MARSoluT
Managed Aquifer Recharge ITN

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MARSoluT

Managed Aquifer Recharge Solutions Training Network

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Contents

Executive Summary **6**

1. Introduction **8**

2. Objectives **10**

3. Review of Regulations and Guidelines Concerning Water Quality for MAR **11**

3.1 International level **12**

3.1.1 The Water Framework Directive (2000/60/CE, WFD) 12

3.1.2 World Health Organization (WHO) 13

3.1.3 European guidelines for water reuse 13

3.2 National level **14**

3.2.1 Brazil 14

3.2.2 Chile 14

3.2.3 Italy 15

3.2.4 Mexico 15

3.2.5 Portugal 15

3.2.6 Thailand 16

3.2.7 The Netherlands 16

3.2.8 USA 16

3.3 Regional level **16**

3.3.1 Arizona (USA) 16

3.3.2 California (USA) 17

3.3.3 Florida (USA) 17

3.4 Local level **17**

3.4.1 Torreele (Belgium) 17

3.4.2 Windhoek (Namibia) 17

3.4.3 The Shafdan (Israel) 18

3.5 Spanish level **18**

3.5.1 MAR in Spain 18

3.5.2 Wastewater reuse in Spain 19

3.6 Analysis of water quality control **25**

4. Modern Water Quality Challenges for Managed Aquifer Recharge 28

4.1 Current context for MAR water quality issues 28

4.2 Towards a risk-based approach 28

4.3 Historical background 29

4.4 The way forward 31

5. Recommendations and Conceptual Models to Regulate Water Quality for MAR 33

5.1 Considerations on the removal of organic pollutants from water during MAR 33

5.2 Recommendations 36

5.2.1 Regulatory framework 36
5.2.2 Water quality standards 38

5.3 Monitored and Intentional Recharge (MIR) 41

5.3.1 Water sources 43
5.3.2 Hydrogeological and environmental conditions 43
5.3.3 MAR Technology 44
5.3.4 MAR Sensors for data gathering 46
5.3.5 Monitoring guidelines 47
5.3.6 Final use of the intentionally recharged water 48
5.3.7 Analytical aspects 48
5.3.8 Risk and/or impact assessment 49
5.3.9 Other aspects and general recommendations 49

6. Water Quality Characterization in MAR and SAT-MAR Sites in Spain 50

6.1 Methodology 50

6.1.1 Evaluation of water quality at Spanish MAR sites 50
6.1.2 Comparison of MAR water sources with MAC-based standards 50

6.2 Evaluation of water quality at Spanish MAR sites 57

6.2.1 The Arabayona MAR site (Salamanca, Spain) 57
6.2.2 The Canal Isabel II ASR Sites (Madrid, Spain) 58
6.2.3 The Careos (Granada, Spain) 59
6.2.4 The Cobre de Las Cruces Copper Mine (Seville, Spain) 61
6.2.5 The El Port de La Selva MAR site (Gerona, Spain) 63
6.2.6 The Guadiana MAR canal (Ciudad Real, Spain) 66

6.2.7 The Los Arenales MAR sites (Segovia and Valladolid, Spain) 67

6.2.8 Mallorca experimental SAT-MAR site (Balearic Islands, Spain)................................ 70

6.5.9 The Sant Vicenç dels Horts MAR site (Barcelona, Spain) 72

6.5.10 The Tenerife pilot SAT-MAR site (Canary Islands, Spain) 74

6.5.11 The Zorrilla urban water buffer (Valladolid, Spain)... 75

6.6 Variability of water quality across MAR sites 77

6.7 Comparison of MAR water sources with MAC-based standards 78

6.8 Preliminary conclusions.. 81

7. Review of Low-cost Techniques to Improve Water Quality in MAR Systems: The Potential of the Biochar 82

8. Conclusions and Recommendations 84

9. References 89

9.1 Literature.. 89

9.2 Web accesses.. 97

Annex 1

Assessing the Potential of Biochar for MAR.. 98

1. Previous studies.. 98

2. Biochar production process 102

2.1 Pre-treatment... 102

2.2 Thermal carbonisation 102

2.3 Post-treatment 104

2.4 Atmospheric modifications and ageing... 105

2.5 Feedstock.. 106

3. Characteristics of biochar 107

3.1 Physical properties 107

3.2 Chemical properties and composition 107

4. Application of biochar to water purification and soil remediation 111

4.1 Heavy metal removal from contaminated water.. 112

4.2 Heavy metal(loids) removal from soils... 115

4.3 Removal of nitrogen and phosphorus from water... 118

4.4 Removal of organic compounds from water... 120

4.6 Removal of organic compounds from soils 124
4.7 Impact of biochar on soil infiltration rate and hydraulic conductivity 125
4.8 Other factors influencing water purification through biochar 125
5. Identified gaps and opportunities 126
6. References 126

Executive Summary

Managed Aquifer Recharge (MAR) is a promising technique for water management. It comprises a group of technologies that enhance the infiltration of various water sources into aquifers. The water stored underground can serve different uses, such as irrigation, industrial and drinking water supply, and the recovery or preservation of environmental assets. Globally, water resources are increasingly under pressure. MAR offers the potential to buffer water resource availability and meet demands in periods of water scarcity. Consequently, the uptake of this technique will likely soar in the next decades due to current pressure on water resources and the consequences of climate change, requiring highly trained practitioners that can provide the knowledge and know-how on MAR implementation. The present report is part of the Managed Aquifer Recharge Solution Training Network (MARSoluT ITN, 2019-2023), which aimed to train experts in MAR.

The report deals with the objectives of work package four (WP4) of the MARSoluT project and aims at helping to improve water quality by optimising MAR design at active MAR sites in Spain. The report tackles four knowledge gaps on MAR in relation to water quality: (i) the need for a review of current regulations on MAR and how they use Maximum Allowable Concentrations (MACs) to prevent water pollution during MAR; (ii) a discussion on the current challenges for MAR water quality; (iii) the lack of a conceptual model that can help in the creation of regulation, rules, and guidelines on MAR; and (iv) the need for testing the efficacy of MACs at the national level with a focus on Spain.

Although this report focuses on Spain, it does not restrict its development to this country and has a relatively broad scope, providing solutions for MAR worldwide. The methodologies in the current report are mostly based on literature review of scientific, technical and regulatory documents and the exploitation of published and unpublished water quality analyses and water quality standards involving MAR.

For the first knowledge gap, a comprehensive review of existing regulations and guidelines for MAR was conducted, and an analysis of MACs in water quality standards from diverse sources globally was completed. To respond to the second knowledge gap, a discussion on modern water quality challenges for MAR is provided, including the context, history, future and the need for a risk-based approach.

The Monitored and Intentional Recharge (MIR) conceptual model is a response to knowledge gap three, comprising a set of nine blocks that elaborates on the most critical aspects that must be considered to draft MAR regulations and guidelines. This section also entails a series of recommendations directed to future regulations on MAR, including developing a common terminology with legal implications, considering a permitting process, new legal development, the inclusion of budgetary aspects, regard to the technical background for authorisation, and the fact that water standards for MAR must be designed at the aquifer level.

