTRIENTS (NITROGEN AND PHOSPORUS), SALINITY AND SODICITY, WASTEWATER TREATMENT PLANT FAILURE, SUSPENDED SOLIDS, GAS GENERATION (PHYSICIAL MOTIVES AND BAD DESIGN)	(ASANO, 1985)
GROUNDWATER RECHARGE FOR WASTEWATER REUSE IN THE DAN REGION PROJECT	INFILTRATION BASINS / SPREADING BASINS	ISRAEL, (1977)	5 YEARS	PROBLEMS - LAND USE (30 HA), LOW INFILTRATION RATES, CLIMATIC CONDITIONS, AND THE FREQUENCY OF BASIN CLEANING, SALINITY, NUTRIENTS (N AND P HIGHER IN WINTER), SUSPENDED SOLIDS (HIGHER IN WINTER), ORGANANIC CHEMICAL COMPOUNDS, WASTEWATER TREATMENT PLANT FAILURE, GEOLOGIGAL HETEROGENEICITY (DIFFERENT GEOLOGICAL MATERIAL LAYERS PRESENT), TRACE ELEMENTS (MAINLY METALS, BUT ALSO MANGANESE AND POTASSIUM)	(ASANO, 1985)
SOIL DEPOSITION OF TRACE METALS DURING GROUNDWATER RECHARGE USING SURFACE SPREADING	SURFACE SPREADING	CALIFORNIA (USA)	20 YEARS	PROBLEMS - SALINITY AND SODICITY, SUSPENDED SOLIDS, TRACE ELEMENTS (OTHERS BUT MAINLY METALS), CLOGGING (NOT SPECIFIED), ORGANIC CHEMICALS, WATER SCARCITY (CLIMATE)	(ASANO, 1985)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
ISSUES IN ARTIFICIAL RECHARGE	GENERAL	NA	NA	PROBLEMS - LONG TIME, CHEMICAL QUALITY ISSUES NOT A PROBLEM – HAS GOOD SOCIAL ACCEPTANCE	(BOUWER, 1996)
ISSUES IN ARTIFICIAL RECHARGE	INFILTRATION BASINS	NA	NA	PROBLEMS – LAND USE, WATER QUALITY, CLOGGING, suspended solids content, ORGANIC COMPOUNDS, FLOODING, DRYING, NUTRIENTS (NITROGEN MAINY), BAD SOIL INFILTRATION RATE AND COMPACTION	(BOUWER, 1996)
ISSUES IN ARTIFICIAL RECHARGE	DEEP WELLS	NA	NA	PROBLEMS – MAIN PROBLEM IS CLOGGING, SUSPENDED SOLIDS, MICROORGANISMS, NUTRIENTS (N AND P), DESIGN AND CONSTRUCTION COSTS, CORROSION NOT A PROBLEM – CAN BE DONE IN ZONES WHERE PERMEABLE SOILS ARE NOT AVAILABLE	(BOUWER, 1996)
ISSUES IN ARTIFICIAL RECHARGE	VADOSE ZONE WELLS	NA	NA	PROBLEMS – CLOGGING, SUSPENDED SOLIDS, NUTRIENTS, MICROORGANISMS, ORGANIC COMPOUNDS, LOW INFILTRATION RATES NOT A PROBLEM - CHEAPER	(BOUWER, 1996)
ISSUES IN ARTIFICIAL RECHARGE	SEEPAGE TRENCHES	NA	NA	PROBLEMS – SUSPENDED SOLIDS ARE USUALLY A PROBLEM, NOT A PROBLEM - CHEAPER	(BOUWER, 1996)
ARTIFICIAL RECHARGE OF GROUNDWATER: HYDROGEOLOGY AND ENGINEERING	SURFACE INFILTRATION	NA	NA	PROBLEMS – FLOOD DANGER, CIVIL WORK FAILURES (OTHERS AND SLOPE), LAND USE, WATER QUALITY PROBLEMS, SUSPENDED SOLIDS, CLOGGING (BIOLOGICAL, MINERAL AND SEDIMENTAL), GAS FORMATION (BACTERIAL MAINLY BUT THER TYPES ARE ALSO QUITE TYPICAL), NUTRIENTS, ORGANIC COMPOUNDS, RISK OF LOW INFILTRATION RATE, CONTAMINANT SPREADING	(BOUWER, 2002)
ARTIFICIAL RECHARGE OF GROUNDWATER: HYDROGEOLOGY AND ENGINEERING	VADOSE-ZONE INFILTRATION	NA	NA	PROBLEMS – VERY LIKELY RISK OF INSUFICIENT SOIL INFILTRATION RATE, LAND USE, PIPELINE FAILURE, GAS ACCUMULATION (PHYSICAL), PIPE FAILURE, MAINLY DISADVANTAGE IS CLOGGING (BIOLOGICAL AND SEDIMENTAL), SUSPENDED SOLIDS CONTENT, NOT PROBLEM - CHEAPER	(BOUWER, 2002)
ARTIFICIAL RECHARGE OF GROUNDWATER: HYDROGEOLOGY AND ENGINEERING	WELLS	NA	NA	PROBLEMS – COMPACTION, CLOGGING (MOST TYPICALL PROBLEM, DUE TO SEDIMENTS BUT ALSO OTHER REASONS LIKE BACTERIA OR PRECIPITATION), WATER QUALITY, NUTRIENTS, SALINITY, MICROBIOLOGICAL PROBLEMS, NOT PROBLEM – LAND USE, INFILTRATION RATE	(BOUWER, 2002)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
ARTIFICIAL RECHARGE OF GROUNDWATER: HYDROGEOLOGY AND ENGINEERING	GENERAL ARTIFICIAL RECHARGE SYSTEMS	NA	NA	THE MAIN ISSUE IN ARTIFICIAL RECHARGE IS CLOGGING, AVAILABILITY OF WATER RESOURCES IS ALSO A PROBLEM WITH CLIMATIC ISSUES, SOCIAL COSTS, ENVIRONMENTAL COSTS, LAND USE, CIVIL WORK PROBLEMS (IN GENERAL, CORROSION),	(BOUWER, 2002)
ARTIFICIAL RECHARGE OF AQUIFERS	INFILTRATION BASINS AND CANALS	SAN JUAN RIVER BASIN (ARGENTINA)	NA	PROBLEMS – SEDIMENTATION OF FINE MATERIAL (CLOGGING, TURBIDITY, ETC.), FLOODING RISK (THE FLOODS MAY INTERFERE WITH THE INFILTRATION BASIN), DEPOSITION PROBLEMS, CORROSION, EROSION PROBLEMS, CIVIL DAMAGE (OTHERS), VANDALISM PROBLEMS (MAY BE CONSIDERED AS TERRORISM?), DROUGH PROBLEMS, DURING DROUGH STAGES THERE MAY BE A SHORTAGE OF WATER RESOURCES TO FEED THE RECHARGE, LACK OF INCENTIVES (LEGISLATIVE AND ECONOMICAL) FOR MAINTENANCE, LACK OF ENOUGH WATER TO HAVE AN ECONOMICALLY FEASIBLE RECHARGE, PROBLEM WITH NUTRIENTS (N AND P), RISK OF AQUIFER DISSOLUTION, LEGISLATION PROBLEMS (OTHERS, RELATED TO ENVIRONMENTAL IMPACT OF THE LANDSCAPE), HIGH THICKNESS AND NOT SHALLOW AQUIFER NOT PROBLEM – LOW MAINTENANCE COSTS, LOW DESIGN AND CONSTRUCTION COSTS, USUALLY THE TECHNICAL KNOWLEDGE OF THIS TECHNOLOGY IS HIGH,	(NATIONS AND PROGRAMME, 2011)
INVESTIGATING THE CAUSES OF WATER-WELL FAILURE IN THE GAOTLHOBOGWE WELLFIELD	DEEP WELLS	SOUTHEAST BOTSWANA	8 YEARS	PROBLEMS – WATER QUALITY (METALS, SALINITY/SODICITY, NITROGEN, PHOSPHORUS, ETC.), LOW QUANTITY OF WATER RESOURCES, PROBLEMS WITH INFILTRATION RATE, RISK OF LOW WATER STORAGE, CHEMICAL CLOGGING (PRECIPITATION OF CALCITE DUE TO WATER MIXTURE), PROBLEMS WITH THE DESIGN AND OPERATION OF THE WELLS	(CHAOKA ET AL. 2006)
AQUIFER STORAGE AND RECOVERY	DEEP WELLS	CALIFORNIA (USA)	NA	PROBLEMS – WATER QUALITY (SUSPENDED SOLIDS, SALINITY/SODICITY, SOCIAL UNACCEPTANCE (TASTE IN WATER), LEGAL CONSTRAINTS (NOT ACCOMPLISHING DRINKING STANDARDS) , MOVILISATION OF TRACE ELEMENTS, PRECIPITATION (CHEMICAL CLOGGING), CLOGGING (SEDIMENT AND MICROBIOLOGICAL), IN GENERAL CLOGGING IS THE MOST TYPICALL PROBLEM, INFILTRATION PROBLEMS, CIVIL WORK FAILURES (LIQUEFACTION), NATURAL HAZARDS (EARTHQUAKE), TERRORISTS ATTACKS	(“USGS CALIFORNIA WATER SCIENCE CENTER” 2015)
TROUBLESHOOTING WATER WELL PROBLEMS	DEEP WELLS	NA	NA	PROBLEMS – IMPROPER WELL DESIGN AND OPERATION, INCOMPLETE WELL DEVELOPMENT, BOREHOLE STABILITY PROBLEMS, INCRUSTATION BUILD-UP (CLOGGING DUE TO CHEMICAL ISSUES WITH WATER), BIOFOULING CLOGGING DUE TO MICROBIOLOGICAL ISSUES), CORROSION, AQUIFER PROBLEMS, OVER PUMPING (SEDIMENT PARTICLE MOVING, SEDIMENTATION, EROSION,	(GOVERNMENT OF ALBERTA, N.D.)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
				COMPACTION), NUTRIENT PROBLEMS (N AND P), GAS GENERATION (BACTERIAL AND INAPROPIATE DESIGN), LACK OF RECHARGE, CLIMATE ISSUES, DROUGH PERIODS, CIVIL WORK FAILURE (PIPES BREAKAGE AND OTHERS), LOW INFILTRATION, WATER QUALITY ISSUES (METALS, NUTRIENTS AND ORGANIC COMPOUNDS)	
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	DEEP WELLS	AUSTRALIA	NA	NOT PROBLEM - low capital costs (managed recharge is often the most economic form of new water supply), no evaporation loss, not algae or mosquitoes (unlike dams), no loss of prime valley floor land (erosion), ability to use saline aquifers that could not be directly used for supplies, potential location close to new water sources, and where demand for water is high, aquifers providing treatment as well as storage, low greenhouse gas emissions compared to remote pumped storages, able to be built to the size required for incremental growth in water demand, provision of emergency and strategic reserves, improved reliability of existing supplies, improved environmental flows in water supply catchments for urban areas	(EPHC/NH MRC/NRM MC, 2008)
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	GENERAL ARTIFICIAL RECHARGE SYSTEMS	AUSTRALIA	NA	DEEP WELLS – PREFERABLY USED WHEN THERE ARE CONFINED AQUIFERS OR SUPERFICIAL CLAY LEVELS, CAN WORK WITH LOW INFILTRATION RATE, LOW LAND USE/COST, EASE OF TRAFFIC ACCESS, COMPATIBILITY OF LAND USE, SUSPENDED SOLIDS AND NUTRIENTS USUALLY LEAD TO CLOGGING PROBLEMS INFILTRATION PONDS – PREFERED WHEN LAND COST/USE IS CHEAP GENERAL INFO - USUALLY ARTIFICIAL RECHARGE HAS GOOD SOCIAL ACCEPTANCE AND SUFICIENT RESIDENCE TIMES FOR WATER, THIS RESIDENCE TIME IMPLIES LESS TREATMENT FOR THE WATER AND LESS RISK FOR PATHOGENS	(EPHC/NH MRC/NRM MC, 2008)
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	GENERAL ARTIFICIAL RECHARGE SYSTEMS	AUSTRALIA	NA	GENERAL INFO – ARTIFIAL RECHARGE DEPENDS MAINLY ON THE AVAILABILITY OF APROPIATE AQUIFERS, SUFFICIENT VOLUMES OF WATER ARE NEEDED TO JUSTIFY THE COSTS OF THE PROJECT, PLACES WITH SURFACE AQUIFERS CAUSE STRUCTURAL PROBLEMS, SALINISATION AND WATERLOGGING.	(EPHC/NH MRC/NRM MC, 2008)
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	DEEP WELLS	Northern Adelaide Plains (AUSTRALIA)	NA	PROBLEMS – SALINITY, AQUIFER HETEROGENITY, WATER MIXTURE, NEED TO HAVE A WATER TREATMENT PLANT (DESIGN AND CONSTRUCTION COSTS, OPERATIONAL COSTS) NOT PROBLEMS – MEET DRINKIG WATER REQUERIMENTS	(EPHC/NH MRC/NRM MC, 2008)
AUSTRALIAN GUIDELINES FOR WATER RECYCLING:	GENERAL ARTIFICIAL	AUSTRALIA	NA	PROBLEMS – PATHOGENS, INORGANIC CHEMICALS, SALINITY AND SODICITY, NUTRIENTS, ORGANIC CHEMICALS, TURBIDITY AND PARTICULATES, RADIONUCLIDES, PRESSURE/FLOW RATES/VOLUMES/LEVELS OF WATER,	(EPHC/NH MRC/NRM MC, 2008)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
MANAGED AQUIFER RECHARGE	RECHARGE SYSTEMS			CONTAMINANT MIGRATION IN FRACTURED AND CARSTIC AQUIFERS, AQUIFER DISSOLUTION, WELL STABILITY, IMPACT ON GROUNDWATER ECOSYSTEMS, GREENHOUSE GASES GENERATION (MICROBIOLOGICAL ISSUES)	
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	GENERAL ARTIFICIAL RECHARGE SYSTEMS	AUSTRALIA	NA	PROBLEMS – INCREASE IRON, MANGANESE, ARSENIC, TRACE SPECIES AND HYDROGEN SULFIDE, SODICITY/SALINITY PROBEMS, NTRIENT ISSUES,	(EPHC/NHMRC/NRMMC, 2008)
MOBILIZATION OF ARSENIC AND OTHER TRACE ELEMENTS DURING AQUIFER STORAGE AND RECOVERY, SOUTHWEST FLORIDA	DEEP WELLS	FLORIDA (USA)	NA	PROBLEMS – ARSENIC, MANGANESE, URANIUM (RADIONUCLIDES), ORGANIC COMPOUNDS, WATER RESIDENCE TIME, AQUIFER AND INPUT WATER CHEMISTRY PROBLEMS (DO, PH, ETC.), AQUIFER MATRIX CHEMISTRY/MINERALOGY, SITE SPECIFIC HIDROGEOLOGY/HIDROCHEMISTRY, WATER MIXTURE	(AIKEN AND KUNIANSKY, 2002)
AUSTRALIAN GUIDELINES FOR WATER RECYCLING: MANAGED AQUIFER RECHARGE	GENERAL ARTIFICIAL RECHARGE SYSTEMS	AUSTRALIA	NA	GENERAL INFO – ABOUT CLOGGING THERE'S INFO FROM 14 INJECTION PLACES THAT SUFERED CLOGGING PROBLEMS. FROM THE 14 SITES, 8 WERE BIOLOGICAL CLOGGING, 9 PHYSICAL CLOGGING AND 1 WAS CHEMICAL CLOGGING (IN SOME CASES THERE WAS A MIXTURE BETWEEN TWO TYUPES OF CLOGGING)	(EPHC/NHMRC/NRMMC, 2008)
SOURCES OF HIGH-CHLORIDE WATER TO WELLS, EASTERN SAN JOAQUIN GROUND-WATER SUBBASIN, CALIFORNIA	DEEP WELLS	CALIFORNIA (USA)	NA	PROBLEMS – SALINITY/SODICITY, CHLORIDE, METALS (ARSENIC, MANGANESE, ETC.), NUTRIENTS (NITRATES), WATER MIXTURE, WATER EVAPORATION	(AIKEN AND KUNIANSKY, 2002)
AQUIFER STORAGE AND RECOVERY FOR THE CITY OF ROSEVILLE: A CONJUNCTIVE USE PILOT PROJECT	DEEP WELLS	CALIFORNIA (USA)	NA	PROBLEMS – ORGANIC CHEMICALS (THM, DBP), DESIGN AND CONSTRUCTION COSTS (PROJECTS OF WATER RECHARGE WITH A COST OF MORE THAN 215 MILLION $), LEGISLATION ISSUES (NATIONAL AND LACK OF COORDINATION), TRACE ELEMENTS (METALS), MECHANICAL COMPLICATIONS (CIVIL WORK FAILURE – OTHERS), SODICITY/SALINITY, MICROBIOLOGICAL ISSUES (LEGISLATION ABOUT BACTERIA INPUT IN THE RECHARGE WATER), WATER MIXTURE, QUALITY ISSUES (IN GENERAL, IT DOESNN'T SPECIFY), AQUIFER THICKNESS AND AQUIFER DEPTH, WATER SCARCITY (DROUGHT) NOT PROBLEM – NATURAL ATENUATION,	(AIKEN AND KUNIANSKY, 2002)
SAN GORGONIO PASS ARTIFICIAL RECHARGE INVESTIGATION	DEEP WELLS	CALIFORNIA (USA) 1997	6 YEARS	PROBLEMS – LOW INFILTRATION RATE, HIGH THICKNESS/NOT SHALLOW AQUIFER, NATURAL HAZARDS (EARTHQUAKES), NUTRIENTS (NITROGEN DUE TO WASTEWATER LEAKAGE)	(FLINT AND ELLETT,