The fourth knowledge gap was addressed through an analysis of source water quality in MAR sites in Spain and a comparison between them and three European MAC-based standards (Italy, Spain, and the Netherlands) to evaluate the efficacy of MAC in dealing with water pollution at MAR sites. This section showed the high variability in terms of water quality at 11 MAR sites and the inadequacy of MAC-based standards to control pollution while allowing for MAR implementation at the national or European levels. This sort of standard could be useful aquifer-wide. This analysis also concluded that focus on quality should be given to the final quality of the water after MAR rather than the original

water quality, and that the attenuation processes in the saturated and unsaturated zones should be regarded. Finally, biochar, a promising low-cost material to remove multiple pollutants during MAR, has been thoroughly studied.

This report also emphasises that, nowadays, MAR is an option, but in the future will likely become a necessity, and that there is a need to continue investing in (1) applied research to improve insights into the development of freshwater cones in saline environments, (2) define measures to increase the efficiency of MAR systems and social acceptance, and (3), consider the beneficial impact of the unsaturated and saturated zones.

1. Introduction

The MARSoluT Interactive Training Network (ITN) was a Marie-Skłodowska Curie doctoral network that aimed at training 12 highly skilled doctoral fellows in Managed Aquifer Recharge (MAR). This goal materialises through PhD theses developed with member and partner institutions. The main objective of all the PhD candidate's research is to provide scientific and technical solutions for MAR.

The PhD candidates' research has also been grouped into four work packages (WPs) which focus on different aspects of MAR, including sustaining high infiltration rates (WP1) or improving water quality for MAR (WP2). The results of the WPs are presented as deliverables submitted to the European Commission. The WPs and PhD researches give answers to knowledge gaps detected by the consortium and, in some cases, continue an active line of research started in previous projects, notably the FP7 MARSOL project (www.marsol.eu[1]). This deliverable (D4.3) is part of WP4 and deals with MAR design and construction criteria. Its specific objectives are:

1. Implementation of monitoring systems.
2. Development of a regional river basin model for scenario analyses.
3. Improving water quality by optimising MAR design at active MAR sites in Spain.
4. Statistical analysis and evaluation of long-term monitoring data and site upgrade of identified hotspots.

The objective of WP4 is reflected in the report title and aims to provide design and conceptual solutions that can help to optimise MAR performance with a focus on Spain.

Four knowledge gaps and an opportunity were identified as adequate research for MARSoluT and this report. The first knowledge gap entails the regulatory framework for MAR. In 2016, MAR was carried out in 62 countries, according to Stefan & Ansems (2018). To date, the number of countries that have created regulatory or guiding documentation for MAR is only around 16. Regulating MAR is crucial for successful experiences. An irresponsible praxis can lead to issues such as water logging and groundwater contamination. Furthermore, an issue concerning water quality and MAR is the fact that some of the existing regulatory frameworks are too stringent, deterring new projects (e.g., the Spanish regulation), or too permissive, failing to control pollution effectively.

The second knowledge gap is a sound discussion of the main modern water quality challenges for MAR and some insight into how to move forward.

The third gap addressed is the lack of guidance on the main aspects to consider when producing documents that aim to regulate or guide MAR implementation. As mentioned above, several countries have created regulations on MAR, but no documents at a higher abstraction level are available.

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[1] Accessed on 19/01/2023

The fourth gap identified is the lack of available information on the types of source water quality for MAR across Spain and whether it is adequate to regulate artificial recharge by a national standard based on maximum allowable concentrations (MACs) of critical water constituents.

The opportunity developed in this report is exploring the potential of biochar to improve water quality in MAR water-spreading methods (e.g., infiltration basins and channels). This material is relatively cheap, can be produced from easily available organic detritus and by-products, and shows great potential to remove pollutants in water and soils.

Based on these gaps and opportunities, this report develops the following research lines:

1. A review of the existing regulations and guides for MAR, with a focus on MAR. This review includes the latest topic on water quality for MAR, such as wastewater reuse and compounds of wastewater.
2. A discussion on pressing issues on water quality for MAR.
3. Recommendations and a conceptual model for creating new regulations and guides on MAR.
4. A study on the different water quality types found in Spain's source water of MAR systems.
5. A white paper on the potential of biochar for MAR will lay down the basis for future research.

The structure of the present deliverable is the following: the report starts with objectives, followed by Section 3, which deals with research line 1 and presents a review of the regulations and guidelines concerning water quality for MAR. The following section (Section 4) discusses modern water quality challenges for MAR (knowledge gap 2). Subquesently, Section 5 involves the third research line by providing recommendations for regulations and guidelines and introducing the Monitored and Intentional Recharge (MIR) conceptual model. A review of the water quality of MAR water sources in Spain (research line 4) is provided in Section 6. The literature review on biochar focusing on MAR, which corresponds to the opportunity (research line 5), is presented in Section 7 and in Annex 1. This report finalises with Conclusions and Recommendations (Section 8) and References (Section 9). The Annex fully develops the topic briefly introduced in Section 5.

2. Objectives

The main objective of this report is to help improving water quality by optimising MAR design at active MAR sites in Spain. To accomplish the aims, there are four specific objectives:

1. Reviewing the state-of-the-art in MAR regulations for water quality worldwide.
2. Providing recommendations and conceptual models that can help producing new regulation and guidelines for MAR.
3. Studying source water quality for MAR at active MAR sites in Spain.
4. Exploring the potential of biochar to improve water quality for MAR.

These targets somewhat expand the description of Deliverable D4.3's content as initially defined in the project's work plan (MARSoluT Grant Agreement).

3. Review of Regulations and Guidelines Concerning Water Quality for MAR

The first step toward proper management of MAR systems and control on water quality is the establishment of regulations and rules. The existing documents that guide and rule the operation of MAR have been reviewed in the framework of the MARSoluT project (Fernández Escalante et al. 2020, 2022). After a careful evaluation of these documents, two proposals have been developed: a series of recommendations on water quality control for artificial recharge (= MAR) (Fernández Escalante et al. 2020), and a conceptual model containing the most relevant aspects to bear into consideration when drafting MAR guidelines (Fernández Escalante et al. 2022). This section presents the preliminary analysis of MAR guiding or regulating documents. **Table 1** and **Figure 1** show the documents reviewed and their geographical distribution, respectively.

Table 1. *Regulation, guidelines and operator rules for managed aquifer recharge. Modified from Fernández Escalante et al. (2022).*

Country	Scope	Soft/hard	Type	Year	MACs	MAR techniques involved
Arizona (USA)	Regional	Hard	Guidelines	1994		ASR, basins
Australia	National	Soft	Guidelines	2009	X	ASR, basins
Brazil	National	Soft	Regulation	2019		
California (USA)	Regional	Hard	Guidelines	2012	X	ASR, SAT-MAR
Chile	National	Soft	Regulation	2013		Multiple
China	National	Soft	Guideline	2014		
Florida (USA)	Regional	Soft	Guidelines	1999	X	ASR, basins
India	National	Soft	Draft Guidelines	2014		Multiple
Italy	National	Hard	Regulation	2016	X	RBF***
Mexico	National	Hard	Regulation	2003, 2009	X	Basins
Windhoek (Namibia)	Local		Guidelines, regulation proposal	2004		Basins, interdunal, ASR
New Zealand	National		Technical guidance	2017	X	
Portugal	National	Hard	Regulation	2000		Multiple
South Africa	National	Hard	Regulation draft	2004		Basins, ASR
Spain	National	Hard	Regulation	2007	X	SAT-MAR (reuse)
Thailand	National	Hard	Guideline	2022	?	
The Netherlands	National	Hard	Regulation (under review)	1993	X	SAT-MAR, dunes, ASR
The Shafdan (Israel)	Local-National**	Hard	Operator rule	1966	X	SAT-MAR, basins
Torreele (Belgium)	Local	Hard	Operator rule	2012	X	SAT-MAR, dunes
USA	National	Soft	Regulation	1974	X	ASR, AR
WFD	International	Soft	Regulation	2000		Basins, ASR
WHO guidelines	International	Soft	Guidelines	2001		SAT-MAR(reuse)

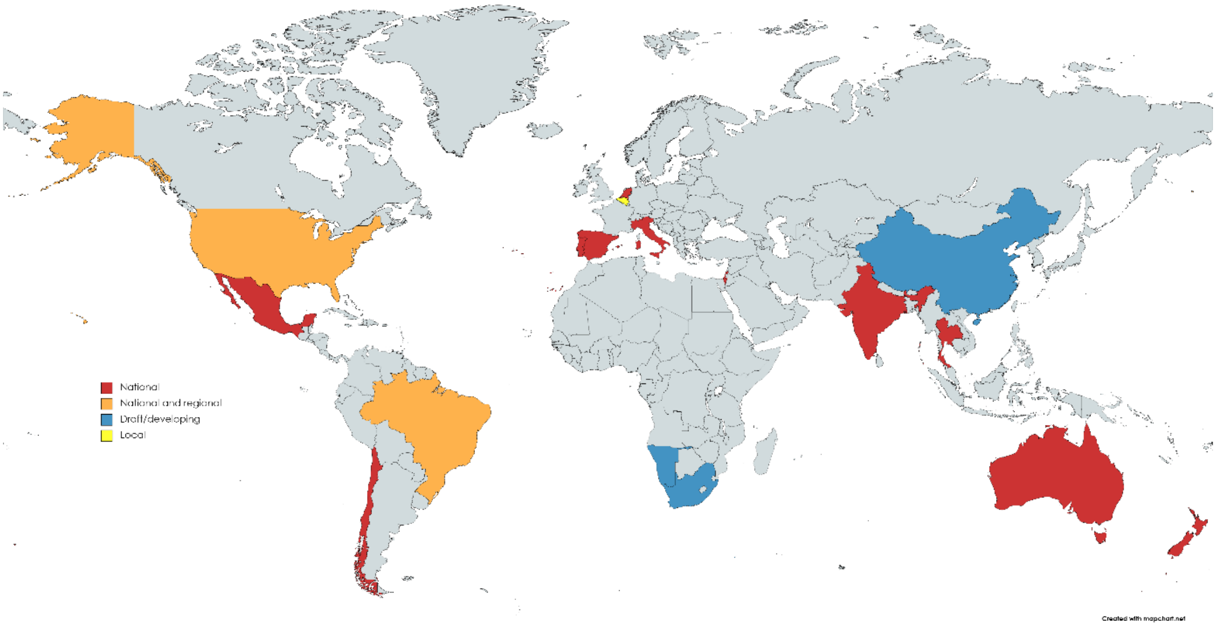

Figure 1. *Geographical distribution of countries and regions with guidelines on MAR. Modified from Fernandez Escalante et al. (2020).*

The preliminary review of documents on MAR will be structured from the international to the local levels. All text between quotation marks has been taken from Fernández Escalante et al. (2020).

3.1 International level

3.1.1 The Water Framework Directive (2000/60/CE, WFD)

"The EU has adopted a suite of legislation that aims at protecting and managing European water bodies. This task began in 1975 with a Directive 75/440/EEC on surface water quality for drinking water abstraction (Council of the European Communities 1975). Groundwater had to wait four years more to receive attention, which came with the Directive 80/68/EEC (Council of the European Communities 1979) on the protection of groundwater against pollution caused by a group of dangerous substances.

Subsequently, the WFD (2000/60/CE) set the first effort to regulate both surface water and groundwater, and their interaction. This effort was broadened through the Guidance Document 17 (European Commission 2007). The text of the 2000/60/ CE contains, at least, five direct references to "artificial recharge" and "reuse" in its articulate. The Article 11(3) (f) introduces a requirement for prior authorisation subjecting MAR to a preventive and limited assessment (in line with Article 4(1) (b) (i)) to ensure that the activity does not hamper its environmental objectives. It demands "controls, including a requirement for prior authorisation of artificial recharge or augmentation of groundwater bodies" and that "these controls shall be periodically reviewed and, where necessary, updated" (MARSOL 2015; European Commission 2012). In short, the WFD impels EU Members to achieve a good qualitative and quantitative status of groundwater bodies. Consequentially, the quality standards of water sources used for MAR are not directly, but indirectly regulated, looking at the effect of MAR on groundwater bodies.

The Groundwater Directive 2006/118/EC (European Parliament and Council of the European Union 2006), in its Article 6(3) (d), develops additional regulations in the form of an exemption to those MAR activities permitted under the WFD. It also considers MAR technologies as a possible measure to achieve the "good status" objectives for water bodies. However, the WFD does not specify implementtation strategies, or adopts a limit value approach, but provides strategies to establish good qualitative (ecological and chemical) and quantitative status of all water bodies. The WFD/GWD requires the achievement of good groundwater qualitative status, including the prohibition of local deterioration. Only a few standards available (nitrate, ammonium, iron, etc.) for MAR are regulated (MARSOL 2016a). The catalogue of priority substances in the field of water policy was released in the Directive 2013/39/CE (European Parliament and Council of the European Union 2013), which was a pioneering text regarding pollutants and water quality standards in Europe, applicable also to MAR. It also includes a document for the implementation of the Directive 91/271/EEC (Council of the European Communities 1991) concerning Urban Waste Water Treatment and possibilities for further reuse. The referred parameters form part of a "minimum list" of quality standards and threshold values, and Member States are bound, through the risk assessment undertaken as part of the development of River Basin Management Plans, to agree to the monitoring of this minimum list of parameters whenever a specific risk is identified. It should also be mentioned the Directive on Environmental Impact Assessment 85/337/EEC (2014/52/EU update) which outlines guidelines for MAR schemes larger than 10 Mm^3."