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
					2005)
The Effects of Artificial Recharge on Groundwater Levels and Water Quality in the West Hydrogeologic Unit of the Warren Subbasin, San Bernardino County, California	DEEP WELLS	CALIFORNIA (USA) 2004	5 YEARS	PROBLEMS – LOW INFILTRATION RATE, RESIDENCE TIME, LAND USE, RISK OF NUTRIENT MOBILISATION, WATER LEVEL DECLINE, NUTRIENTS (NITROGEN), ORGANIC CHEMICALS, WATER SCARCITY (DROUGHTS AND RAINFALL PERIODICITY), EVAPORATION, SEDIMENTATION, EROSION, REGIONAL HYDROGEOLOGY WATER IMBALANCE, NO PROBLEM – NATURAL ATENUATION	(U.S. GEOLOGICAL SURVEY, 2013)
HYDRO-LOGIC EFFECTS OF ARTIFICIAL-RE CHARGE EXPERIMENTS WITH RECLAIMED WATER AT EAST MEADOW, LONG ISLAND, NEW YORK	INFILTRATION BASINS	NEW YORK (USA) 1982	2 YEARS	PROBLEMS – LAND USE, GAS GENERATION (PHYSICAL MOTIVES AND BAD DESIGN), LOW INFILTRATION RATES, SUSPENDED SOLIDS, CLOGGING (PHYSICAL AND BIOLOGICAL), MECHANICAL FAILURES, PONDING (UNWANTED WATER ACCUMULATION), MICROBIOLOGICAL ISSUES, DEVELOPMENT OF INSECT POPULATIONS, WATER QUALITY ISSUES (MAINLY MICROBIOLOGICAL, NUTRIENTS AND MAYBE OTHER WATER CHEMICAL COMPOUNDS), SALINITY/SODICITY, METALS, SLOPE FACTOR ISSUES (MOUNDING), WATER MIXING, ORGANIC CHEMICALS (ORGANIC MATTER), INORGANIC CHEMICALS, INEFICIENT NATURAL ATTENUATION (DUE TO SHORT RESIDENCE TIME, NOT ENOUGH REACTION OF THE GEOLOGICAL MATERIALS OR DUE TO THE HIGH TREATMENT OF THE INJECTED WATER)	(SCHNEIDER ET AL., 1987)
HYDRO-LOGIC EFFECTS OF ARTIFICIAL-RE CHARGE EXPERIMENTS WITH RECLAIMED WATER AT EAST MEADOW, LONG ISLAND, NEW YORK	DEEP WELLS	NEW YORK (USA) 1982	2 YEARS	PROBLEMS – SUSPENDED SOLIDS (TURBIDITY), CLOGGING (BACTERIAL, PHYSICAL AND CHEMICAL), METALS (IRON), SALINITY/SODICITY, LESS EFFICIENT TO MOVE LARGE QUANTITIES OF WATER THAN THE INFILTRATION BASINS, CLOGGING IS MORE A PROBLEM IN WELLS THAN IN BASINS, SLOPE FACTOR ISSUES (MOUNDING), INEFICIENT NATURAL ATTENUATION (DUE TO SHORT RESIDENCE TIME, NOT ENOUGH REACTION OF THE GEOLOGICAL MATERIALS OR DUE TO THE HIGH TREATMENT OF THE INJECTED WATER)	(SCHNEIDER ET AL., 1987)
THE ATLANTIS WATER RESOURCE MANAGEMENT SCHEME: 30 YEARS OF ARTIFICIAL GROUNDWATER RECHARGE	INFILTRATION BASINS	SOUTH AFRICA (1980)	30 YEARS	PROBLEMS – CLOGGING (PHYSICAL, BIOLOGICAL AND CHEMICAL), METAL CONTENT (IRON), NOT ENOUGH WATER QUANTITY, ORGANIC MATTER, LOW INFILTRATION RATE, HIGH MAINTENANCE COSTS, GROUNDWATER POLLUTION, APPEREANCE OF ALIEN VEGETAL SPECIES, MICROBIOLOGICAL ISSUES, LAND OWNERSHIP PROBLEMS (IS NOT UNDER THE SAME LEGAL MANAGEMENT THAN THE REST OF THE RECHARGE FACILITY)	(SCHNEIDER ET AL., 1987)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
				NOT PROBLEM – LOW SALINITY	
THE ATLANTIS WATER RESOURCE MANAGEMENT SCHEME: 30 YEARS OF ARTIFICIAL GROUNDWATER RECHARGE	DEEP WELLS	SOUTH AFRICA (1980)	30 YEARS	PROBLEMS – CLOGGING (PHYSICAL, BIOLOGICAL AND CHEMICAL), METAL CONTENT (IRON), NOT ENOUGH WATER QUANTITY, ORGANIC MATTER, LOW INFILTRATION RATE, HIGH MAINTENANCE COSTS, DROUGH CONDITIONS, OVERPUMPING WATER (IMBALANCE BETWEEN THE WATER INJECTION AND PUMPING), GAS GENERATION (DUE TO PHYSICAL PROPERTIES AND INEFICIENT DESIGN), GROUNDWATER POLLUTION, SALINITY/SODICITY PROBLEMS, MICROBIOLOGICAL ISSUES, LAND OWNERSHIP PROBLEMS (IS NOT UNDER THE SAME LEGAL MANAGEMENT THAN THE REST OF THE RECHARGE FACILITY)	(TREDOUX AND CAIN, 2010)
Recycling Polokwane's treated wastewater	INFILTRATION PONDS	SOUTH AFRICA	NA	PROBLEMS – HIGH THICKNESS AND NOT SHALLOW AQUIFER, EVAPORATION OF WATER (WATER LOSS), NUTRIENT PROBLEMS (MAINLY NITROGEN)	(TREDOUX AND CAIN, 2010)
Small-scale borehole injection in Namaqualand	DEEP WELLS	SOUTH AFRICA (1999)	3 YEARS	PROBLEMS – LOW INFILTRATION RATE, SALINITY/SODICITY, CLOGGING (PHYSICAL)	(TREDOUX AND CAIN, 2010)
Calvinia: Trial borehole injection tests and water quality assessment in fractured mudstones	DEEP WELLS	SOUTH AFRICA	NA	PROBLEMS – LOW WATER STORAGE TIME (RESIDENCE TIME), HIGH WATER PH (WATER QUALITY PROBLEMS), HIGH FLUORIDE CONCENTRATIONS, HIGH ARSENIC CONCENTRATIONS, HIGH SULFATE CONCENTRATIONS, OXYGEN PENETRATION (REDOX PROCESSES), ENTRANCVE OF GAS FROM THE ATHMOSPHERE (DUE TO PHYSICAL MOTIVES AND BAD DESIGN).	(TREDOUX AND CAIN, 2010)
Prince Albert: Borehole injection feasibility study in fractured sandstones	DEEP WELLS	SOUTH AFRICA	NA	PROBLEMS – MICROBIOLOGICAL ISSUES, HIGH FLUORIDE CONCENTRATIONS, NUTRIENTS (MAINLY NITROGEN), CLOGGING (BIOLOGICAL AND CHEMICAL), IRON CONTENT, LOW QUANTITY WATER AVAILABLE (CLIMATE), LOW PERMEABILITY RATES,	(TREDOUX AND CAIN, 2010)
BITOU MUNICIPALITY GROUNDWATER MANAGEMENT AND ARTIFICIAL RECHARGE FEASIBILITY STUDY	DEEP WELLS	SOUTH AFRICA	2 YEARS	PROBLEMS – WATER SCARCITY (WWTP FAILURE OR TOO LOW SUPPLY LIMIT), SALINITY/SODICITY, IRON CONTENT, AND ORGANIC MATTER, WATER MIXTURE (CHEMICAL REACTIONS), CLOGGING (CHEMICAL AND BIOLOGICAL), WATER IMBALANCE BETWEEN INJECTION AND WATER INPUT (NOT ENOUGH WATER FROM REGIONAL HYDROGEOLOGY), LEGAL CONSTRAINTS (OTHERS – ENVIRONMENTAL)	(TREDOUX AND CAIN, 2010)
Artificial recharge of the Windhoek	DEEP WELLS	NAMIBIA	NA	PROBLEMS – SODICITY/SALINITY, HIGH SULFATE CONCENTRATIONS, HIGH IRON CONCENTRATIONS, PRESENCE OF A DISPOSAL SITE WHICH IS THE SOURCE OF ORGANIC POLLUTANTS INFILTRATION	(TREDOUX AND CAIN,

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aquifer, Namibia: Water quality considerations					2010)
In the Face of Changing Climate: Groundwater Development through Artificial Recharge in Hard Rock Terrain of Kumaun Lesser Himalaya	INFILTRATION BASINS	KUMAUN LESSER HIMALAYA	NA	PROBLEMS - LOW CONDUCTIVITY OF THE WATER, FLOODS, DROUGHS, HIGH THICKNESS AND NOT SHALLOW AQUIFER, CIVIL WORK FAILURES (OTHERS – HIGH STEEP SLOPES), WATER SCARCITY (CLIMATE, DUE TO THE FACT THAT RAINFALL IS THE ONLY SOURCE OF WATER FOR THE RECHARGE)	(TRIPATHI, 2016)
ASSESSING RISK OF CLOGGING IN COMMUNITY SCALE MANAGED AQUIFER RECHARGE SITES FOR DRINKING WATER IN THE COASTAL PLAIN OF SOUTH-WEST BANGLADESH	INFILTRATION PONDS AND INFILTRATION WELLS	BANGLADESH	NA	PROBLEMS – LOW INFILTRATION RATE, CIVIL WORK FAILURE (OTHERS – MAINLY RELATED TO THE MINAROLOGY OF THE TERRAIN), HIGH TURBIDITY (SUSPENDED SOLIDS), HIGH SULFATES, HIGH NUTRIENTS (PHOSPHORUS MAINLY), MICROBIOLOGICAL ISSUES, CLOGGING (PHYSICAL TYPE MAINLY), ORGANIC MATTER CONTENT, FILTER EFFICIENCY ISSUES, RESIDENCE TIME, NUTRIENTS (NITROGEN), CLOGGING (BIOLOGICAL), AQUIFER HETEROGENEICITY (DIFFERENT GEOLOGICAL MATERIAL LAYERS ON THE AQUIFER), WATER MIXTURE, SALINITY/SODICITY ISSUES	(SULTANA AND AHMED, 2016)
Investigation of recharge dynamics and flow paths in a fractured crystalline aquifer in semi-arid India using borehole logs: implications for managed aquifer recharge	PERCOLATION TANK	INDIA (HYDERABAD)	NA	PROBLEMS – GEOLOGIGAL HETEROGENEICITY (DIFFERENT GEOLOGICAL MATERIAL LAYERS PRESENT), LOW INFILTRATION RATE, FLOODS, DROUGHS, NOT SHALLOW AQUIFER/GEOLOGY THICKNESS, NOT ENOUGH WATER (CLIMATE), WATER MIXING	(ALAZARD ET AL., 2016)
Impact of a Storm-Water Infiltration Basin on the Recharge Dynamics in a Highly Permeable Aquifer	INFILTRATION BASIN	ITALY	NA	PROBLEMS – LEGAL CONSTRAINTS, CLOGGING (PHYSICAL AND BIOLOGICAL), SUSPENDED SOLIDS, NOT PROBLEM – HIGH RECHARGE RATE (PRECIPITATION), HIGH AMOUNT OF WATER AVAILABLE, HIGH INFILTRATION RATE	(MASETTI ET AL., 2016)
An innovative artificial recharge system to enhance groundwater storage in basaltic terrain: example from Maharashtra, India	RECHARGE SHAFTS AND SUBSURFACE DAMS	INDIA	NA	PROBLEM – LOW INFILTRATION RATE, EXCESIVE WITHDRAWAL, WATER IMBALANCE (INPUT/OUTPUT OF WATER), WATER SCARCITY (CLIMATE), DROUGHS, EROSION ISSUES, SUSPENDED SOLIDS	(BHUSARI ET AL., 2016)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
Integrated frameworks for assessing and managing health risks in the context of managed aquifer recharge with river water	SURFACE WATER FROM A RIVER (INFILTRATION BASINS)	FINLAND	NA	PROBLEMS – MICROBIOLOGICAL ISSUES, NUTRIENTS, CONTAMINANTS (ORGANIC AND INORGANIC), LACK OF COORDINATION (POLITICAL CONCERNS), ECONOMIC COSTS (DESIGN/CONSTRUCTION AND OPERATION), ORGANIC MATTER, PERSISTENT ORGANIC POLUTANTS, LACK OF KNOWLEDGE, COST-BENEFIT IMBALACE RELATED TO OTHER WATER RESOURCES OPTIONS (WHICH WOULD BE BETTER OR CHEAPER),	(ASSMUTH ET AL., 2016)
The effects of artificial recharge of groundwater on controlling land subsidence and its influence on groundwater quality and aquifer energy storage in Shanghai, China	DEEP WELLS	CHINA	NA	PROBLEMS – SURFACE COVER OF HARD AND LOW INFILTRATION RATE GEOLOGICAL MATERIALS, COMPACTION, SUBSIDENCE ISSUES, GEOLOGICAL LAYERS OVERLAPPING (NOT A CONTINOUS AQUIFER BUT THE DISPOSITION OF DIFFERENT GEOLOGICAL MATERIAL LAYERS), AQUIFER TOO DEEP, CONTAMINANT MIGRATION, SULFATES INCREASE, ORGANIC CHEMICALS INCREASE (ORGANIC CONTAMINANTS POPS), NUTRIENT ISSUES (MAINLY NITROGEN), ORGANIC MATTER, CLOGGING (CHEMICAL AND BIOLOGICAL)	(SHI ET AL., 2016)
Impact of managed aquifer recharge on the chemical and isotopic composition of a karst aquifer, Wala reservoir, Jordan	DEEP WELLS	JORDAN, 40 KM NEAR AMMAN	NA	PROBLEMS – LIMITED KNOWLEDGE ABOUT HYDRAULIC AND GEOLOGIC CHARACTERISTICS OF THE ZONE, WATER SCARCITY (CLIMATE), KARSTIC AQUIFER ISSUES (DISSOLUTION), HYDROLOGICAL IMBALANCE, SALINITY ISSUES (BUT NOT DUE TO SODICITY), SULFATE ISSUES, NUTRIENTS, CHLORIDE, CLOGGING (PHYSICAL), SUSPENDED SOLIDS, LOW INFILTRATION RATE	(XANKE ET AL., 2015)
Natural attenuation of chlorobenzene in a deep confined aquifer during artificial recharge process	NA	SOUTH-WEST CHINA	NA	PROBLEMS – ORGANIC CHEMICALS (POPS), SUSPENDED SOLIDS, CHLORIDE, LAND USE PROBLEMS (USES OF LAND FOR AGRICULTURE, INDUSTRY AND RESIDENTIAL HAVE DETERIORATED WATER QUALITY), WATER USES (INDUSTRY, URBAN AND AGRICULTURE),	(HE ET AL., 2016)
Artificial recharge of the phreatic aquifer in the upper Friuli plain, Italy, by a large infiltration basin	INFILTRATION BASIN	ITALY	NA	PROBLEMS – LOW PERMEABILITY, NUTRIENT ISSUES (NITROGEN MAINLY), SULFATES, OVERLAPPING OF DIFFEREND GEOLOGICAL LAYERS (WITH CLAY), GEOLOGICAL/HYDRAULIC INFORMATION, HYDRAULIC IMBALANCE (INPUT OUTPUT OF THE RECHARGE IS NEGATIVE) NOT PROBLEM – LOW SALINITY	(TEATINI ET AL., 2015)
Water Quality of the Little Arkansas River and Equus Beds Aquifer Before and Concurrent with Large-Scale	DEEP WELLS	USA (KANSAS) 1995	6 YEARS	PROBLEMS – CHLORIDE, NUTRIENT ISSUES (MAINLY NITROGEN), TRACE ELEMENTS PROBLEMS (METALS MAINLY), NOT ENOUGH WATER RECHARGED (WATER INPUT IS TOO LOW COMPARED TO THE EXTRACTION AND THE TOTAL VOLUME OF THE AQUIFER), ORGANIC CHEMICALS (POPS), MICROBIOLOFGICAL ISSUES (FECAL BACTERIA)	(GALLEGOS AND VARELA, 2015)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
Artificial Recharge, South-Central Kansas, 1995–2012					
ARTIFICAL RECHARGE IN LAS VEGAS VALLEY, CLARK COUNTY NEVADA	INJEECTION WELLS / DEEP WELLS	USA (LAS VEGAS)	NA	PROBLEMS – HIGH THICKNESS AND NOT SHALLOW AQUIFER, SULFATE CONTENT, SODIUM CONTENT, CHLORIDE CONTENT, WATER MIXTURE, LOW WELL RECHARGE YIELD (PROBABLY DUE TO CLOGGING BUT UNKNOWN TYPE), ECONOMIC CONSTRAINTS (OPERATONAL)	(KATZER AND BROTHERS, 1989)
Water Quality Changes Related to the Development of Anaerobic Conditions During Artificial Recharge	INFILTRATION BASINS	USA (TEXAS)	NA	PROBLEMS – LOW INFILTRATION RATE, SODICITY/SALINITY ISSUES, HIGH SULFATE, HIGH CHLORIDE, VEGETATION/ALGAE GROWTH, GENERATION OF METABOLITES (H2S), LOW PH, CLOGGING (BIOLOGICAL) NOT PROBLEM – LOW SUSPENDED SOLIDS CONTENT	(WOOD AND BASSETT, 1975)
A thirty year artificial recharge experiment in coastal aquifer in an arid zone: The Teboulba aquifer system (Tunisian Sahel)	DEEP WELLS / INJECTION WELLS	TUNISIA (SAHEL) 1972 - 2002	30 years	PROBLEMS – WATER SCARCITY (DUE TO CLIMA AND PRECIPITATION), LOW QUANTITY OF WATER RESOURCES AVAILABLE FOR RECHARGE, HIGH SALINITY/SODICITY, LOW INFILTRATION RATE, LOW POROSITY, REGIONAL HYDROGEOLOGY PROBLEMS (NEGATIVE INPUT/OUTPUT RATIO) NOT PROBLEM – CHEAPER WATER PRICES, COMPARED TO OTHER TECHNOLOGIES THE PRICES AND COSTS (DESIGN/CONSTRUCTION AND OPERATION) ARE BETTER IN AQUIFER ARTIFICIAL RECHARGE	(BOURI AND DHIA, 2010)
Estimating groundwater recharge induced by engineering systems in a semiarid area (southeastern Spain)	INFILTRATION BASINS (VIA CHECK DAMS AND GRAVEL PITS)	SPAIN (ALMERIA)	NA	PROBLEMS – HIGH SLOPE, WATER SCARCITY (CLIMATE), CLOGGING (PHYSICAL) NOT PROBLEM – GOOD INFILTRATION RATE	(MARTÍN-ROSALES ET AL., 2007)
Quantitative PCR Monitoring of Antibiotic Resistance Genes and Bacterial Pathogens in Three European Artificial Groundwater Recharge Systems	RIVER INFILTRATION	SPAIN (SABADELL)	1 YEAR	PROBLEMS – MICROBIOLOGICAL ISSUES, LEGAL CONSTRAINTS (DOESN'T COMPLY WITH DRINKING STANDARDS)	(BÖCKELMANN ET AL., 2009)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
Quantitative PCR Monitoring of Antibiotic Resistance Genes and Bacterial Pathogens in Three European Artificial Groundwater Recharge Systems	DEEP WELLS	ITALY (NARDÒ)	1 YEAR	PROBLEMS – LOW PH (POSSIBLY METAL DISSOLUTION AND MOBILISATION), WATER MIXTURE, MICROBIOLOGICAL ISSUES, WATER SCARCITY (CLIMATE), LEGAL CONSTRAINTS (DOESN'T COMPLY WITH DRINKING STANDARDS)	(BÖCKELMANN ET AL., 2009)
Quantitative PCR Monitoring of Antibiotic Resistance Genes and Bacterial Pathogens in Three European Artificial Groundwater Recharge Systems	INFILTTRATION BASINS	BELGIUM /TORREELE)	1 YEAR	PROBLEMS – WATER MIXTURE, MICROBIOLOGICAL ISSUES, DESIGN AND CONSTRUCTION COSTS, OPERATIONAL COSTS (REVERSE OSMISIS AND ULTRAFILTRATION TREATMENTS),	(BÖCKELMANN ET AL., 2009)
Modeling Seasonal Redox Dynamics and the Corresponding Fate of the Pharmaceutical Residue Phenazone During Artificial Recharge of Groundwater	DEEP WELLS	GERMANY (BERLIN)	NA	PROBLEMS – CLOGGING (UNKNOWN TYPE), LOW INFILTRATION RATE (PERIODICALLY CHANGING THIS RATE DUE TO CLOGGING ISSUES), NUTRIENTS, LOW NATURAL ATENUATION	(GRESKOWIAK ET AL., 2006)
Integrated Water Management for the 21st Century: Problems and Solutions	NA	NA	NA	PROBLEMS – LEGAL (OWNERSHIP,REUSE), CONTAMINATION (EXTERNAL POLUTANTS AND WASTE WATER RECHARGED POLLUTANTS), SALINITY, WATER SHORTAGE DUE TO CLIMATE CHANGE, FLOODING DUE TO CLIMATE CHANGE, NOT ENOUGH WATER EXTRACTED FROM MAR.	(BOUWER, 2002)
Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations Takashi	SURFACE SPREADING AND INJECTION WELLS	NA	NA	PROBLEMS – LEGAL (HEALTH LAWS), CONTAMINATION (EXTERNAL, TRACE CONTAMINANTS, ETC.), LACK OF KNOWLEDGE ABOUT THE RISKS AND PROBLEMS,	(ASANO AND COTRUVO, 2004)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
Future management of aquifer recharge	ALL	NA	NA	PROBLEMS – WATERLOGGING, DAMAGE TO STRUCTURES, FLOODING, SOIL SALINISATION, LEGAL ISSUES, WATER QUALITY, LACK OF KNOWLEDGE	(DILLON, 2005)
Managed Aquifer Recharge: an assessment of its role and effectiveness in watershed management	INFILTRATION BASIN AND CHECK DAMS	KOLWAN VALLEY 1998	NA	PROBLEMS – WATER SCARCITY (TO INFILTRATE), LACK OF INFORMATION, LACK OF WORKFORCE, MAINTENANCE COSTS, LEGAL ISSUES, OWNERSHIP ISSUES, COST-BENEFIT SHRING ISSUES, TENSIONS BETWEEN GOVERNMENT/AGENCIES/PEOPLE, INCREASED WATER ABSTRACTION, CLIMATE CHANGE ISSUES, CLOGGING.	(GALE ET AL., 2006)
Managed Aquifer Recharge: an assessment of its role and effectiveness in watershed management	CHECK DAM AND PERCOLATION TANK	SATLASANA (MUMANVAS, BHANAVAS 1, BBHANAVAS 2 AND SAMRAPUR) 2001-2003	NA	PROBLEMS – INVESTEMENT COSTS ISSUES, LAND USE (19,5 KM2), CLOGGING, LOW WATER RETENTION, HIGH FLUORIDE, HIGH NA, HIGH NO3-,	(GALE ET AL., 2006)
Managed Aquifer Recharge: an assessment of its role and effectiveness in watershed management	INFILTRATION BASIN AND CHECK DAM	COIMBATORE (KARNAMPET TAI, KODAGIPALAYA1 AND KODANGIPALAYAM 2)	NA	PROBLEMS – LAND USE, SOCIAL ACCEPTANCE, HIGH COSTS, LEGAL ISSUES, OWNERSHIP ISSUES, LACK OF MAINTENANCE (DUE TO COSTS, LACK OF KNOWLEDGE AND UNWILLINGNESS), LOW INFILTRATION RATES (MAINLY DUE TO CLOGGING), HIGH CONCENTRATIONS OF BA, FE AND NO3-	(GALE ET AL., 2006)
Organic micropollutant removal from wastewater effluent-impacted drinking water sources during bank filtration and artificial recharge	BANK FILTRATION AND INFILTRATION BASIN	GERMANY 2002	3 YEARS	PROBLEMS – VERY HIGH RETENTION TIME FOR BANK FILTRATION, VERY SHORT RETENTION TIME FOR INFILTRATION BASIN, BOTH HAD PROBLEMS WITH WATER QUALITY (MICROPOLLUTANTS, MOSTLY PHARMACEUTICAL PRODUCTS).	(MAENG ET AL., 2010)