3.1.2 World Health Organization (WHO)

"The WHO Guidelines for the Safe Use of Wastewater, Excreta and Greywater, third edition, have been published in four volumes which describe policy-related issues (vol. 1), wastewater reuse in agriculture (vol. 2), and aquaculture (vol. 3) and the use of excreta and greywater in agriculture (vol. 4). These guidelines establish a framework, which allows assessing socio-cultural, environmental, economic and policy aspects of "aquifer recharge", including public health risk, risk assessment, regulation, public concerns and communication chapters, and paying special consideration to the reuse of reclaimed water (Yuan et al. 2016). Finally, they encourage countries to adapt the guidelines to "their own social, cultural, economic and environmental conditions" (Ensink & van der Hoek 2009). They are deemed as less strict than those existing in some USA states and in the EU (Yuan et al. 2016). The approach is international, and the guidelines are primarily used in developing countries and as a baseline in jurisdictions without any specific MAR regulation."

3.1.3 European guidelines for water reuse

In August 2022, the European Commission published the "Guidelines to support the application of Regulation 2020/741 on minimum requirements for water reuse" in the journal of the European Union. These guidelines "seek to facilitate and encourage the practice of reusing water for irrigation in agriculture" (European Commission 2022). The guideline provides rules for two main aspects:

- A uniform set of water quality requirements for safely using treated wastewater from urban environments in the agricultural and irrigation context. The water quality requirements in the document imply that water intended for agricultural reuse must undergo treatment beyond the level set forth by Directive 91/271/EEC, which governs urban waste water treatment.

- A risk management approach that addresses potential health and environmental risks, minimum monitoring requirements and rules for permitting and information transparency, borrowing some aspects from the Australian guidelines for MAR.

Some comments on these guidelines and a hypothetical European directive for MAR were developed in the article by Fernández Escalante et al. (2021).

3.2 National level

3.2.1 Brazil

"The National Water Resources Council (CNRH) Resolution 153/2013 regulates MAR at the national level as defined in article 2: "unnatural introduction of water into an aquifer, by planned anthropic intervention, by the construction of structures designed for this purpose". This resolution requires MAR projects to have a license from the State Water Management body Authority and studies which certify its technical, economic, health and environmental feasibility (article 5). Another requirement outlined in this resolution is that recharging water must not compromise the aquifer water quality. After the implementation of MAR, the legal officer must maintain a Good Practices Register System (article 9)."

Shubo et al. (2020) provide an overview of managed aquifer recharge in Brazil, providing a review of laws at the federal and state level. At the federal level, four legal documents dealing with groundwater mention MAR. Between 2001 and 2008, several resolutions by the Water Resources National Council provided the national regulatory framework for MAR, which requires, as stated in the text above, no changes in the native groundwater quality, monitoring and permitting.

The same authors compile laws at the state level, which have been developed predominantly in semi-arid regions of the country. State rules for MAR comply with the national requirements and, in some cases, are more stringent. Shubo et al. (2020) highlight the legal framework for MAR in Pernambuco and Ceará, which promote MAR through tax rebate schemes.

3.2.2 Chile

"The "Decreto 203 - Reglamento Sobre Normas de Exploración y Explotación de Aguas Subterráneas" (Decree 203 - Regulation on Norms for the Exploration and Exploitation of Groundwater) (Ministerio de Obras Públicas 2014), in its articles 47 and 48, "regulations on standards", rules the authorisation and the permit systems and defines the required monitoring during MAR operations. Nevertheless, this decree does not provide any water quality standard."

The Chilean National Irrigation Commission from the Ministry of Agriculture and SCIRO Chile have also developed a methodological guideline on the operational framework for MAR projects (CNR & SCIRO 2020). It is intended to provide irrigation organisations, such as water users, with an overview of potential MAR methods to increase groundwater availability. The document is scoped to scheme recharging unconfined aquifers, diverting surface water as source water for MAR, and irrigation as the final use. This guideline elaborates on MAR methods and their technical aspects (costs, water source, design and construction, etc.).

3.2.3 Italy

"In this country, under the "Decreto 2 maggio 2016, n. 100" (Ministero dell'Ambiente e della Tutela del Territorio e del Mare, 2016) regulation, aquifer recharge is allowed for improving the quality status of the groundwater bodies as per the WFD, and as far as the water employed comes from water bodies which are in good chemical status still according to the WFD/GWD. Recharge is only allowed for groundwater bodies not in good status, or for groundwater bodies in good status but with a standing/negative trend in the presence of pollutants. As per the source water, which can only come from surface water or groundwater bodies in good chemical status, this regulation considers the maximum concentration allowed for several substances and parameters (PADs) as defined in the WFD and the Groundwater Directive. Therefore, these quality standards are well adapted to Riverbank Filtration (RBF) and infiltration basins specially allocated near the riverbanks. The Italian regulation also requires one-year monthly hydrodynamic and hydrochemical characteristics monitoring of the aquifer and the donor water body, not only during project design, but during MAR system operation, establishing a quality baseline. Besides, the regulation requires continuous high-frequency monitoring during MAR operations in order to stop operations in case of quality failure. The regulation mentions for its application MAR technologies such as, but not limited to, spreading methods, recharging wells, riverbank filtration, forested infiltration areas, etc. A review on the implementation of MAR in Italy can be found in Rossetto & Bonari (2014) in Acque Sotterranee, Italian Journal of Groundwater special issue on MAR (Vol 3, no 3, 2014)."

3.2.4 Mexico

"The "Norma Oficial Mexicana NOM-014-CONAGUA-2003" (Official Mexican law norm NOM-014-CONAGUA-2003) (Conagua 2009) establishes a water quality standard with maximum allowed values for 95 different compounds and parameters. The "Norma 15" addresses the MAR methodology without any mention to PAD (Conagua 2009). This law concerns treated wastewater and river water as sources and addresses infiltration ponds. The final use of water entailed is, generally, irrigation."

3.2.5 Portugal

"The Decree-Law 69_2000 of the Ministerio do Ambiente e do Ordenamiento do Territorio (2000) specifies the necessity of an environmental impact assessment for "Groundwater abstraction or artificial recharge of groundwater where the annual volume of water abstracted or recharged is equivalent or greater than 10 million m^3/year". The Water Law (Lei 58_2005) (Assembleia da República, 2005) has a reference to MAR in article 30-3: "Prohibition of direct discharges of pollutants in groundwater … and control of artificial recharge of groundwater, including the establishment of a licensing regime". Therefore, there are no PADs published, but this decree outlines the intention of a proper regulation to address them."

In December 2022, the Portuguese national Assembly issued the "Resolução da Assembleia da República n.º 86/2022, de 26 de dezembro" (Resolution of the Assembly of the Republic no. 86/2022, of 26 December), a resolution that "recommends the Government to encourage artificial recharge of aquifers to enhance water efficiency".