TITLE	RECHARGE TYPE	PLACE & TIME	DURATION OF THE PROJECT	MAIN PROBLEMS	REFERENCE
Biogeochemical Processes during the Infiltration of River Water into an Alluvial Aquifer	RIVERBANK FILTRATION	FRANCE	NA	PROBLEMS – SEDIMENTS WHERE WATER INFILTRATES ARE CONTAMINATED WITH ZINC AND CADMIUM	(SITE, 1993)
Use of static Quantitative Microbial Risk Assessment to determine pathogen risks in an unconfined carbonate aquifer used for Managed Aquifer Recharge Simon	INJECTION WELLS	AUSTRALIA	NA	PROBLEMS – CHEMICAL CLOGGING	(TOZE ET AL., 2010)
Study of the feasibility of an aquifer storage and recovery system in a deep aquifer in Belgium	INJECTION WELLS	BELGIUM	NA	PROBLEMS – QUALITY ISSUES DUE TO WATER MIXING, LOW AMOUNT OF RECOVERED WATER, QUALITY ISSUES (PHOSPHATE, WATER COLOUR, DOC), CLOGGING (PHYSICAL AND BIOLOGICAL).	(VANDENBOHEDE ET AL., 2008)
Effectiveness of riverbank filtration for removal of nitrogen from heavily polluted rivers: a case study of Kuihe River, Xuzhou, Jiangsu, China	RIVERBANK FILTRATION	CHINA	NA	PROBLEMS – QUALITY ISSUES (HIGH NITROGEN CONCENTRATIONS), LOW DEGRADATION OF POLLUTANTS	(WU ET AL., 2007)

Definition of all MAR events considered

LEG Legal constraints - Changes in the legislation or failures to comply with its requirements (especially for health or environmental legislation).

TER Territorial constraints

EU European

NAT National

REG Regional/Local

SC Scope of legislation – Depending on the legislation type, its restrictions and risk probabilities can be significantly different.

HTH Health legislation

OTH Others – Mainly environmentally related legislation that can pose some kind of restrictions to the operation of the Mar facility.

ECO Economic constraints

MAC Macroeconomic constraints – Restrictions related to global effects on economy like crisis, changes in currency value, increase of the petroleum price, etc. That may cause a reduction on the interest in recharging water or a reduction on the quantity recharged.

MIC Microeconomic constraints

NEWR Not enough water to recharge due to other economical uses

IND Industrial use

AGR Agricultural use

DOM Domestic use

COST Cost restriction

LWP Low price of water – MAR has fixed costs and the water that produces has a fixed price, however other water sources can have a variable price that may be cheaper than the water obtained by MAR sources and therefore, the incentive for developing MAR is lowered.

HCST High installation cost

MAIN

T High maintenance cost/maintenance requirements

FUND Lack of private/public funding

SO Social unacceptance – Neighbors and other citizens may dislike MAR due to their own opinions according to safety, health, noise, etc.

HTHR Health risk perception

HCOS

T High cost perception

BRH Behavioral requirements – MAR as any technical facility has safety procedures and a code of conduct for the workers and people related to the facility operation. Thus implying that people may be unwilling to accept a MAR facility because they fear a facility that needs safety requirements like these.

CHILD Children surveillance

FAIR Fair distribution of treated wáter

EFECT Perception of effectiveness

GOV Governance

CORD Lack of coordination

NTK Non-technical knowledge

SD Structural Damages

FL Flooding

NH Natural hazards (e.g. earthquake)

TA Terrorism activities/Vandalism

CV Civil work failures

SLP Slope stability – Mostly for surface infiltration, it implies that the water recharge or accumulation in storage ponds may cause instabilities in the slopes and possibly causing landfalls or wall breakages.

PB Pipe breakage

OTH Others

AD Aquifer dissolution (e.g. in karstic aquifer)

QUAT Not enough water recharged

LWIP Low quality water

BIO Sanitary/biological restrictions (e.g. due the pathogens)

PHY Physical restrictions

TP Turbidity/particles

CHE Chemical restrictions

MET Metals (e.g. arsenic, manganese)

SL Salinity and sodicity

NUT Nutrients (nitrogen, phosphorous)

OC Organic chemicals (pollutants, EOCs)

RN Radionuclides

WS Water scarcity

CLIM Climate

DRO Droughts

WWTP Waste water treatment plant failure

LAND Desalination plant failure

RIV River regulation

CLOG Clogging

PCL Physical clogging

FDP Failure deposition pond (particles from diverted water) – The particles may not be sedimented efficiently and still be present in the recharged water, diminishing and difficulting the entrance of water during recharge operations.

PPF Pipe filter fails

RT Residence time – Not enough residence time may cause an inefficient reduction and degradation of contaminants and pathogens.

SFP Source fine particles (generation inside MAR facility)

TD Transport sedimentation (erosion or deposition from recharge pond)

DP Deposition

ER Erosion

BCL Bioclogging

CCL Chemical clogging

EV Evaporation (excess)

WMX Water mixtures – The combination of the aquifer natural water and the injected water may cause precipitation of minerals and therefore chemical clogging, reducing the amount of water recharged into the aquifer.

MIC Microbial population catalysis – Microbial population may cause changes in the water chemistry which in turn can imply precipitation of minerals or other byproducts (microbial biofilms) which can reduce recharged water.

COM Compaction

GAS Generation of gas (e.g. bubble formation)

PHM Physical Motives

BAC Bacterial processes

ID Inappropriate design

QUAL Unacceptable quality of water at sensitive location

AN Inefficient natural attenuation

OM Organic matter

EOC Emerging organic compounds

UN Nutrients

MET Generation of metabolites – The chemicals injected or already present in the aquifer may be degraded and then transformed into another compounds which may be equally or more dangerous than the previous ones, therefore affecting the quality of the water.

NC Nitrogen cycle (NO2 -, N2O…)

EOC Emerging organic compounds

H2S Other nutrient cycles (H2S)

MOB Mobilization

MET Metals

ST Specific targets – A MAR project can be done for many reasons but there is always one or a couple of them that are the main ones for the project. Those reasons may have specific objectives that need to be achieved in order to have a successful MAR project.

SWB Seawater barriers

PROT Protected water body

WL Water levels

RIV River

SPR Spring

WET Wetland

RISKMAR APP MANUAL

The programming language of the MAR-RISKAPP was Visual Basic. Which is based on the usage of macros, which are usually short programing code lines that are used to give some kind of orders to the program in order to do some specific calculations or to set automatically some kind of properties for the working environment (among other kind of possibilities) and objects.

The result was the MAR-RISKAPP tool which allows the user to define four probability categories (high risk, medium risk, low risk and no risk) of failure for each type MAR event and therefore calculate the risk of a general MAR failure (representing the different probabilities within a fault tree).

The MAR-RISKAPP was structured in four main steps: 1) HOME, 2) INPUT, 3) RESULTS and 4) GRAPHICAL RESULTS.

The application starts with the HOME step. This first stage shows the name of the tool, the creators and the main institutions involved in it, with a clear indication that the tool was developed within the framework of project MARSOL. From this starting point, there are two possible ways to proceed: 1) HELP (which sends the user to a general explanation of the tool and its operational set can be found), and 2) START (which sends the user to the second step of the tool – INPUT).

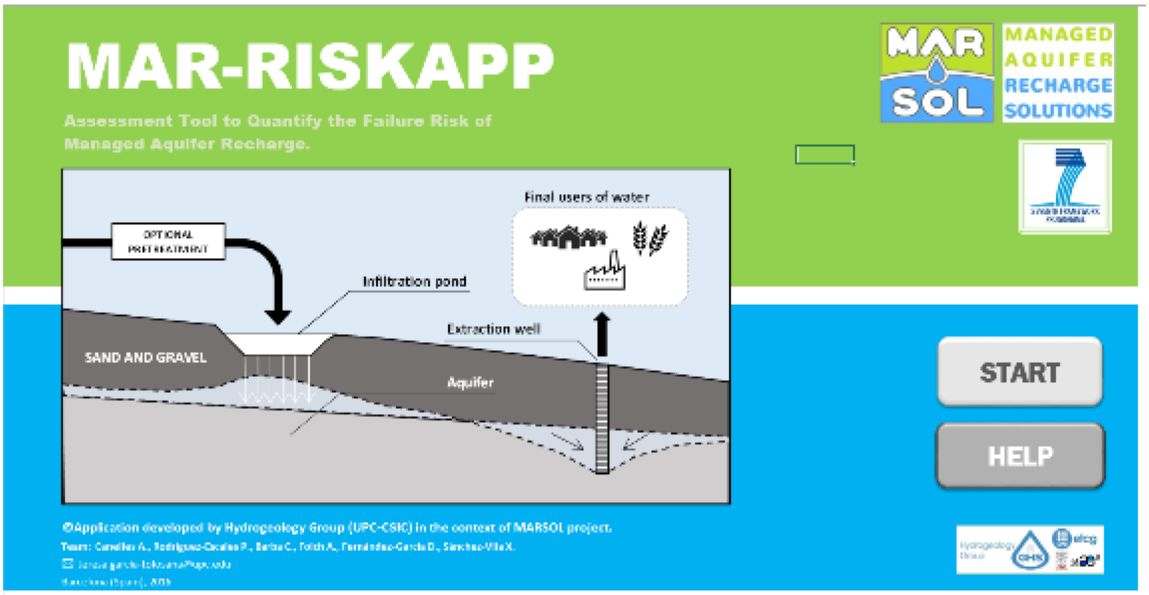


Figure S2.6. *Home layout visualization.*

The second step of the tool is INPUT. At this point, the user has to choose the risk category of the different events for both non-technical and technical issues (the Input sheet can be seen in Figure S3.2). This step implies that data has to be filled in four different sheets: 1) NON-TECHNICAL CONSTRAINTS - DESIGN AND CONSTRUCTION (Figure S3.3), 2) TECHNICAL CONSTRAINTS - DESIGN AND CONSTRUCTION (Figure S3.4), 3) NON-TECHNICAL CONSTRAINTS – OPERATION (Figure S3.5) and 4) TECHNICAL CONSTRAINTS – OPERATION (Figure S3.6). Where the user has to answer for all the events by writing an “X” on the risk category that they think it is the most adequate.