3.2.6 Thailand

In 2022, the Ministry of Natural Resources and Environment of Thailand developed "the Standard Guidelines for Artificial Groundwater Recharge" (Department of Groundwater Resources (DGR) 2022), a document that is expected to tap into the country's potential to increase groundwater availability through MAR.

3.2.7 The Netherlands

"The Infiltratiebesluit Bodembescherming (Infiltration Decree Soil Protection) (Minister van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, 1993), updated in 2009, sets forth 65 maximum allowed values for water infiltration through the soil from a surface water body. Additionally, it lists a series of compounds which might be hazardous and gives the provincial executive the competences to rule over these compounds when they are not in negligible concentrations. This regulation additionally considers the end of an infiltration scheme and requires an assessment of the impacts on the soil. If the impacts are negative, remediation is compulsory. This case is a good example of how the high level framework outlined in the WFD and GWD is applied. In particular, these parameters should have been identified as part of the risk assessment undertaken during the development of River Basin Management Plan (risk to achieve good qualitative status). This decree is currently under a new revision. The water source implied is treated wastewater; the MAR technologies addressed are ASR and interdune infiltrations and the final uses of water are irrigation, wetlands restoration and the avoidance of saline water intrusion."

3.2.8 USA

"The Underground Injection Control Regulations and Safe Drinking Water Act Provisions (US EPA 1974) are a collection of rules which apply to every state in the USA unless a state has its own and more strict regulation (Dillon et al. 2019). One of its objectives is to prevent the endangerment of underground water drinking sources as a consequence of water injection through wells (Maliva, 2020). Therefore, this normative considers MAR systems such as ASR and Aquifer Recharge (AR). It rules the approval and permitting of water injection schemes, as well as their design and operation standards definition. It controls drinking water pollution through maximum contaminant thresholds, which might be determined at the wellhead or some distance away from it, recognising the removal of pollutants through the soil natural attenuation capacity (Maliva 2020). An updated list of the water quality standards for the recharging water (US EPA 2019) is provided in the Annex."

3.3 Regional level

3.3.1 Arizona (USA)

"This section of the Title 45 (water) belonging to the Arizona statute, sets the definition, mechanism and process to obtain permits of groundwater recharge and Aquifer Storage and Recovery (ASR) (Arizona State Legislature 1994). Additionally, this law defines the ownership of the artificially stored water in the aquifer (Dillon et al. 2019). The water sources considered are treated wastewater, river and rainwater; the guidelines are directed to borehole injection in ASR schemes, infiltration ponds and canals, and the final use of water is varied, with particular regard to the irrigation of golf courses."

3.3.2 California (USA)

"The "Groundwater Replenishment Using Recycled Water" law explicitly addresses the low-threat ASR projects. It defines the permitting process, the requirements and the water quality standards in water injected and recovered from aquifers (State Water Resources Control Board 2012). Furthermore, the California Department of Public Health (2014) has established a series of rules regarding the replacement of groundwater with recycled water. These include multi-barrier criteria to ensure the safety of the recovered water, hearings before the implementation of a project of this nature and the concept of dilution to remove pollutants reducing the necessity of upgrading wastewater reclamation projects (Yuan et al. 2016). It also requires pilot-testing before full-scale implementation. The water quality standards presented in the Annex correspond to those in the Draft Proposed Groundwater Recharge Regulation (State of California, 1993). The water sources considered are treated wastewater, river and rain water; the MAR technologies addressed are borehole injection (ASR), infiltration ponds and canals, and the final uses of water are multiple."

3.3.3 Florida (USA)

"The regulation Reuse of Reclaimed Water and Land Application sets the requirements to recharge aquifers with reclaimed water via injection wells or infiltration basins (Florida Department of Environmental Protection 1999). For example, for spreading basins, it requests a minimum of secondary treatment and disinfection. For injection wells, the water quality requirements and the pre-treatment are a function of the quality of the native groundwater (Yuan et al. 2016). Furthermore, these water quality standards involve the treatment capacity of the infiltrating medium as well (National Research Council 1998). Apart from controlling reclaimed water reuse, the state of Florida also regulates how to caution areas with water supply problems, and to meet the needs with reclaimed water to a certain extent (National Research Council 1998). The source of water encompassed by this regulation is treated wastewater; the MAR technologies addressed are borehole injection (ASR) and infiltration ponds, and the final uses of water are multiple."

3.4 Local level

3.4.1 Torreele (Belgium)

"The Torreele wastewater treatment plant infiltrates effluents through the dunes of the St. André Watershed, constituting a SAT-MAR project. Before infiltration, water is subject to membrane filtration techniques, which account for the stringent water quality standard set in the project. Such standard consist of a collection of nine parameters applied in the whole Flanders Region (Van Houtte 2005), with specific settings. The water source considered is treated wastewater, the MAR technologies addressed by the rules are wells and dunes, and the final use of water is the indirect potable re-use through artificial recharge of the dune aquifer of St-André."

3.4.2 Windhoek (Namibia)

"A draft of water quality standards and regulations are being set by the municipality of Windhoek, the local water supplier in charge of the MAR system and the water affairs department. This draft establishes water quality guidelines with MACs for six parameters, namely dissolved organic carbon (DOC), assimilable organic carbon (AOC), electrical conductivity (EC), chloride, sulphate and nitrite/ nitrate. It also set forth a series of principles which must be complied. For instance, MAR should not have a significant negative impact or bring about health risk for the residents in city (GRN 2020). The water sources entailed are multiple (e.g. river water and rainwater); the MAR technologies considered are primarily wells (ASR), and interdune infiltration ponds. The intended end uses of the water are irrigation and environmental purposes."

3.4.3 The Shafdan (Israel)

"The Shafdan is a SAT-MAR project in which water from the metropolitan area of Tel Aviv (Israel) is reclaimed by way of a wastewater treatment plant and infiltration basins (Goren et al. 2014). This project, which started in 1963, has set 25 MACs, specifying the quality that water must comply prior with infiltration through the soil. Israel's National Water Company, Mekorot, has a certain capacity on regulations drafting and applies these quality standards in all the MAR projects in the country, whilst their proposed list of MACs is finally regulated by the government. The water source is primarily treated wastewater and to a minor extent desalinated water. The MAR technologies involved are infiltration ponds and ASR, and the final uses of water are irrigation, services for the city and barriers against saline water intrusion."

3.5 Spanish level

3.5.1 MAR in Spain

"The Royal Decree 1620/2007 for water reuse (BOE 2007) is specifically designed for water reuse. It stipulates the water quality standards in MAR considering two situations, either direct percolation (surface recharge using the unsaturated zone as a natural filter) or direct recharge (i.e. injection), either in the unsaturated area at a certain depth (not specified) or directly below the phreatic level. The water quality standards comprehend six parameters, with a particular focus on biological compounds, given the origin of the water (wastewater treatment plants). The water sources are treated wastewater, river and rainwater; the main MAR technologies encompassed are infiltration ponds and canals, and eventually injection boreholes. The intended end use of water is irrigation, and in some cases, water supply for big cities."