Only one “X” has to be written at each line, as the person filling the sheet must select one of the following four categories of risk: no risk, high risk, medium risk, or low risk. In the Input worksheet, there is a button of instructions; when this button is clicked, a pop-up text box is shown (which indicates the order that the four input sheets should be filled and some explanation about their meaning). In addition, each input sheet has its own instruction button, which explains the user by using text and images, how to fill the surveys from each input worksheet. Finally, when all the input sheets have been filled, the user can run the Results button in order to go the RESULTS sheet (or if the user need help, the Help button can bring him/her to the Help sheet, or if the user wants to go back to the HOME sheet, he/she can press the BACK TO HOME button).

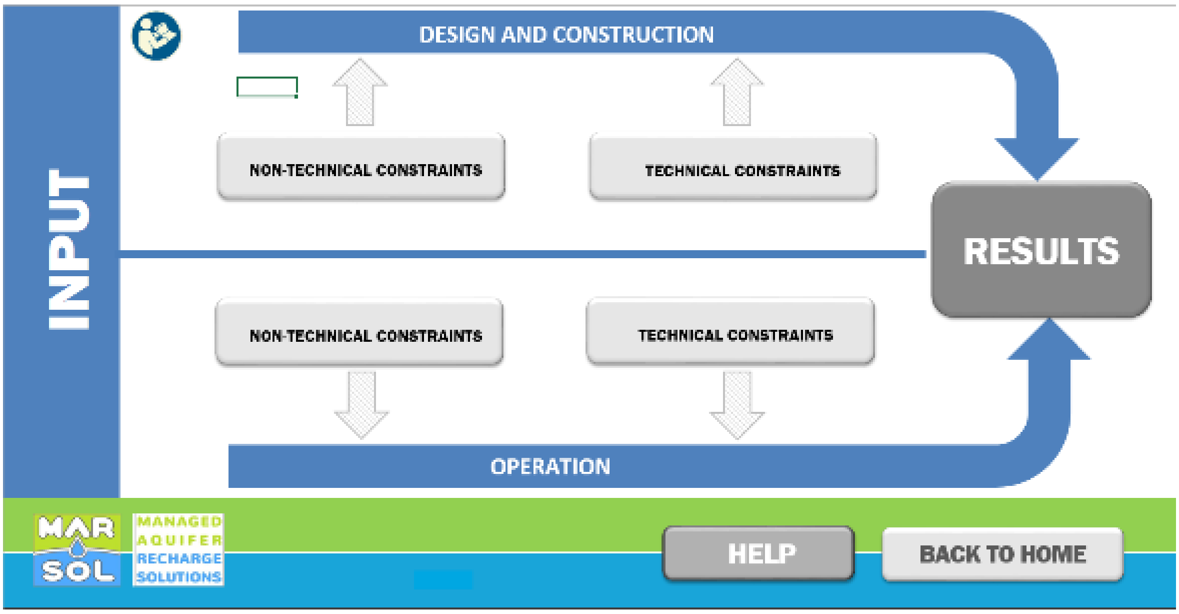
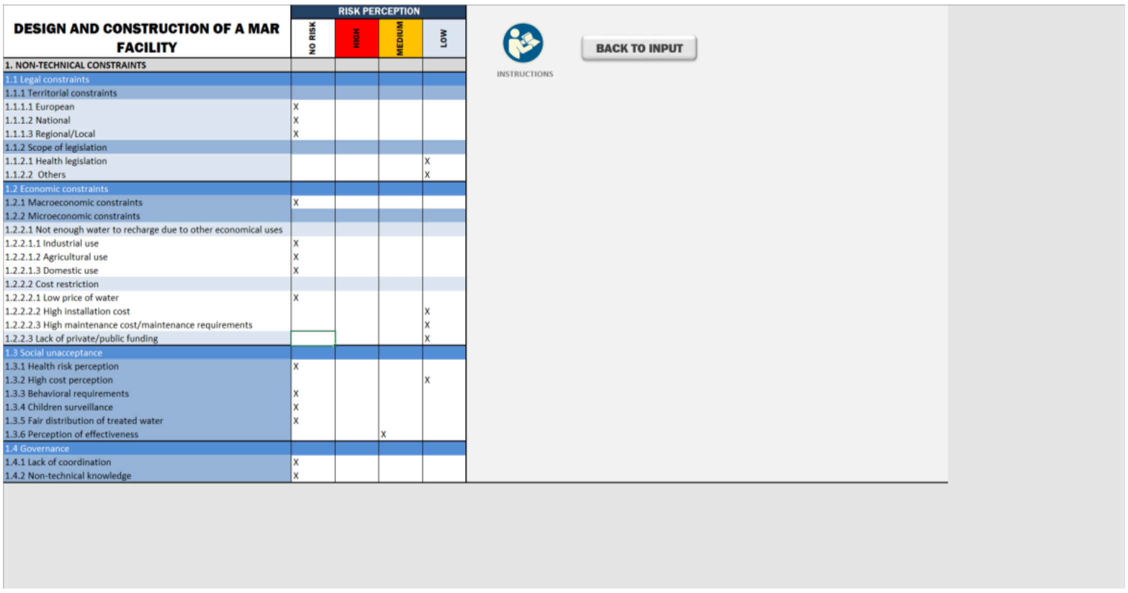
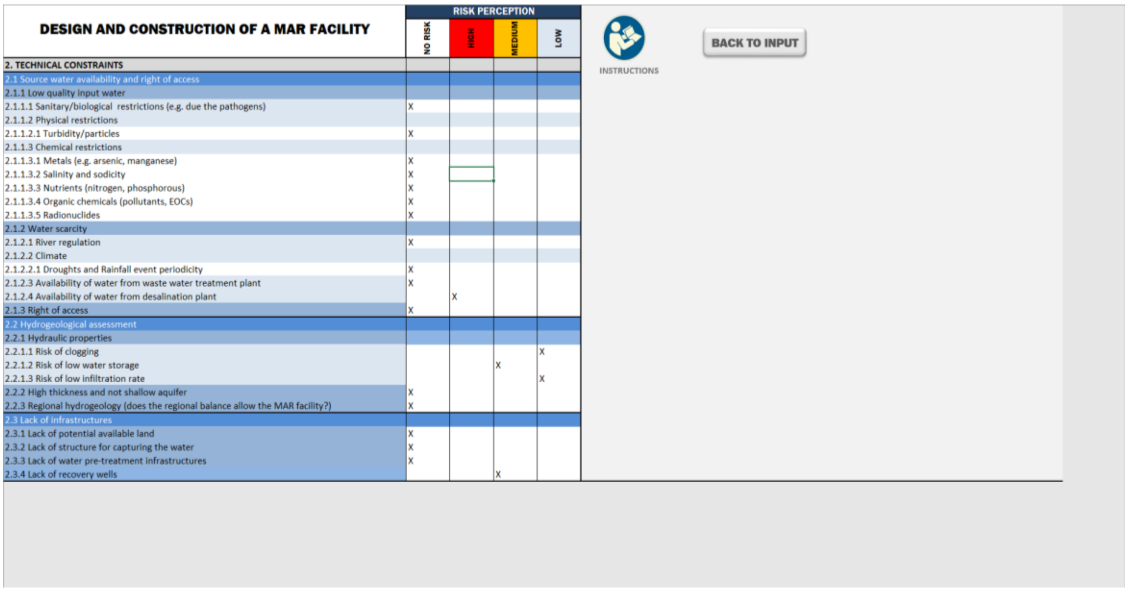


Figure S2.7. *Input layout visualization*



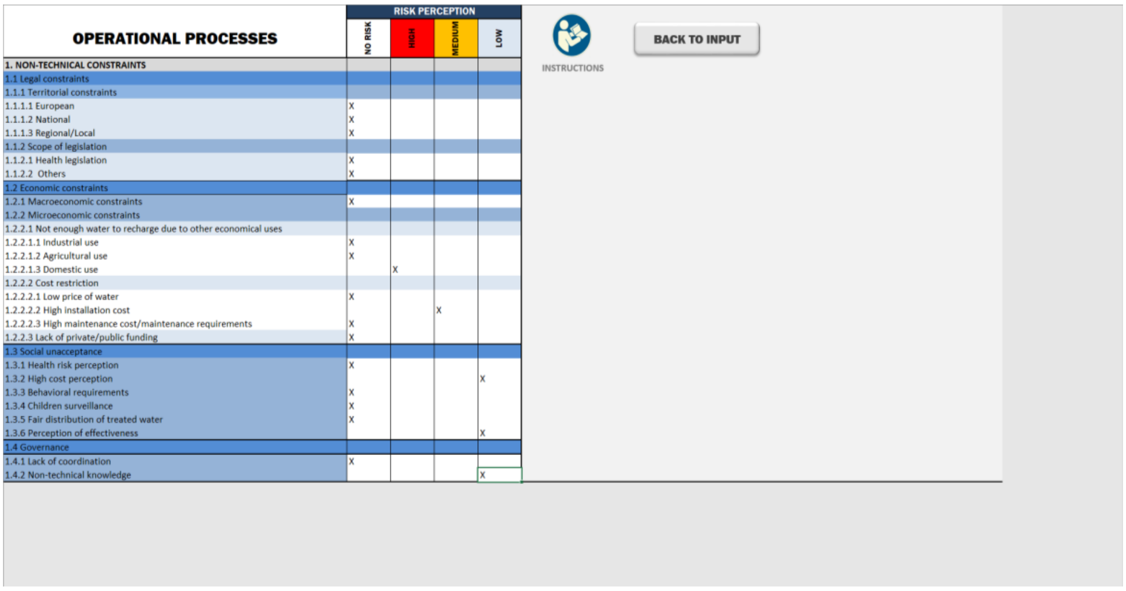
DESIGN AND CONSTRUCTION OF A MAR FACILITY	RISK PERCEPTION			
	NO RISK	HIGH	MEDIUM	LOW
1. NON-TECHNICAL CONSTRAINTS				
1.1 Legal constraints				
1.1.1 Territorial constraints				
1.1.1.1 European	X			
1.1.1.2 National	X			
1.1.1.3 Regional/Local	X			
1.1.2 Scope of legislation				
1.1.2.1 Health legislation				X
1.1.2.2 Others				X
1.2 Economic constraints				
1.2.1 Macroeconomic constraints	X			
1.2.2 Microeconomic constraints				
1.2.2.1 Not enough water to recharge due to other economical uses				
1.2.2.1.1 Industrial use	X			
1.2.2.1.2 Agricultural use	X			
1.2.2.1.3 Domestic use	X			
1.2.2.2 Cost restriction				
1.2.2.2.1 Low price of water	X			
1.2.2.2.2 High installation cost				X
1.2.2.2.3 High maintenance cost/maintenance requirements				X
1.2.2.3 Lack of private/public funding				X
1.3 Social unacceptance				
1.3.1 Health risk perception	X			
1.3.2 High cost perception				X
1.3.3 Behavioral requirements	X			
1.3.4 Children surveillance	X			
1.3.5 Fair distribution of treated water	X			
1.3.6 Perception of effectiveness			X	
1.4 Governance				
1.4.1 Lack of coordination	X			
1.4.2 Non-technical knowledge	X			

Figure S2.8. *Non-technical constraints – Design and construction, sheet visualization.*



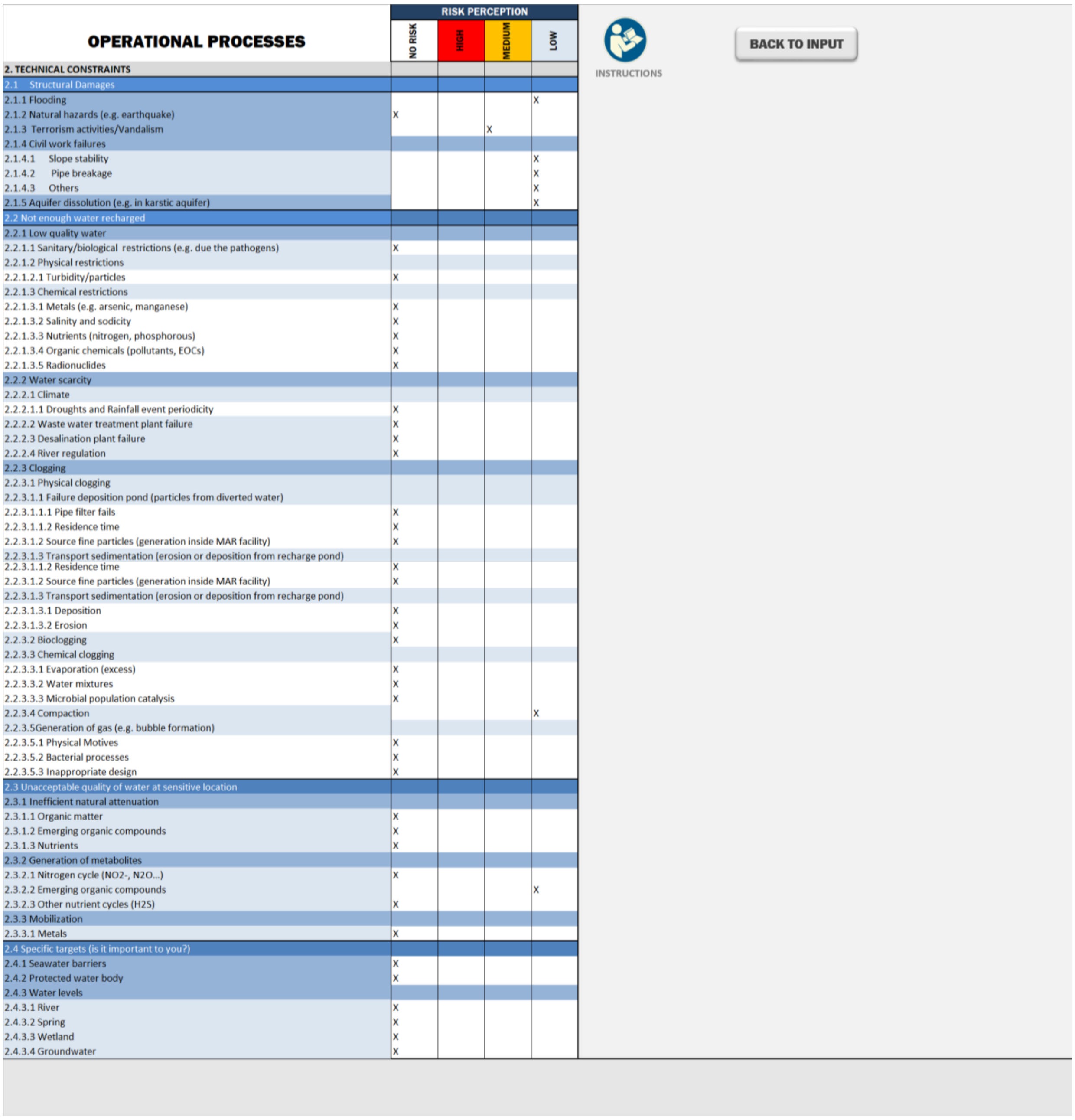
DESIGN AND CONSTRUCTION OF A MAR FACILITY	RISK PERCEPTION			
	NO RISK	HIGH	MEDIUM	LOW
2. TECHNICAL CONSTRAINTS				
2.1 Source water availability and right of access				
2.1.1 Low quality input water				
2.1.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	X			
2.1.1.2 Physical restrictions				
2.1.1.2.1 Turbidity/particles	X			
2.1.1.3 Chemical restrictions				
2.1.1.3.1 Metals (e.g. arsenic, manganese)	X			
2.1.1.3.2 Salinity and sodicity	X			
2.1.1.3.3 Nutrients (nitrogen, phosphorous)	X			
2.1.1.3.4 Organic chemicals (pollutants, EOCs)	X			
2.1.1.3.5 Radionuclides	X			
2.1.2 Water scarcity				
2.1.2.1 River regulation	X			
2.1.2.2 Climate				
2.1.2.2.1 Droughts and Rainfall event periodicity	X			
2.1.2.3 Availability of water from waste water treatment plant	X			
2.1.2.4 Availability of water from desalination plant		X		
2.1.3 Right of access	X			
2.2 Hydrogeological assessment				
2.2.1 Hydraulic properties				
2.2.1.1 Risk of clogging				X
2.2.1.2 Risk of low water storage			X	
2.2.1.3 Risk of low infiltration rate				X
2.2.2 High thickness and not shallow aquifer	X			
2.2.3 Regional hydrogeology (does the regional balance allow the MAR facility?)	X			
2.3 Lack of infrastructures				
2.3.1 Lack of potential available land	X			
2.3.2 Lack of structure for capturing the water	X			
2.3.3 Lack of water pre-treatment infrastructures	X			
2.3.4 Lack of recovery wells			X	

Figure S2.9. *Technical constraints – Design and construction, sheet visualization.*



OPERATIONAL PROCESSES	RISK PERCEPTION			
	NO RISK	HIGH	MEDIUM	LOW
1. NON-TECHNICAL CONSTRAINTS				
1.1 Legal constraints				
1.1.1 Territorial constraints				
1.1.1.1 European	X			
1.1.1.2 National	X			
1.1.1.3 Regional/Local	X			
1.1.2 Scope of legislation				
1.1.2.1 Health legislation	X			
1.1.2.2 Others	X			
1.2 Economic constraints				
1.2.1 Macroeconomic constraints	X			
1.2.2 Microeconomic constraints				
1.2.2.1 Not enough water to recharge due to other economical uses				
1.2.2.1.1 Industrial use	X			
1.2.2.1.2 Agricultural use	X			
1.2.2.1.3 Domestic use		X		
1.2.2.2 Cost restriction				
1.2.2.2.1 Low price of water	X			
1.2.2.2.2 High installation cost			X	
1.2.2.2.3 High maintenance cost/maintenance requirements	X			
1.2.2.3 Lack of private/public funding	X			
1.3 Social unacceptance				
1.3.1 Health risk perception	X			
1.3.2 High cost perception				X
1.3.3 Behavioral requirements	X			
1.3.4 Children surveillance	X			
1.3.5 Fair distribution of treated water	X			
1.3.6 Perception of effectiveness				X
1.4 Governance				
1.4.1 Lack of coordination	X			
1.4.2 Non-technical knowledge				X