At the moment this deliverable has been released, Spanish Government is about to publish the modified version of the Water Act (Law 29/1985, modified in the Royal Legislative Decree (Real Decreto Legislativo or RDL 1/2001)), and of the regulation implementing it, Royal Decree 849/1986 (RDPH). After the period of public participation (with contributions from MARSoluT consortium members), some MAR-related modifications are expected, e.g. the term "gestionada" (managed) is proposed as a synonym of "recarga artificial" or artificial recharge.

MARSoluT members proposed to include a point 5 in the article 258.3 of the Water Act, literally "Any surplus water volume of appropriate quality shall be suitable for managed (or artificial) aquifer recharge". This point was also proposed for the Peruvian water regulations, and is expecting a top ranking decision makers' final decision.

According to the draft of the Spanish Groundwater Action Plan 2023-2030 (currently in draft version and under public participation period), MAR is still slightly considered in Spanish regulations. The MACs limits published in the Royal Decree 1620/2007 for water reuse and artificial recharge are expecting the publication of the imminent Directive about "artificial recharge and water reuse for agricultural uses".

According to the Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse, cradle of the future water reuse and artificial recharge Directive, MACs are not considered any longer at European Level, being regulations rather based in risk assessment approaches, and (apparently) an excessive application of the precautionary principle.

In summary, future or even imminent Spanish water regulations include:

Background on MAR in the Spanish regulatory framework, and how water quality is regarded avoiding MAC limits and in consonance with the rest of the EU members. Meanwhile limits are established for spills, applying very stringent maximum allowable concentrations (MACs).

Water reuse in Spain and its relation to MAR included in the Water Act and RDPH (revised), in the National Water Reuse Plan 2010-2015, and in the National Plan for Purification, Sanitation Efficiency, Saving and Reusing (DSEAR).

Review of the novel Spanish Groundwater Action Plan 2023-2030, which will be published in the next few weeks, and it considers MAR briefly, appearing the term "recarga artificial o gestionada" three times:

a. Pg. 63: *Artificial or managed aquifer recharge, in its many different forms, is one of the techniques to be valued in water resources management.*
b. Pg. 76: *Consideration and appropriate regulatory treatment of artificial or managed aquifer recharge.*
c. Pg. 90 (repeated): *Consideration and appropriate regulatory treatment of artificial or managed aquifer recharge.*

Therefore, Managed Aquifer Recharge application must improve within Spanish water-related regulations, due to the fact that its consideration is still below current water management necessities, and specially, below the climate change´s adaptation demands.

3.5.2 Wastewater reuse in Spain

Two policies have focused on promoting wastewater reuse at the national level. The first of these policies was the National Water Reuse Plan (2010-2015), which tried to involve regional and river basin authorities towards building infrastructure and capacity for wastewater reuse. Among other objecttives, this plan aimed at creating financial instruments to promote wastewater reuse, replace the source of concessions from conventional to treated wastewater in cases of non-potable use, promote good practices, and raise awareness about the benefits of using recycled water. All these objectives had to consider the WFD (European Parliament and Council of the European Union 2000), which commands the good status of water bodies in the EU (Jodar-Abellán et al. 2019).

In 2021, the National Plan for Purification, Sanitation Efficiency, Saving and Reusing (NPPSSR) was enacted by the national government (MITERD 2021). This plan constitutes a response to a series of opportunities to improve sanitation and water reuse in the country. One of its pillars is to promote wastewater reuse, stating that "The priority objective is to favour the use of these non-conventional resources in substitution of resources of other origins that are other resources that are applied to existing uses, mainly irrigation, and whose extraction puts pressure on the environment". Among other objectives, this plan also aims to analyse the potential for water reuse in Spanish river basins and its impact on the allocation and reserve of water resources; to prioritise reuse actions aimed at achieving the good status of water bodies; to improve the regulatory and financial framework for reuse (Revision and adaptation of RD 1620/2007 to Regulation 2020/741); to develop a section dedicated to reusing on the MITECO website; and to carry out a communication campaign on consuming recycled water (MITERD 2021).

Water reuse started in Spain in 1970 in Las Palmas (Canary Islands) with effluent from the Barranco Seco wastewater treatment plant. The additional water was used in agricultural irrigation (Jódar-Abellán et al. 2019). Ever since, wastewater reuse in Spain has increased, driven by water scarcity and the over-allocation of conventional water sources. The total national volume of water reuse rose until 2005, when it stabilised at around 500 Mm^3 (**Figure 2**). However, in 2018, the volume of treated wastewater (481 Mm^3) was considerably below the targeted volumes by the National Plan for Water Reuse which were 998 and 1,403 Mm^3 in 2015 and 2021, respectively (MITERD 2021). Nonetheless, Spain is the European Union country with the largest share of reused treated wastewater and ranks among the top ten globally (Jódar-Abellán et al. 2019).

Moreover, the potential of Spain for wastewater reuse is the highest among European countries. It was estimated at 1,200 Mm^3 per year in 2025 (AQUAREC). In economic terms, according to Pistocchi et al. (2017), Spain could provide more than 1,500 Mm^3 of reclaimed water at a marginal cost below 0.25 €/m^3.

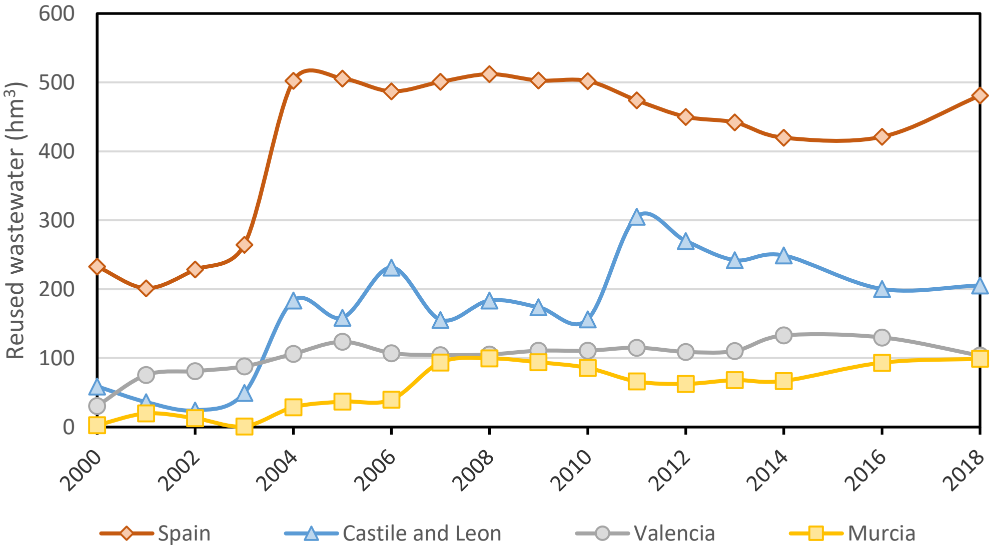

Figure 2. *Reused wastewater for Spain and three regions of the country. Own elaboration based on INE information.*

Two regions of Spain stand out by the considerable percentages of wastewater reuse, namely Murcia and Valencia. Between 2000 and 2018, the share of recycled water in these regions increased by 3.4 and 37 times, reaching 43% and 95%, respectively (**Figure 3**).

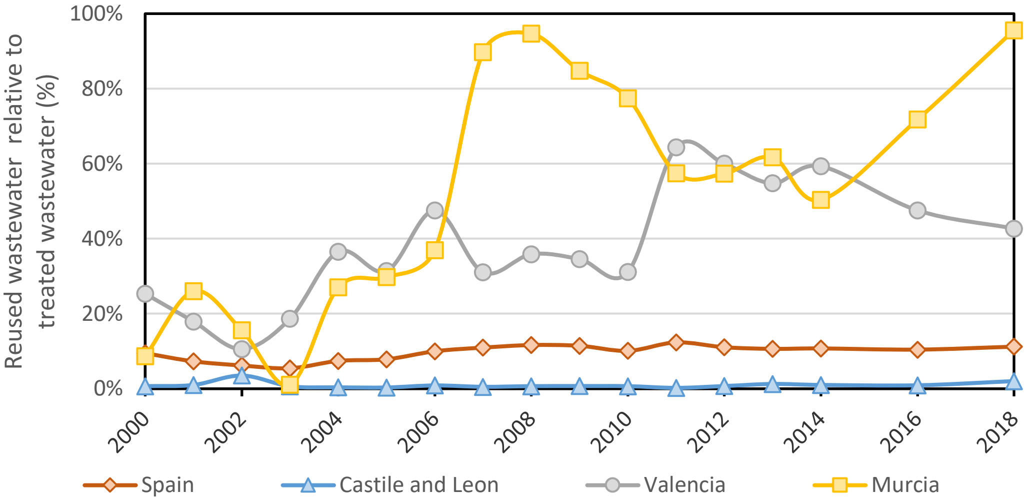

Figure 3. *Percentage of reused treated wastewater in Spain and a few of its regions. Own elaboration based on INE information.*

The main final uses for recycled wastewater in Spain are agriculture (45%), parks and recreational area (36%), industry (10%), and the cleaning of sewerage and urban streets (7%) (**Figure 4**) (Jódar-Abellán et al. 2019). However, other sources point out that the actual figures for water reuse in agriculture could reach 70% and up to 80% when forest irrigation is taken into account (Jódar-Abellán et al. 2019).

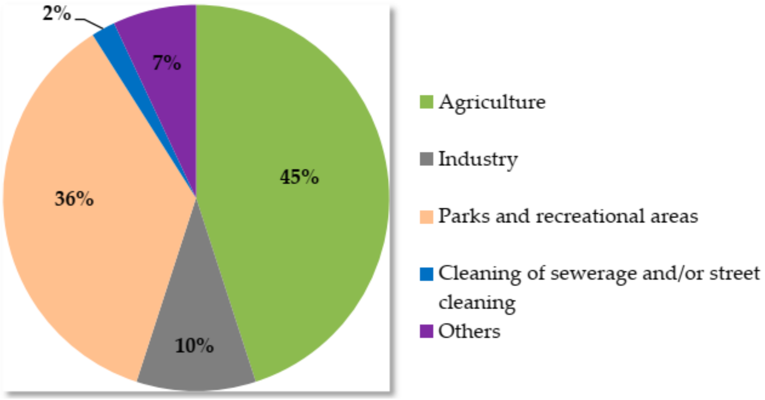

Figure 4. *Primary uses of reclaimed water in Spain (Jódar-Abellán et al. 2019).*

Water reuse can be a great ally in improving sanitation. In Spain, there is a deficit in the investment for sanitation, especially in villages with middle to low populations. About 12% of wastewater lacks secondary treatment, and 34% requires more stringent treatment (OECD 2019). This lack of treatment breaches Directive 91/271/CEE (Council of the European Communities 1991), which establishes the minimum requirements for the collection, treatment and disposal of wastewater in the European Union.

Furthermore, wastewater treatment should be in line with the Water Framework Directive 2000/60/CE (European Parliament and Council of the European Union 2000), which commands member states to guarantee water bodies' good quantitative and qualitative status.

According to directive 91/271/CEE, small villages (<2,000 PE) require appropriate wastewater treatment. "The treatment of urban wastewater by any process and/or disposal system which after discharge allows the receiving waters to meet the relevant quality objectives and the relevant provisions of this and other Community Directives" (Council of the European Communities 1991). Spain applies the same discharge limits set by Directive 91 /271/CEE for medium and large cities (>2,000 PE) and 3 million PE without coverage (Aragón et al. 2013).

Small villages are particularly behind in terms of water sanitation. For instance, small villages constitute 96% of the wastewater (WW) discharge points in Castile and Leon (CyL), and it's estimated that only 40-50% of the population in these urban conglomerates have adequate sanitation (Huertas et al. 2013; Aragón et al. 2013). Some of the challenges for the implementation of wastewater treatment in small villages in CyL are: Numerous spread urban nuclei with small populations; scarce economic resources; some of these urban settlements are located within protected areas (more stringent quality requirements); more variability in discharge and contaminant concentration; less dilution of contaminants; around 50% of small villages don't count with WWT. However, small towns have a more negligible environmental impact overall as their contaminant load is lower than in areas with larger populations. In fact, 19 urban areas of CyL account for 60% of the region's water pollution (Huertas et al. 2013).

Solutions coping with wastewater treatment in small villages in Spain should bear the following aspects: simplicity of operation, meaning that operation time, staff, training and technical requirements should be the lowest possible, as well as the number and use of electromechanical devices and facilities. The method employed should be able to treat a considerable amount of water and should comply with minimum quality requirements even when part of the system fails (García et al. 2001; Huertas et al. 2013).

Some steps in the correct direction towards adequate sanitation are taking place. Between 2010 and 2013, the Confederación Hidrográfica del Duero (CHD) built 14 pilot wastewater treatment plants in small villages in Castile and Leon, considering low-cost and flexible technologies. Some employed technologies included artificial wetlands, septic tanks, filter trenches, green filters, and lagooning (Primo 2013). The CHD and the Centro de Estudios y Experimentación de Obras Públicas (CEDEX) assessed eight of these projects for two years, concluding the adequacy and efficiency of the tested technologies[2].

Wastewater could become a reliable and plentiful source of water for MAR. Henao Casas et al. (2022b) explored the potential to conduct artificial recharge in the Los Arenales MAR sites in Spain using wastewater and diminishing reliance on surface water bodies. The following is the explanation of the methodology the authors used and their main findings:

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[2] https://www.chduero.es/proyecto-piloto-tratamiento-vertidos

"According to Representative Concentration Pathway (RCP) 8.5 climate projections by Guerreiro et al. (2017) and Cruz-García et al. (2016), the Douro River flow is expected to decrease by around 71% in autumn and up to 91% in winter. A similar decrease could occur in the rivers providing water for MAR under the expected decline of precipitation by 5% in the Douro River basin.