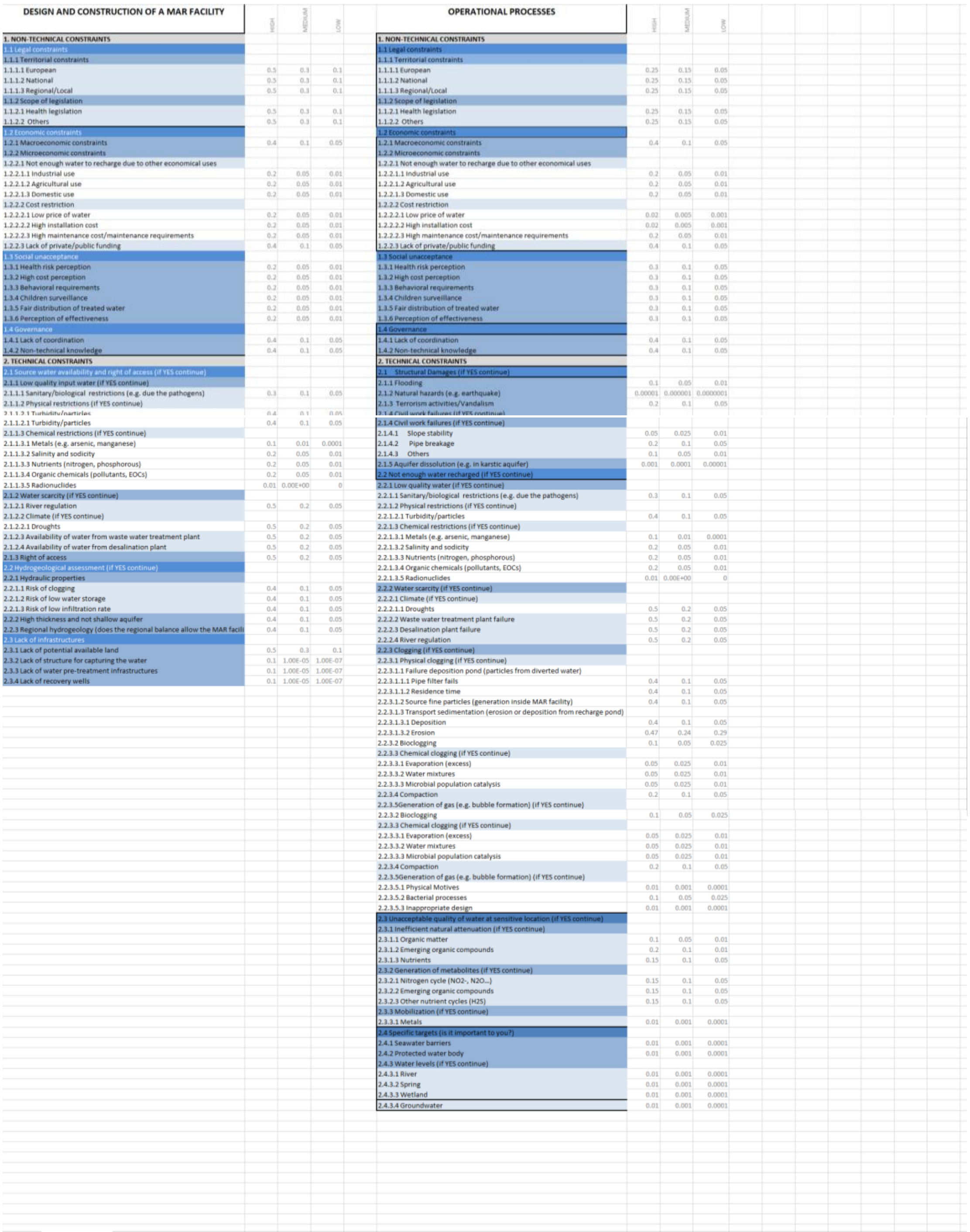
Figure S2.10. *Non-technical constraints – Operation, sheet visualization.*



OPERATIONAL PROCESSES	RISK PERCEPTION			
	NO RISK	HIGH	MEDIUM	LOW
2. TECHNICAL CONSTRAINTS				
2.1 Structural Damages				
2.1.1 Flooding				X
2.1.2 Natural hazards (e.g. earthquake)	X			
2.1.3 Terrorism activities/Vandalism			X	
2.1.4 Civil work failures				
2.1.4.1 Slope stability				X
2.1.4.2 Pipe breakage				X
2.1.4.3 Others				X
2.1.5 Aquifer dissolution (e.g. in karstic aquifer)				X
2.2 Not enough water recharged				
2.2.1 Low quality water				
2.2.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	X			
2.2.1.2 Physical restrictions				
2.2.1.2.1 Turbidity/particles	X			
2.2.1.3 Chemical restrictions				
2.2.1.3.1 Metals (e.g. arsenic, manganese)	X			
2.2.1.3.2 Salinity and sodicity	X			
2.2.1.3.3 Nutrients (nitrogen, phosphorous)	X			
2.2.1.3.4 Organic chemicals (pollutants, EOCs)	X			
2.2.1.3.5 Radionuclides	X			
2.2.2 Water scarcity				
2.2.2.1 Climate				
2.2.2.1.1 Droughts and Rainfall event periodicity	X			
2.2.2.2 Waste water treatment plant failure	X			
2.2.2.3 Desalination plant failure	X			
2.2.2.4 River regulation	X			
2.2.3 Clogging				
2.2.3.1 Physical clogging				
2.2.3.1.1 Failure deposition pond (particles from diverted water)				
2.2.3.1.1.1 Pipe filter fails	X			
2.2.3.1.1.2 Residence time	X			
2.2.3.1.2 Source fine particles (generation inside MAR facility)	X			
2.2.3.1.3 Transport sedimentation (erosion or deposition from recharge pond)				
2.2.3.1.1.2 Residence time	X			
2.2.3.1.2 Source fine particles (generation inside MAR facility)	X			
2.2.3.1.3 Transport sedimentation (erosion or deposition from recharge pond)				
2.2.3.1.3.1 Deposition	X			
2.2.3.1.3.2 Erosion	X			
2.2.3.2 Bioclogging	X			
2.2.3.3 Chemical clogging				
2.2.3.3.1 Evaporation (excess)	X			
2.2.3.3.2 Water mixtures	X			
2.2.3.3.3 Microbial population catalysis	X			
2.2.3.4 Compaction				X
2.2.3.5Generation of gas (e.g. bubble formation)				
2.2.3.5.1 Physical Motives	X			
2.2.3.5.2 Bacterial processes	X			
2.2.3.5.3 Inappropriate design	X			
2.3 Unacceptable quality of water at sensitive location				
2.3.1 Inefficient natural attenuation				
2.3.1.1 Organic matter	X			
2.3.1.2 Emerging organic compounds	X			
2.3.1.3 Nutrients	X			
2.3.2 Generation of metabolites				
2.3.2.1 Nitrogen cycle (NO2-, N2O…)	X			
2.3.2.2 Emerging organic compounds				X
2.3.2.3 Other nutrient cycles (H2S)	X			
2.3.3 Mobilization				
2.3.3.1 Metals	X			
2.4 Specific targets (is it important to you?)				
2.4.1 Seawater barriers	X			
2.4.2 Protected water body	X			
2.4.3 Water levels				
2.4.3.1 River	X			
2.4.3.2 Spring	X			
2.4.3.3 Wetland	X			
2.4.3.4 Groundwater	X			

Figure S2.11. *Technical constraints – Operation, sheet visualization.*

The third step is RESULTS. This part shows the user the numerical results of the risk assessment (Figure S3.8). The risk assessment is calculated within the same Results sheet by applying the values present in the A PRIORI CRITERIA sheet (Figure S3.7) which are chosen depending on the risk category selected from the INPUT step. Note that the a priori criteria are site dependent. For that, the MAR facility managerd must define each a priori criteria based on their knowledge about the site and its particular idiosyncrasies. As a default, A PRIORI CRITERIA values are provided in MAR-RISKAPP based on experience from a number of sites worldwide. A prior values are probability numbers (ranging in the interval [0-1] that indicate the probability (from a period of 2-6 years) that the MAR facility fails due to that particular individual event.

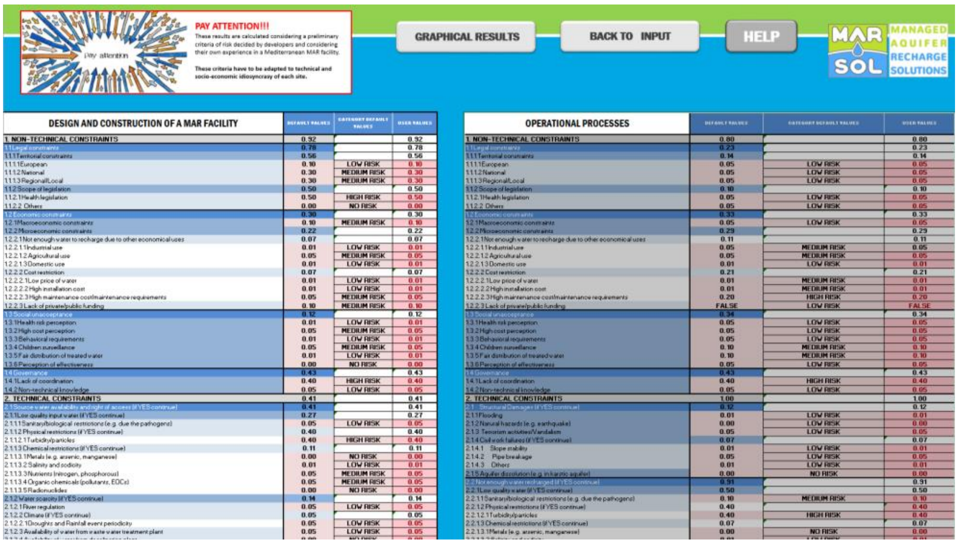


DESIGN AND CONSTRUCTION OF A MAR FACILITY	HIGH	MEDIUM	LOW
1. NON-TECHNICAL CONSTRAINTS			
1.1 Legal constraints			
1.1.1 Territorial constraints			
1.1.1.1 European	0.5	0.3	0.1
1.1.1.2 National	0.5	0.3	0.1
1.1.1.3 Regional/Local	0.5	0.3	0.1
1.1.2 Scope of legislation			
1.1.2.1 Health legislation	0.5	0.3	0.1
1.1.2.2 Others	0.5	0.3	0.1
1.2 Economic constraints			
1.2.1 Macroeconomic constraints	0.4	0.1	0.05
1.2.2 Microeconomic constraints			
1.2.2.1 Not enough water to recharge due to other economical uses			
1.2.2.1.1 Industrial use	0.2	0.05	0.01
1.2.2.1.2 Agricultural use	0.2	0.05	0.01
1.2.2.1.3 Domestic use	0.2	0.05	0.01
1.2.2.2 Cost restriction			
1.2.2.2.1 Low price of water	0.2	0.05	0.01
1.2.2.2.2 High installation cost	0.2	0.05	0.01
1.2.2.2.3 High maintenance cost/maintenance requirements	0.2	0.05	0.01
1.2.2.3 Lack of private/public funding	0.4	0.1	0.05
1.3 Social unacceptance			
1.3.1 Health risk perception	0.2	0.05	0.01
1.3.2 High cost perception	0.2	0.05	0.01
1.3.3 Behavioral requirements	0.2	0.05	0.01
1.3.4 Children surveillance	0.2	0.05	0.01
1.3.5 Fair distribution of treated water	0.2	0.05	0.01
1.3.6 Perception of effectiveness	0.2	0.05	0.01
1.4 Governance			
1.4.1 Lack of coordination	0.4	0.1	0.05
1.4.2 Non-technical knowledge	0.4	0.1	0.05
2. TECHNICAL CONSTRAINTS			
2.1 Source water availability and right of access (if YES continue)			
2.1.1 Low quality input water (if YES continue)			
2.1.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	0.3	0.1	0.05
2.1.1.2 Physical restrictions (if YES continue)			
2.1.1.2.1 Turbidity/particles	0.4	0.1	0.05
2.1.1.3 Chemical restrictions (if YES continue)			
2.1.1.3.1 Metals (e.g. arsenic, manganese)	0.1	0.01	0.0001
2.1.1.3.2 Salinity and sodicity	0.2	0.05	0.01
2.1.1.3.3 Nutrients (nitrogen, phosphorous)	0.2	0.05	0.01
2.1.1.3.4 Organic chemicals (pollutants, EOCs)	0.2	0.05	0.01
2.1.1.3.5 Radionuclides	0.01	0.00E+00	0
2.1.2 Water scarcity (if YES continue)			
2.1.2.1 River regulation	0.5	0.2	0.05
2.1.2.2 Climate (if YES continue)			
2.1.2.2.1 Droughts	0.5	0.2	0.05
2.1.2.3 Availability of water from waste water treatment plant	0.5	0.2	0.05
2.1.2.4 Availability of water from desalination plant	0.5	0.2	0.05
2.1.3 Right of access	0.5	0.2	0.05
2.2 Hydrogeological assessment (if YES continue)			
2.2.1 Hydraulic properties			
2.2.1.1 Risk of clogging	0.4	0.1	0.05
2.2.1.2 Risk of low water storage	0.4	0.1	0.05
2.2.1.3 Risk of low infiltration rate	0.4	0.1	0.05
2.2.2 High thickness and not shallow aquifer	0.4	0.1	0.05
2.2.3 Regional hydrogeology (does the regional balance allow the MAR facili	0.4	0.1	0.05
2.3 Lack of infrastructures			
2.3.1 Lack of potential available land	0.5	0.3	0.1
2.3.2 Lack of structure for capturing the water	0.1	1.00E-05	1.00E-07
2.3.3 Lack of water pre-treatment infrastructures	0.1	1.00E-05	1.00E-07
2.3.4 Lack of recovery wells	0.1	1.00E-05	1.00E-07

OPERATIONAL PROCESSES	HIGH	MEDIUM	LOW
1. NON-TECHNICAL CONSTRAINTS			
1.1 Legal constraints			
1.1.1 Territorial constraints			
1.1.1.1 European	0.25	0.15	0.05
1.1.1.2 National	0.25	0.15	0.05
1.1.1.3 Regional/Local	0.25	0.15	0.05
1.1.2 Scope of legislation			
1.1.2.1 Health legislation	0.25	0.15	0.05
1.1.2.2 Others	0.25	0.15	0.05
1.2 Economic constraints			
1.2.1 Macroeconomic constraints	0.4	0.1	0.05
1.2.2 Microeconomic constraints			
1.2.2.1 Not enough water to recharge due to other economical uses			
1.2.2.1.1 Industrial use	0.2	0.05	0.01
1.2.2.1.2 Agricultural use	0.2	0.05	0.01
1.2.2.1.3 Domestic use	0.2	0.05	0.01
1.2.2.2 Cost restriction			
1.2.2.2.1 Low price of water	0.02	0.005	0.001
1.2.2.2.2 High installation cost	0.02	0.005	0.001
1.2.2.2.3 High maintenance cost/maintenance requirements	0.2	0.05	0.01
1.2.2.3 Lack of private/public funding	0.4	0.1	0.05
1.3 Social unacceptance			
1.3.1 Health risk perception	0.3	0.1	0.05
1.3.2 High cost perception	0.3	0.1	0.05
1.3.3 Behavioral requirements	0.3	0.1	0.05
1.3.4 Children surveillance	0.3	0.1	0.05
1.3.5 Fair distribution of treated water	0.3	0.1	0.05
1.3.6 Perception of effectiveness	0.3	0.1	0.05
1.4 Governance			
1.4.1 Lack of coordination	0.4	0.1	0.05
1.4.2 Non-technical knowledge	0.4	0.1	0.05
2. TECHNICAL CONSTRAINTS			
2.1 Structural Damages (if YES continue)			
2.1.1 Flooding	0.1	0.05	0.01
2.1.2 Natural hazards (e.g. earthquake)	0.00001	0.000001	0.0000001
2.1.3 Terrorism activities/Vandalism	0.2	0.1	0.05
2.1.4 Civil work failures (if YES continue)			
2.1.4.1 Slope stability	0.05	0.025	0.01
2.1.4.2 Pipe breakage	0.2	0.1	0.05
2.1.4.3 Others	0.1	0.05	0.01
2.1.5 Aquifer dissolution (e.g. in karstic aquifer)	0.001	0.0001	0.00001
2.2 Not enough water recharged (if YES continue)			
2.2.1 Low quality water (if YES continue)			
2.2.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	0.3	0.1	0.05
2.2.1.2 Physical restrictions (if YES continue)			
2.2.1.2.1 Turbidity/particles	0.4	0.1	0.05
2.2.1.3 Chemical restrictions (if YES continue)			
2.2.1.3.1 Metals (e.g. arsenic, manganese)	0.1	0.01	0.0001
2.2.1.3.2 Salinity and sodicity	0.2	0.05	0.01
2.2.1.3.3 Nutrients (nitrogen, phosphorous)	0.2	0.05	0.01
2.2.1.3.4 Organic chemicals (pollutants, EOCs)	0.2	0.05	0.01
2.2.1.3.5 Radionuclides	0.01	0.00E+00	0
2.2.2 Water scarcity (if YES continue)			
2.2.2.1 Climate (if YES continue)			
2.2.2.1.1 Droughts	0.5	0.2	0.05
2.2.2.2 Waste water treatment plant failure	0.5	0.2	0.05
2.2.2.3 Desalination plant failure	0.5	0.2	0.05
2.2.2.4 River regulation	0.5	0.2	0.05
2.2.3 Clogging (if YES continue)			
2.2.3.1 Physical clogging (if YES continue)			
2.2.3.1.1 Failure deposition pond (particles from diverted water)			
2.2.3.1.1.1 Pipe filter fails	0.4	0.1	0.05
2.2.3.1.1.2 Residence time	0.4	0.1	0.05
2.2.3.1.2 Source fine particles (generation inside MAR facility)	0.4	0.1	0.05
2.2.3.1.3 Transport sedimentation (erosion or deposition from recharge pond)			
2.2.3.1.3.1 Deposition	0.4	0.1	0.05
2.2.3.1.3.2 Erosion	0.47	0.24	0.29
2.2.3.2 Bioclogging	0.1	0.05	0.025
2.2.3.3 Chemical clogging (if YES continue)			
2.2.3.3.1 Evaporation (excess)	0.05	0.025	0.01
2.2.3.3.2 Water mixtures	0.05	0.025	0.01
2.2.3.3.3 Microbial population catalysis	0.05	0.025	0.01
2.2.3.4 Compaction	0.2	0.1	0.05
2.2.3.5Generation of gas (e.g. bubble formation) (if YES continue)			
2.2.3.2 Bioclogging	0.1	0.05	0.025
2.2.3.3 Chemical clogging (if YES continue)			
2.2.3.3.1 Evaporation (excess)	0.05	0.025	0.01
2.2.3.3.2 Water mixtures	0.05	0.025	0.01
2.2.3.3.3 Microbial population catalysis	0.05	0.025	0.01
2.2.3.4 Compaction	0.2	0.1	0.05
2.2.3.5Generation of gas (e.g. bubble formation) (if YES continue)			
2.2.3.5.1 Physical Motives	0.01	0.001	0.0001
2.2.3.5.2 Bacterial processes	0.1	0.05	0.025
2.2.3.5.3 Inappropriate design	0.01	0.001	0.0001
2.3 Unacceptable quality of water at sensitive location (if YES continue)			
2.3.1 Inefficient natural attenuation (if YES continue)			
2.3.1.1 Organic matter	0.1	0.05	0.01
2.3.1.2 Emerging organic compounds	0.2	0.1	0.01
2.3.1.3 Nutrients	0.15	0.1	0.05
2.3.2 Generation of metabolites (if YES continue)			
2.3.2.1 Nitrogen cycle (NO2-, N2O...)	0.15	0.1	0.05
2.3.2.2 Emerging organic compounds	0.15	0.1	0.05
2.3.2.3 Other nutrient cycles (H2S)	0.15	0.1	0.05
2.3.3 Mobilization (if YES continue)			
2.3.3.1 Metals	0.01	0.001	0.0001
2.4 Specific targets (is it important to you?)			
2.4.1 Seawater barriers	0.01	0.001	0.0001
2.4.2 Protected water body	0.01	0.001	0.0001
2.4.3 Water levels (if YES continue)			
2.4.3.1 River	0.01	0.001	0.0001
2.4.3.2 Spring	0.01	0.001	0.0001
2.4.3.3 Wetland	0.01	0.001	0.0001
2.4.3.4 Groundwater	0.01	0.001	0.0001

Figure S2.12. *Expert Criteria values for the Llobregat site.*

The initial prior values are presented in the DEFAULT VALUE column, and are blocked to changes by the user. Next to this column, there is the CATEGORY DEFAULT VALUES column, which indicates the risk category that the user selected in the INPUT sheets. There is also a third column called USER VALUES, that can be modified by the user in order to change the specific risk values (from the DEFAULT VALUES column) if the user has better data than the default calculations for a specific study site (but does not want to change the a priori criteria values). This third column is the one that will be used in the following calculations, so the user has to be fully aware that its modification has direct consequences on the results. The tool indicates the user if these USER VALUES have been modified or not from the default ones (this is done by filling the USER VALUES cells with red color, to indicate that both columns have the same values). Similarly, to the other steps, a HELP button can be found, and also some instructions pop-up (Figure S3.9) if the instructions button is clicked. The user can change some data from the INPUT by clicking the BACK TO INPUT button. If everything is correct, the user can go to the next step by clicking the GRAPHICAL RESULTS button.



PAY ATTENTION!!!

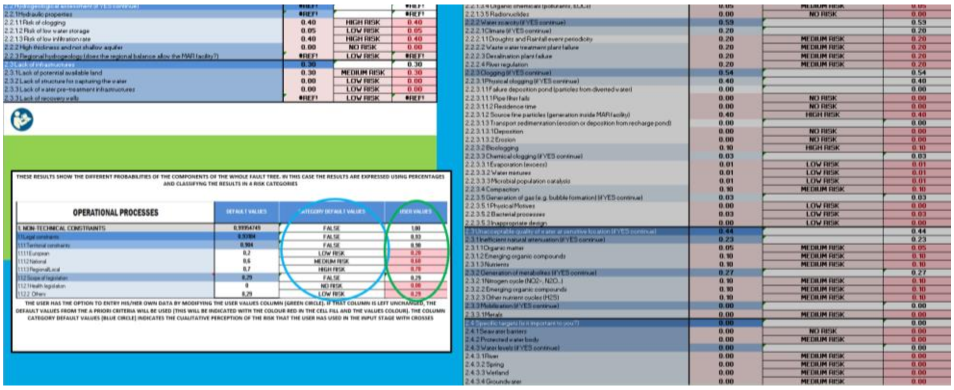
These results are calculated considering a preliminary criteria of risk decided by developers and considering their own experience in a Mediterranean MAR facility.

These criteria have to be adapted to technical and socio-economic idiosyncrasy of each site.

DESIGN AND CONSTRUCTION OF A MAR FACILITY	DEFAULT VALUES	CATEGORY DEFAULT VALUES	USER VALUES
1. NON-TECHNICAL CONSTRAINTS	0.92		0.92
1.1 Legal constraints	0.78		0.78
1.1.1 Territorial constraints	0.56		0.56
1.1.1.1 European	0.10	LOW RISK	0.10
1.1.1.2 National	0.30	MEDIUM RISK	0.30
1.1.1.3 Regional/Local	0.30	MEDIUM RISK	0.30
1.1.2 Scope of legislation	0.50		0.50
1.1.2.1 Health legislation	0.50	HIGH RISK	0.50
1.1.2.2 Others	0.00	NO RISK	0.00
1.2 Economic constraints	0.30		0.30
1.2.1 Macroeconomic constraints	0.10	MEDIUM RISK	0.10
1.2.2 Microeconomic constraints	0.22		0.22
1.2.2.1 Not enough water to recharge due to other economical uses	0.07		0.07
1.2.2.1.1 Industrial use	0.01	LOW RISK	0.01
1.2.2.1.2 Agricultural use	0.05	MEDIUM RISK	0.05
1.2.2.1.3 Domestic use	0.01	LOW RISK	0.01
1.2.2.2 Cost restriction	0.07		0.07
1.2.2.2.1 Low price of water	0.01	LOW RISK	0.01
1.2.2.2.2 High installation cost	0.01	LOW RISK	0.01
1.2.2.2.3 High maintenance cost/maintenance requirements	0.05	MEDIUM RISK	0.05
1.2.2.3 Lack of private/public funding	0.10	MEDIUM RISK	0.10
1.3 Social unacceptance	0.12		0.12
1.3.1 Health risk perception	0.01	LOW RISK	0.01
1.3.2 High cost perception	0.05	MEDIUM RISK	0.05
1.3.3 Behavioral requirements	0.01	LOW RISK	0.01
1.3.4 Children surveillance	0.05	MEDIUM RISK	0.05
1.3.5 Fair distribution of treated water	0.01	LOW RISK	0.01
1.3.6 Perception of effectiveness	0.00	NO RISK	0.00
1.4 Governance	0.43		0.43
1.4.1 Lack of coordination	0.40	HIGH RISK	0.40
1.4.2 Non-technical knowledge	0.05	LOW RISK	0.05
2. TECHNICAL CONSTRAINTS	0.41		0.41
2.1 Source water availability and right of access (if YES continue)	0.41		0.41
2.1.1 Low quality input water (if YES continue)	0.27		0.27
2.1.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	0.05	LOW RISK	0.05
2.1.1.2 Physical restrictions (if YES continue)	0.40		0.40
2.1.1.2.1 Turbidity/particles	0.40	HIGH RISK	0.40
2.1.1.3 Chemical restrictions (if YES continue)	0.11		0.11
2.1.1.3.1 Metals (e.g. arsenic, manganese)	0.00	NO RISK	0.00
2.1.1.3.2 Salinity and sodicity	0.01	LOW RISK	0.01
2.1.1.3.3 Nutrients (nitrogen, phosphorous)	0.05	MEDIUM RISK	0.05
2.1.1.3.4 Organic chemicals (pollutants, EOCs)	0.05	MEDIUM RISK	0.05
2.1.1.3.5 Radionuclides	0.00	NO RISK	0.00
2.1.2 Water scarcity (if YES continue)	0.14		0.14
2.1.2.1 River regulation	0.05	LOW RISK	0.05
2.1.2.2 Climate (if YES continue)	0.05		0.05
2.1.2.2.1 Droughts and Rainfall event periodicity	0.05	LOW RISK	0.05
2.1.2.3 Availability of water from waste water treatment plant	0.05	LOW RISK	0.05

OPERATIONAL PROCESSES	DEFAULT VALUES	CATEGORY DEFAULT VALUES	USER VALUES
1. NON-TECHNICAL CONSTRAINTS	0.80		0.80
1.1 Legal constraints	0.23		0.23
1.1.1 Territorial constraints	0.14		0.14
1.1.1.1 European	0.05	LOW RISK	0.05
1.1.1.2 National	0.05	LOW RISK	0.05
1.1.1.3 Regional/Local	0.05	LOW RISK	0.05
1.1.2 Scope of legislation	0.10		0.10
1.1.2.1 Health legislation	0.05	LOW RISK	0.05
1.1.2.2 Others	0.05	LOW RISK	0.05
1.2 Economic constraints	0.33		0.33
1.2.1 Macroeconomic constraints	0.05	LOW RISK	0.05
1.2.2 Microeconomic constraints	0.29		0.29
1.2.2.1 Not enough water to recharge due to other economical uses	0.11		0.11
1.2.2.1.1 Industrial use	0.05	MEDIUM RISK	0.05
1.2.2.1.2 Agricultural use	0.05	MEDIUM RISK	0.05
1.2.2.1.3 Domestic use	0.01	LOW RISK	0.01
1.2.2.2 Cost restriction	0.21		0.21
1.2.2.2.1 Low price of water	0.01	MEDIUM RISK	0.01
1.2.2.2.2 High installation cost	0.01	MEDIUM RISK	0.01
1.2.2.2.3 High maintenance cost/maintenance requirements	0.20	HIGH RISK	0.20
1.2.2.3 Lack of private/public funding	FALSE	LOW RISK	FALSE
1.3 Social unacceptance	0.34		0.34
1.3.1 Health risk perception	0.05	LOW RISK	0.05
1.3.2 High cost perception	0.05	LOW RISK	0.05
1.3.3 Behavioral requirements	0.05	LOW RISK	0.05
1.3.4 Children surveillance	0.10	MEDIUM RISK	0.10
1.3.5 Fair distribution of treated water	0.10	MEDIUM RISK	0.10
1.3.6 Perception of effectiveness	0.05	LOW RISK	0.05
1.4 Governance	0.43		0.43
1.4.1 Lack of coordination	0.40	HIGH RISK	0.40
1.4.2 Non-technical knowledge	0.05	LOW RISK	0.05
2. TECHNICAL CONSTRAINTS	1.00		1.00
2.1 Structural Damages (if YES continue)	0.12		0.12
2.1.1 Flooding	0.01	LOW RISK	0.01
2.1.2 Natural hazards (e.g. earthquake)	0.00	LOW RISK	0.00
2.1.3 Terrorism activities/Vandalism	0.05	LOW RISK	0.05
2.1.4 Civil work failures (if YES continue)	0.07		0.07
2.1.4.1 Slope stability	0.01	LOW RISK	0.01
2.1.4.2 Pipe breakage	0.05	LOW RISK	0.05
2.1.4.3 Others	0.01	LOW RISK	0.01
2.1.5 Aquifer dissolution (e.g. in karstic aquifer)	0.00	NO RISK	0.00
2.2 Not enough water recharged (if YES continue)	0.91		0.91
2.2.1 Low quality water (if YES continue)	0.50		0.50
2.2.1.1 Sanitary/biological restrictions (e.g. due the pathogens)	0.10	MEDIUM RISK	0.10
2.2.1.2 Physical restrictions (if YES continue)	0.40		0.40
2.2.1.2.1 Turbidity/particles	0.40	HIGH RISK	0.40
2.2.1.3 Chemical restrictions (if YES continue)	0.07		0.07
2.2.1.3.1 Metals (e.g. arsenic, manganese)	0.00	NO RISK	0.00

Figure S2.13. Results (upper part) sheet visualization.



THESE RESULTS SHOW THE DIFFERENT PROBABILITIES OF THE COMPONENTS OF THE WHOLE FAULT TREE. IN THIS CASE THE RESULTS ARE EXPRESSED USING PERCENTAGES AND CLASSIFYNG THE RESULTS IN 4 RISK CATEGORIES

OPERATIONAL PROCESSES	DEFAULT VALUES	CATEGORY DEFAULT VALUES	USER VALUES
1. NON-TECHNICAL CONSTRAINTS	0,99954749	FALSE	1.00
1.1 Legal constraints	0,93084	FALSE	0.93
1.1.1 Territorial constraints	0,904	FALSE	0.90
1.1.1.1 European	0,2	LOW RISK	0.20
1.1.1.2 National	0,6	MEDIUM RISK	0.60
1.1.1.3 Regional/Local	0,7	HIGH RISK	0.70
1.1.2 Scope of legislation	0,29	FALSE	0.29
1.1.2.1 Health legislation	0	NO RISK	0.00
1.1.2.2 Others	0,29	LOW RISK	0.29

THE USER HAS THE OPTION TO ENTRY HIS/HER OWN DATA BY MODIFYING THE USER VALUES COLUMN (GREEN CIRCLE). IF THAT COLUMN IS LEFT UNCHANGED, THE DEFAULT VALUES FROM THE A PRIORI CRITERIA WILL BE USED (THIS WILL BE INDICATED WITH THE COLOUR RED IN THE CELL FILL AND THE VALUES COLOUR). THE COLUMN CATEGORY DEFAULT VALUES (BLUE CIRCLE) INDICATES THE CUALITATIVE PERCEPTION OF THE RISK THAT THE USER HAS USED IN THE INPUT STAGE WITH CROSSES

Figure S2.14. *Results (bottom part) sheet visualization.*

The fourth step of the MAR-RISKAPP is the graphical results (Figure S3.10), displaying the numerical results shown in the previous step into graphs and tables. This step is divided into four points: 1) Operational pivot-table results (Figure S3.11), 2) Design and construction pivot-table results (Figure S3.12), 3) Operational fault tree (Figure S3.13) and 4) Design and construction fault tree (Figure S3.14). As in the other steps, there is a button with instructions, only if the user needs some help or orientation with the results from this step. For both pivot-tables, the results are structured in four categories of risk (high, medium, low, and no-risk). Inside each category, risk values are displayed in decreasing order (from high to low risk values). Also, both pivot-tables have a button to go back to the graphical results main sheet. For both fault trees, each point from the survey is presented by using a rectangle. For each point, risk value is showed on the bottom-left part of the rectangle and also is coloured according to risk categories. Finally, both fault-trees have a button to go back to the graphical results main sheet and a button to print the fault tree in a PDF file.

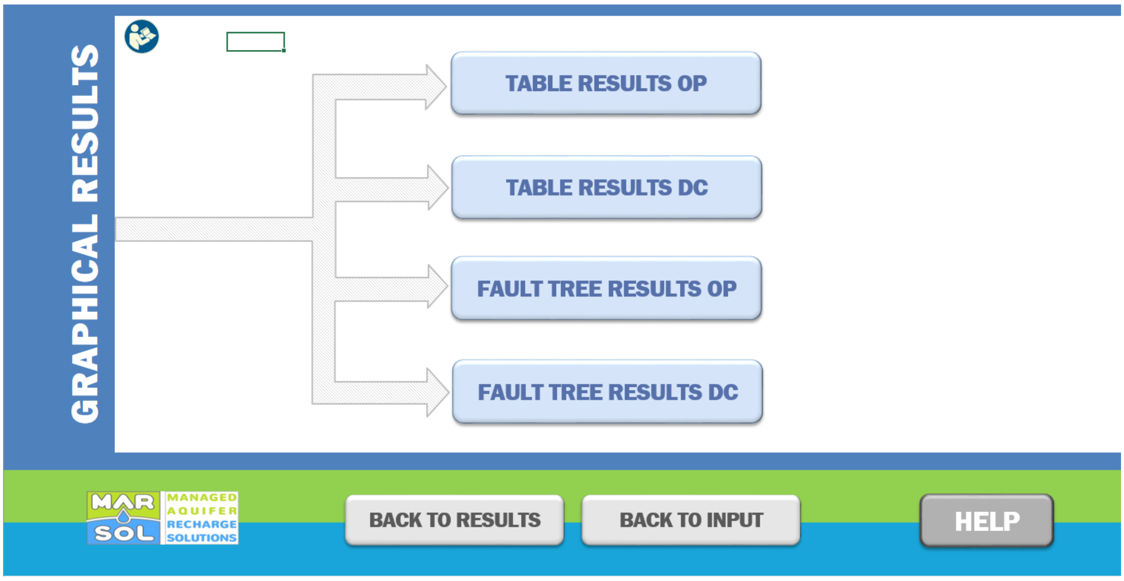
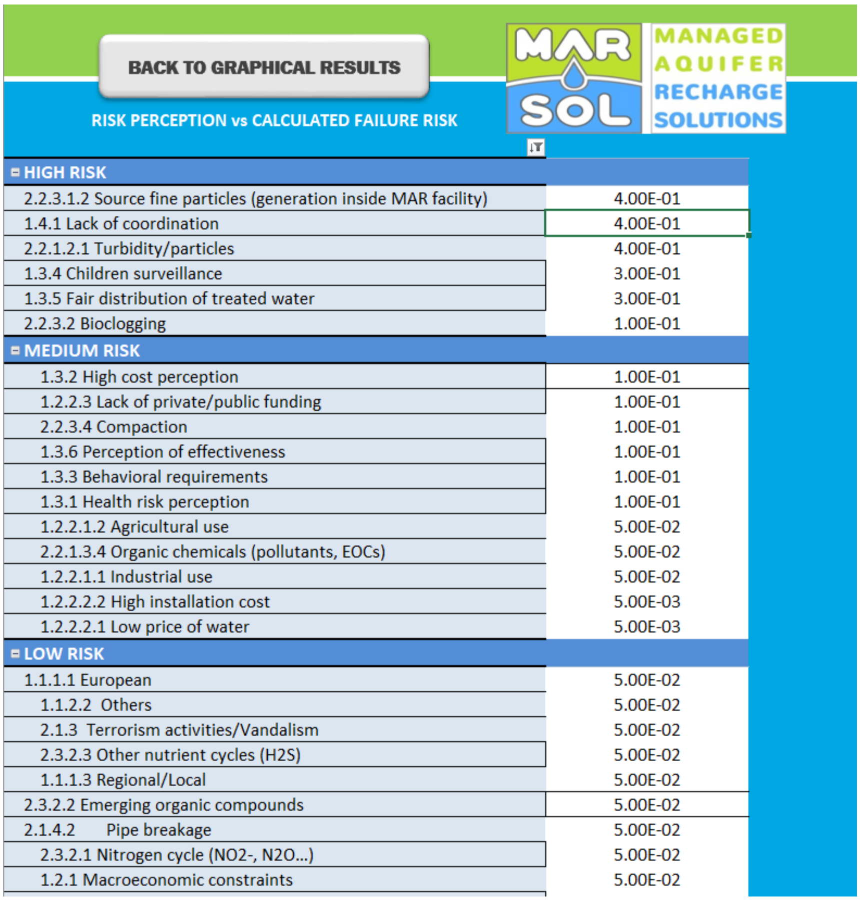


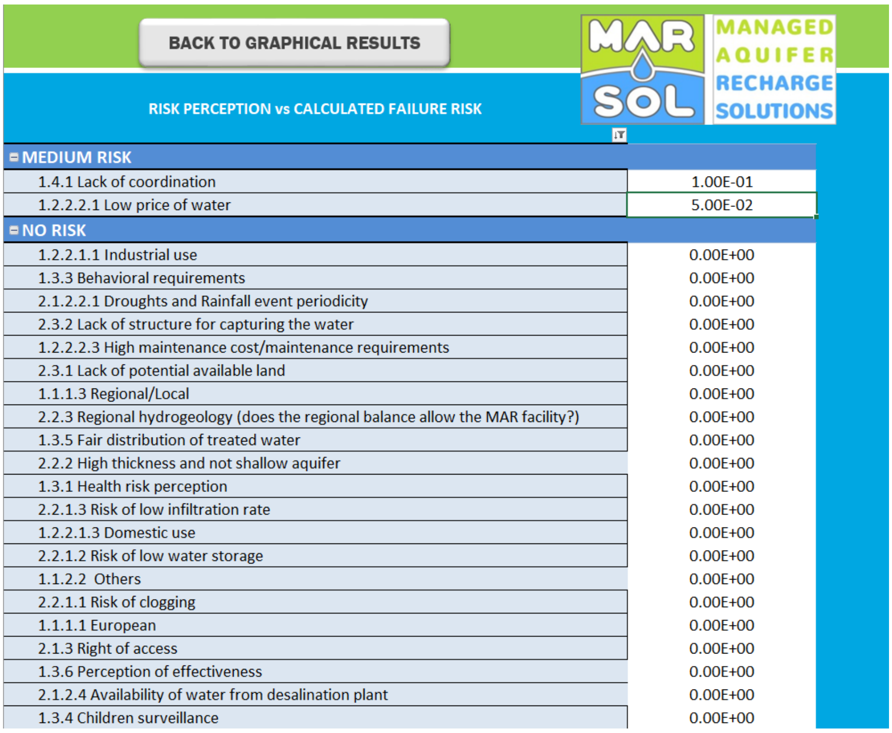
Figure S2.15. *Graphical results sheet visualization.*



RISK PERCEPTION vs CALCULATED FAILURE RISK

⊟ HIGH RISK	
2.2.3.1.2 Source fine particles (generation inside MAR facility)	4.00E-01
1.4.1 Lack of coordination	4.00E-01
2.2.1.2.1 Turbidity/particles	4.00E-01
1.3.4 Children surveillance	3.00E-01
1.3.5 Fair distribution of treated water	3.00E-01
2.2.3.2 Bioclogging	1.00E-01
⊟ MEDIUM RISK	
1.3.2 High cost perception	1.00E-01
1.2.2.3 Lack of private/public funding	1.00E-01
2.2.3.4 Compaction	1.00E-01
1.3.6 Perception of effectiveness	1.00E-01
1.3.3 Behavioral requirements	1.00E-01
1.3.1 Health risk perception	1.00E-01
1.2.2.1.2 Agricultural use	5.00E-02
2.2.1.3.4 Organic chemicals (pollutants, EOCs)	5.00E-02
1.2.2.1.1 Industrial use	5.00E-02
1.2.2.2.2 High installation cost	5.00E-03
1.2.2.2.1 Low price of water	5.00E-03
⊟ LOW RISK	
1.1.1.1 European	5.00E-02
1.1.2.2 Others	5.00E-02
2.1.3 Terrorism activities/Vandalism	5.00E-02
2.3.2.3 Other nutrient cycles (H2S)	5.00E-02
1.1.1.3 Regional/Local	5.00E-02
2.3.2.2 Emerging organic compounds	5.00E-02
2.1.4.2 Pipe breakage	5.00E-02
2.3.2.1 Nitrogen cycle (NO2-, N2O...)	5.00E-02
1.2.1 Macroeconomic constraints	5.00E-02

Figure S2.16. *Operational pivot-table results sheet visualization.*



RISK PERCEPTION vs CALCULATED FAILURE RISK

⊟ MEDIUM RISK	
1.4.1 Lack of coordination	1.00E-01
1.2.2.2.1 Low price of water	5.00E-02
⊟ NO RISK	
1.2.2.1.1 Industrial use	0.00E+00
1.3.3 Behavioral requirements	0.00E+00
2.1.2.2.1 Droughts and Rainfall event periodicity	0.00E+00
2.3.2 Lack of structure for capturing the water	0.00E+00
1.2.2.2.3 High maintenance cost/maintenance requirements	0.00E+00
2.3.1 Lack of potential available land	0.00E+00
1.1.1.3 Regional/Local	0.00E+00
2.2.3 Regional hydrogeology (does the regional balance allow the MAR facility?)	0.00E+00
1.3.5 Fair distribution of treated water	0.00E+00
2.2.2 High thickness and not shallow aquifer	0.00E+00
1.3.1 Health risk perception	0.00E+00
2.2.1.3 Risk of low infiltration rate	0.00E+00
1.2.2.1.3 Domestic use	0.00E+00
2.2.1.2 Risk of low water storage	0.00E+00
1.1.2.2 Others	0.00E+00
2.2.1.1 Risk of clogging	0.00E+00
1.1.1.1 European	0.00E+00
2.1.3 Right of access	0.00E+00
1.3.6 Perception of effectiveness	0.00E+00
2.1.2.4 Availability of water from desalination plant	0.00E+00
1.3.4 Children surveillance	0.00E+00

Figure S2.17. *Design and construction pivot-table results sheet visualization.*

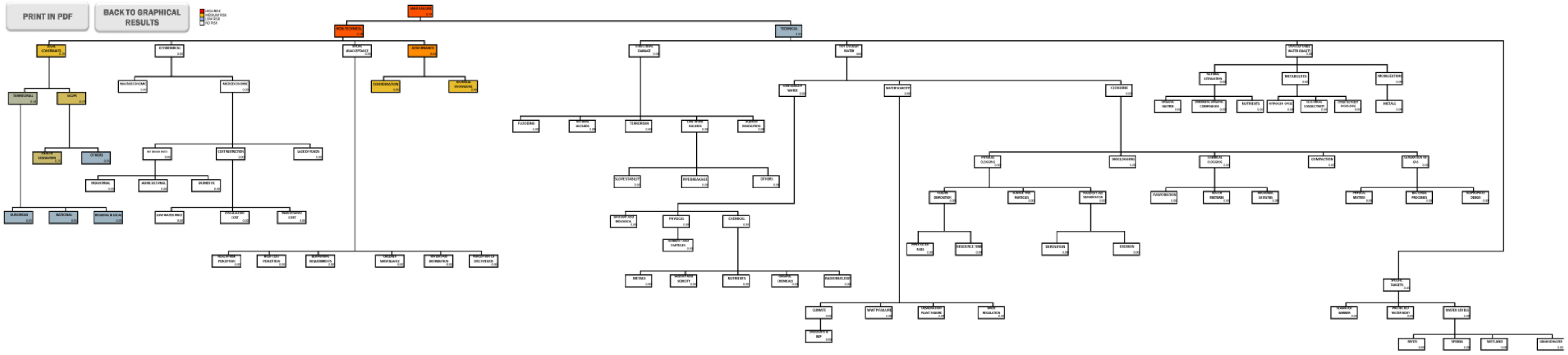


Figure S2.18. Operational fault-tree results sheet visualization.

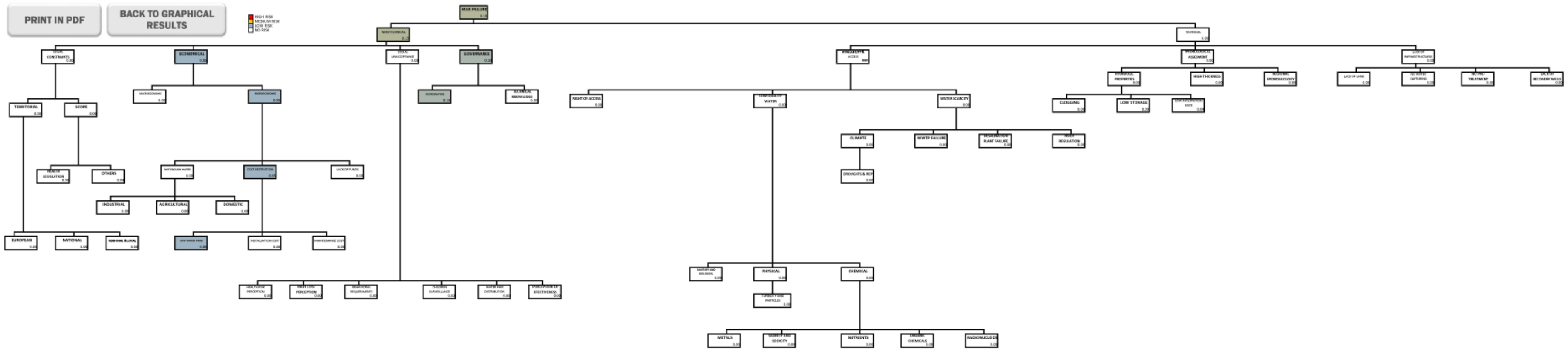


Figure S2.19. *Design and construction sheet visualization.*

Appendix for Chapter 3

Column experiment details (Modrzyński et al, 2021)

1. Barrier materials and packing

The barriers used in the study were made of sand mixed with compost (organic matter contents of 0.6% and 25.5%, and pH of 8.4 and 7.8, respectively; pH measured with deionized water in proportion of material:water of 1:2.5). The materials originated from a field-trial MAR facility in Palamós, Spain (Valhondo et al., 2020). The non-commercial compost material was produced by a local farmer by mixing green and brown crop residues in the area. The purpose of our study, however, was not to closely mimic this field site, but to disclose the effect of compost amended reactive barriers on pollutant removal processes occurring in the top layer of a constructed MAR facility. As always with model systems, some parameters will differ from those under field conditions. In our case these could include fluctuations in infiltration rate, pollutant concentration and temperature.

The barriers were created by packing Plexiglas columns (see below) with either pure sand, or a mixture of sand with 10% or 50% compost (v/v; Figure 1). On top of each barrier, a layer of sand was added, to prevent floating of any components of the barrier like e.g. plant material. The bottom of each column, beneath the barrier, was packed with a layer of coarse quartz sand, to ensure homogeneous outflow of the columns, and reduce risk of clogging. All columns were wet-packed (columns filled with water before adding barrier) to avoid capture of air bubbles.

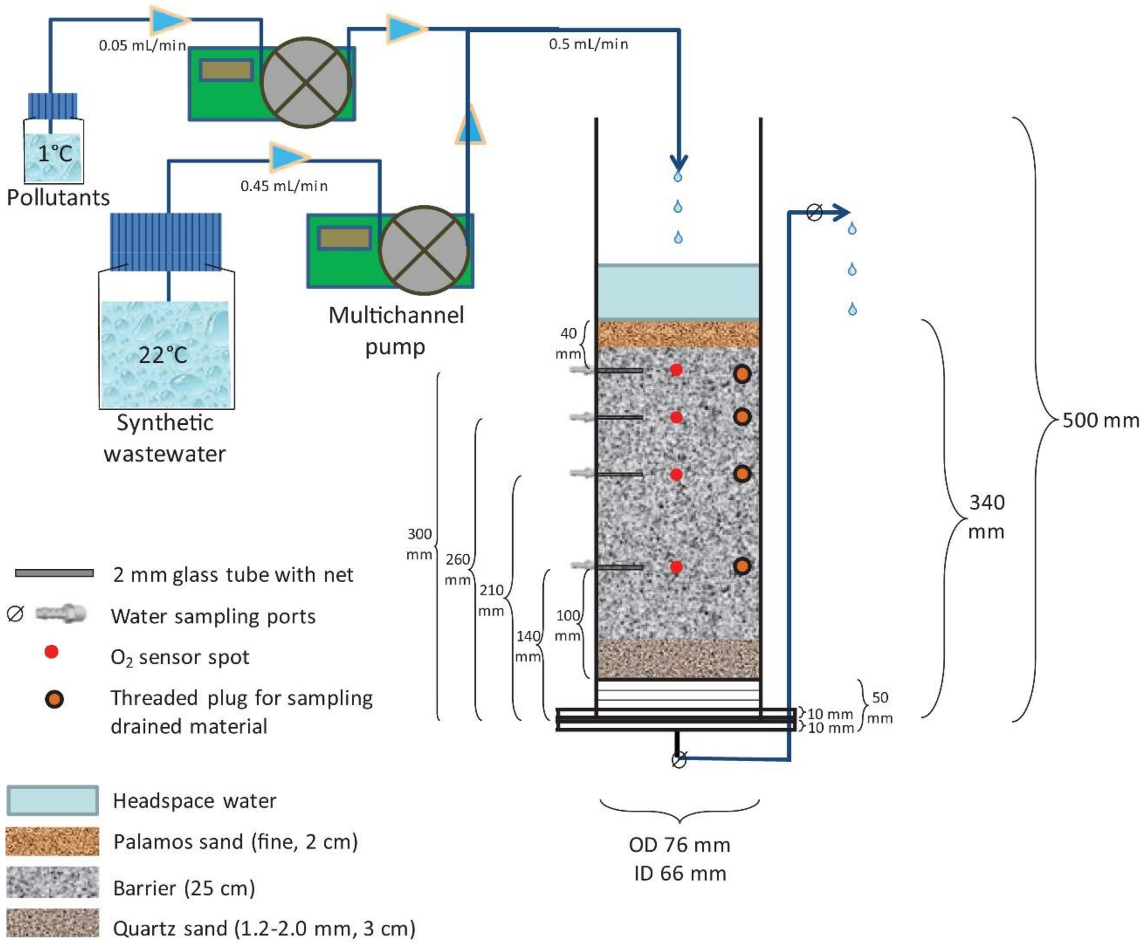


Figure S3.1. Schematic presentation of the column system.

2. Column conditions

The columns were equipped with side ports allowing for sampling of water and barrier material, as well as oxygen sensors (PreSense, Germany) located at 4, 8, 13 and 20 cm depth below the top of the barrier (Fig. 1). Inoculation (microbial seeding) of selected barriers was done with fresh activated sludge from a local wastewater treatment plant (Biofos Lynetten, Copenhagen) by passing 1 L of a decanted fraction through the columns over 10 h at 1.67 mL/min.

Duplicate columns were prepared for each of the five treatments: 1) sand, inoculated; 2) 10% compost, inoculated; 3) 50% compost, inoculated; 4) sand, not inoculated; and 5) 10% compost, not inoculated. The columns were operated for 17 weeks in the dark at 22 °C. The flow was a top to bottom gravity flow of 0.5 mL/min, resulting in an empty-bed residence time of approximately 30 h in the barrier (33 h including the quartz sand at the outlet). The columns were fed with a synthetic treated wastewater solution composed of two separate solutions mixed in a ratio of 9:1 at the columns inlet to obtain the desired final concentrations (Table S1). The first solutions contained phosphate buffer (3 mM, pH 7.5) and essential micronutrients, and was kept at 22 °C. The other solution was a mixture of ammonium as the sole source of N (2 mg N/L), yeast extract (1.5 mg DOC/L; Difco) and humic acids (2 mg DOC/L; humic acid sodium salt, Sigma-Aldrich) serving as organic carbon sources, and five OMPs (Table S1, spiked to 1 µg/L each except of paracetamol that was spiked to 2 µg/L), prepared at sterile conditions, kept at 1 °C and exchanged weekly to prevent biodegradation. The latter solution was transferred with tubes made of polytetrafluoroethylen (PTFE, Teflon®) and Viton (passing through peristaltic pump) to prevent sorption of OMPs; otherwise, polyethylene and silicone tubing was used. The composition of the synthetic wastewater effluent was based on analyses of N species and inorganic elements in samples of secondary effluent from wastewater treatment plants in Copenhagen, Denmark (Lynetten) and Palamós, Spain. The concentration of OMPs was chosen to be representative of typical OMP concentrations in treated wastewater. The concentrations were not expected to affect the microbial communities in the barrier, as even for antibiotics, minimal selective concentrations are normally much higher than 1 µg/L (Stanton et al., 2020) and specifically for sulfonamide antibiotics such as sulfamethoxazole, effect concentrations are reported to be orders of magnitudes higher (Bengtsson-Palme and Larsson, 2016).

A tracer test with tritiated water (3H2O, Moravek, USA) was conducted before pollutants and organic matter was included in the influent by applying a flow of 0.5 mL/min just after packing the columns. The headspace water level was then lowered to 1 mm above the column material and 600 µL 3H2O (3 × 106 DPM/mL) was distributed across the surface. Outlet fractions of 7 mL were then collected in a fraction collector for 56 h and 3H2O in selected fractions were quantified by liquid scintillation counting of 1 mL subsamples (Tri-Carb 2810 TR, PerkinElmer). The tracer test was repeated just before termination of the experiment (after the last sampling of water but before disassembling the columns and splitting the column material).

The flow through in the barrier material was controlled by gravity in the columns like in full-scale MAR systems. Clogging was checked by measuring the height of the water column above the barrier while keeping the outflow level constant. Except for some clogging in the outlet tubes of the 50% compost columns, clogging was not a big issue. However, there was an increase in headspace height and hence a decreased ability for the water to pass the barrier over time in five of the 10 columns. The columns with increased headspace height represented all barrier compositions (and treatments) and it is therefore not possible to conclude how the tested barrier compositions affect clogging tendencies relative to one another.

3. Sampling and analyses

a. Quantification of organic micropollutants

All OMPs and internal standards were or analytical purity grade ((≥98%). The stock solutions of the OMPs were prepared in HPLC-grade acetonitrile or methanol and the working solution was stored at −20 °C. Diluted working solutions were prepared on daily basis, and kept refrigerated up to 48 h.

For OMPs quantification, 10 mL of sample was taken into baked glass vials, spiked with 20 µl internal standard mix (to reach 1 µg/L in the final sample) and acidified with H2SO4 to pH = 6.0. The samples were processed on solid-phase extraction (SPE) cartridges (HLB Oasis 60 mg, Waters) conditioned with 2 mL methanol and 2 × 2 mL milliQ water. After loading, the samples were passed through the cartridge at 1 mL/min, followed by 2 mL milliQ water and cartridge drying under vacuum for 3 min. Elution was done with 2 × 1.5 mL methanol at 1 mL/min. The collected eluent was dried under a nitrogen stream at 30 °C. The samples were reconstituted in 0.2 mL methanol and 0.8 mL of 2 mM ammonium acetate (pH = 5.0). OMPs were quantified using ultra-high-pressure liquid chromatography tandem mass spectrometry (Supplementary section 2).

b. N-species quantification

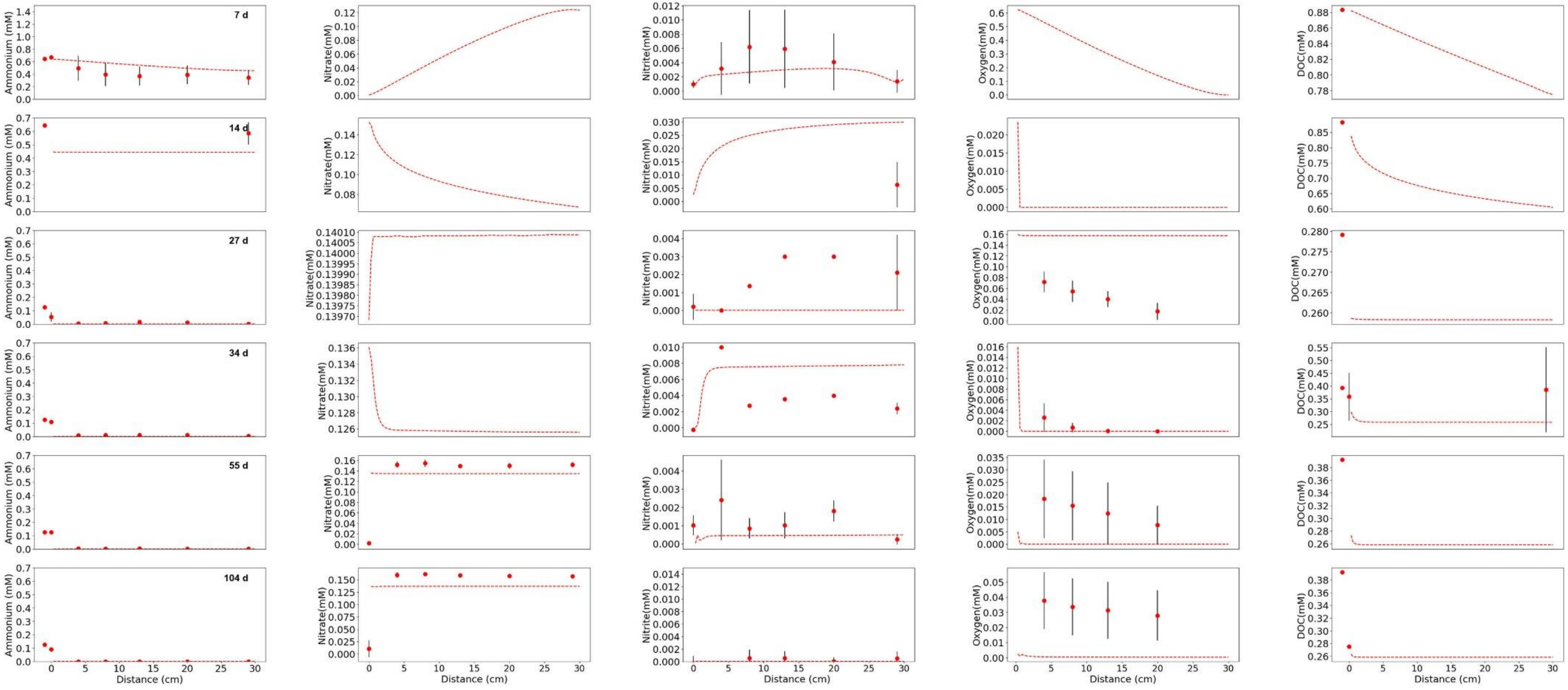
Spectrophotometric kits were used to analyze ammonium (Merck Spectroquant 1.14752, Merck KGaA, Germany) and nitrite (Merck Spectroquant 1.14776) on a spectrophotometer (UV-1800, Shimadzu, Japan). The limits of quantification derived from standard curves in tap water and milliQ water were 0.02 mg/L ammonium-N and 0.01 mg/L nitrite-N. Nitrate was analyzed by anion chromatography (Metrohm 819 IC detector with a Metrosep A 150/4.0 column, Metrohm, Switzerland) with a limit of quantification of 0.01 mg/L nitrate-N. Ammonium and nitrite samples were stored cold and analyzed on the day of sampling while nitrate samples were kept frozen until analysis.

c. DNA extraction and quantitative PCR analysis

For DNA extraction, samples of barrier material were taken from drained columns using threaded side ports (Fig. 1). Samples of ~0.3 g were stored in DNA- and DNase-free tubes at −20 °C until extraction. DNA was extracted using the Dneasy PowerSoil kit (Qiagen, Germany) and a Precellys homogenizer (Bertin Instruments, France) set at 5500 rpm, 2 × 30 s. The concentration of DNA was quantified using a Qubit Fluorometer (Invitrogen, CA, US), and quality was verified by gel electrophoresis. To determine the genetic potential for ammonium oxidation by bacteria and archaea as well as complete ammonium oxidation (comammox), denitrification, and dissimilatory nitrate reduction to ammonium (DNRA), the abundances of the functional genes amoA (ammonium monooxygenase in ammonium oxidizing bacteria and archaea (AOB and AOA)), comammox amoA, clade A and B (in comammox bacteria), nirK and nirS (dissimilatory nitrite reductase, denitrification), and nrfA (ammonium forming nitrite reductase, DNRA) were measured by quantitative PCR (qPCR). The abundance of total bacteria was determined by qPCR of the 16S rRNA gene. The qPCRs were performed in independent duplicate runs containing 0.4–1 ng template DNA, iQ SYBR Green Supermix (Bio-Rad, CA, USA) and 0.1% BSA in a total reaction volume of 15 µl. Information about primer sequences and concentrations and thermal cycling conditions can be found in Table S4. Standard curves were based on serial dilutions of linearized plasmids containing fragments of the specific genes. To exclude the possibility of PCR inhibition, a plasmid specific qPCR assay with T7 and SP6 primers was performed containing the pGEM-T plasmid (Promega, WI, USA) together with sample DNA. Inhibition of the PCR reaction was not detected.

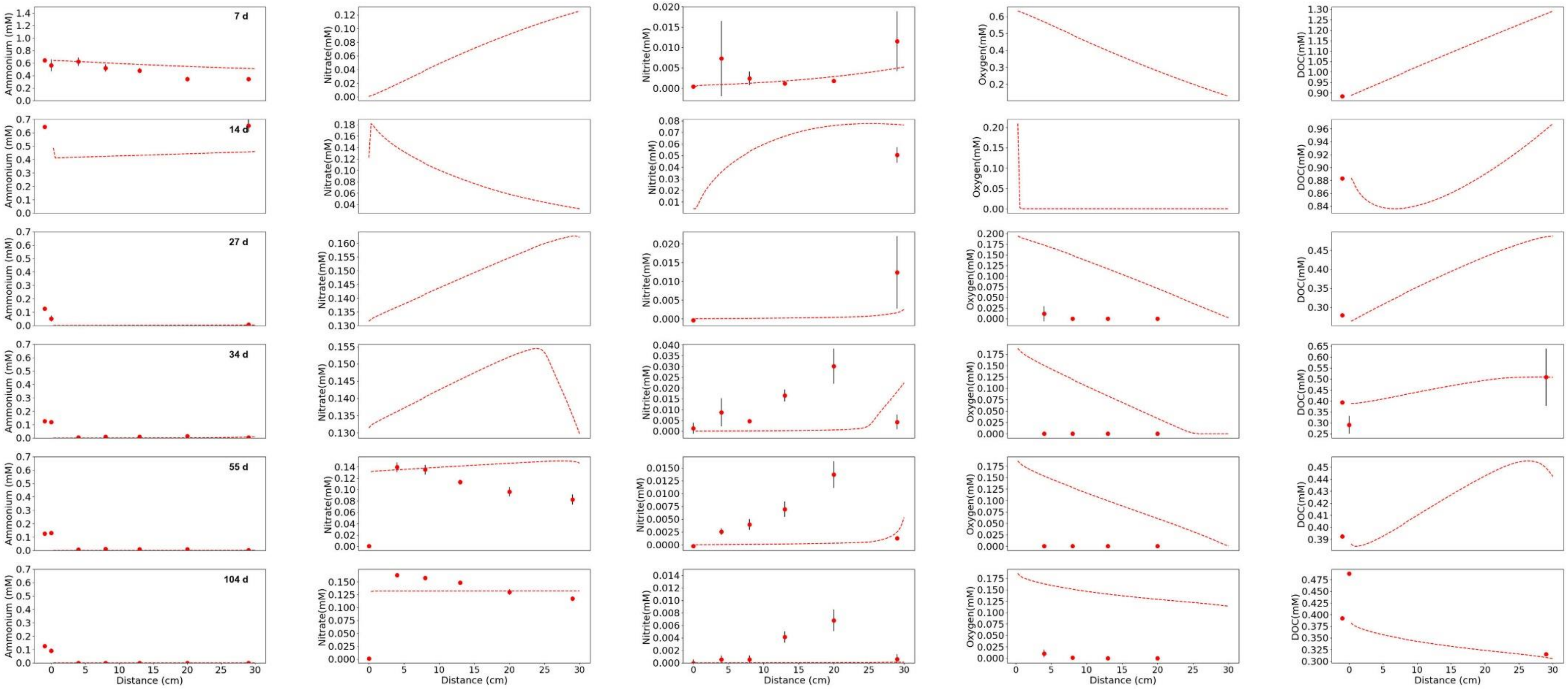
Appendix for Chapter 3

Figures with profile information



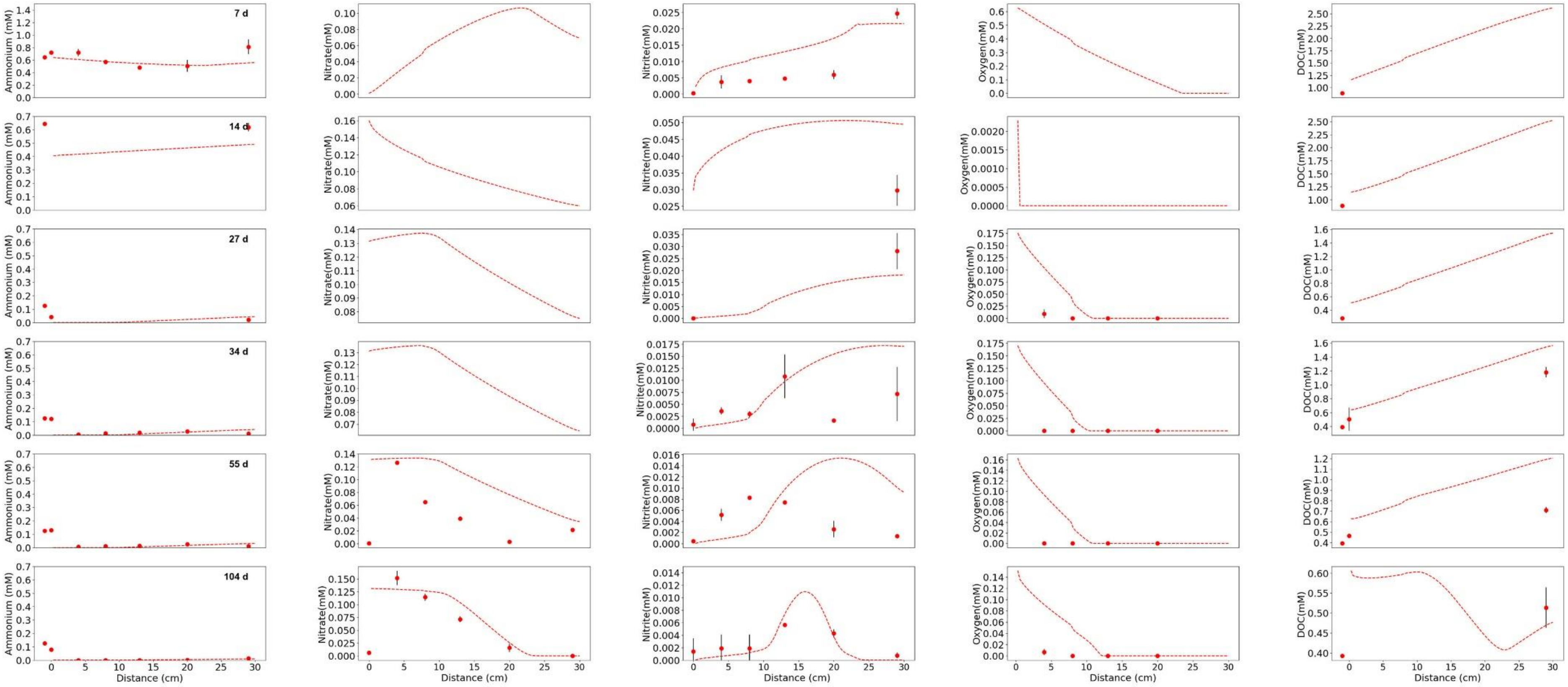
Nutrient profile data (points) and model results (dashed lines) for 100% sand column data.

Figure S4.1. Nutrient profile data (points) and model results (dashed lines) for 100% sand column data.



Nutrient profile data (points) and model results (dashed lines) for 10% compost column data.

Figure S4.2. Nutrient profile data (points) and model results (dashed lines) for 10% compost column data.



Nutrient profile data (points) and model results (dashed lines) for 50% compost column data.

Figure S4.3. Nutrient profile data (points) and model results (dashed lines) for 50% compost column data.

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