We estimate the volume of wastewater produced in the LAGB (Los Arenales groundwater body) that could be treated and recharged in the Los Arenales MAR systems, potentially replacing river water as the main source in the face of decreasing river flow. We consider two primary sources of wastewater: (i) household and industrial sewage and (ii) stormwater. We estimate the wastewater produced by industry and households in each municipality through Equation (1):

$$V_R = V_D\ P\ DF\ (1 - SL) \qquad (1)$$

where V_R is the household and industrial sewage potentially available for reuse, V_D is the average drinking water supply per inhabitant per year (170 litres/inhabitant day for urban areas with little commercial activity), P is the population, DF is the discharge factor representing the fraction of drinking water that goes into the sewage system (80%), and SL is the sewage system losses (15%). We estimate the reusable wastewater in the LAGB by adding the individual contributions of the municipalities in the region, computed through Equation (1). We obtain urban agglomerations in the LAGB and their corresponding populations from the 2018 Geographic Information Database of Reference Populations ofthe National Geographic Institute (IGN).

We estimate stormwater as the product of the average annual precipitation and the urban area, considering paved surfaces such as roads and rooftops. We compute the average annual precipitation in the LAGB using Thiessen polygons and rainfall data between 1985 and 2020 from meteorological stations of the Spanish Meteorological Agency (AEMET) (2444, 2422, 2150H, 2503X, 2117D) and InfoRiego, a system for irrigation recommendation by the Spanish Ministry of Natural Resources and Environment Agriculture and the JCyL (SG01, SG02, VA102, VA03, VA06, AV01). We use three information sources to obtain urban area, resulting in three estimations of potentially recyclable stormwater: continuous and discontinuous urban fabric area from (i) SIOSE and (ii) CLC for 2014 and 2018, respectively, and (iii) 85% of the urban agglomeration area reported in the Geographic Information Database of Reference Populations by the IGN, assuming that the remaining 15% of the area corresponds to green urban spaces."

"Our calculations indicate that there is likely 2.9 Mm^3 year^{-1} of wastewater from households and industries in the LAGB. We estimated recyclable stormwater at 19.9 Mm^3 year^{-1}, 15.6 Mm^3 year^{-1}, and 10.1 Mm^3 year^{-1}, using IGN, CLC, and SIOSE urban area information, respectively. The total recyclable water lies between 22.8 Mm^3 year^{-1} and 13.1 Mm^3 year^{-1} (**Figure 5**). The potentially reusable wastewater is between 4.8 and 2.7 times the average MAR in the period 2002-2020 (Avg. MAR, **Figure 5a, b**).

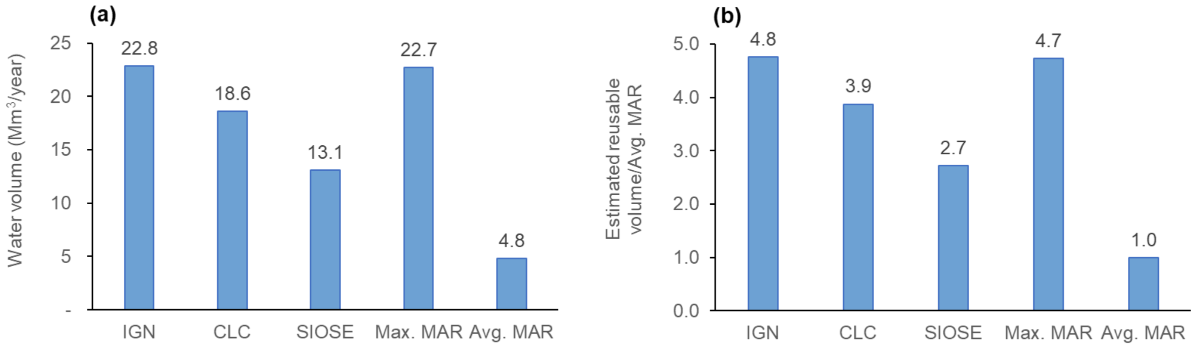


Figure 5. *“Potential recyclable wastewater: (a) in absolute values, and (b) as a percentage of the average managed aquifer recharge (MAR) volume between 2002 and 2020 (Avg. MAR). Max. MAR refers to the maximum annual allowed diversion of river water for MAR in El Carracillo and Santiuste together. Sources of urban area extension: IGN: National Geographic Institute; CLC: CORINE Land Cover; and SIOSE: Spanish Land Occupation Information System. From Henao Casas et al. (2022b).*

If the actual urban area in the LAGB corresponds to the value reported by the IGN, the estimated reusable water (22.8 Mm^3 $year^{-1}$) could cover the maximum allowed annual diversion of river water for MAR in EL Carracillo (14.2 Mm^3 $year^{-1}$) and Santiuste (8.5 Mm^3 $year^{-1}$) combined (22.7 Mm^3 $year^{-1}$) (Max. MAR, **Figure 5a, b**). Note that the maximum allowed annual diversions of river water for MAR constitute a limit aiming to respect ecological flow and downstream users. Actual diversion volumes are often <50% ofthe maximum allowed volumes. Some of the estimated recyclable water might not be harnessed due to water quality issues or logistical, practical, and financial constraints, aswell as further losses in the collection system or to evaporation.

Replacing river water surpluses with recycled wastewater entirely or partially couldalso contribute to increasing water security against drought, which can further deplete available surface water in the area.

There is a need for wastewater treatment in CyL, and a favourable technical and regulatory environment for reuse. In this region, 50% of small villages (>2000 equivalent inhabitants) lack wastewater treatment. This situation breaches the European directive 91/271/CEE (adopted in the Spanish regulation through the 11/1995 Royal Decree), which requires adequate wastewater treatment in nearly all urban agglomerations by 1 January 2006, at the latest. Furthermore, planning wastewater treatment witha focus on reuse in villages lacking this service would align with Spanish and European efforts towards a circular economy, including one of the first regulatory frameworks for wastewater reuse (Spanish Royal Decree 1620/2007), two national plans for recycling water (The National Water Reuse Plan 2010-2015 and the National Plan for Purification,Sanitation Efficiency, Saving, and Reusing), and the European Directive on Minimum Requirements for Water Reuse. Similarly, Spain has an extensive experience in thisregard, as one of the top ten countries in water reuse percentage worldwide and the countrywith the highest wastewater reuse rate in the European Union."

3.6 Analysis of water quality control

Fernández Escalante et al. (2020) analysed how water quality is controlled in the existing MAR guiding and regulating documents. This analysis focused on the maximum allowable concentration (MAC) of multiple parameters and is presented below. Text between quotation marks is from Fernández Escalante et al. (2020):

"From the collection of 18 regulations/guidelines/operator rules gathered, ten present specific water quality standards (for water to be injected or infiltrated), whose compilation is presented in the Annex. The number of parameters regulated by the different standards shows a remarkable difference, from six in Spain´s internal regulation (independently of the constraint of the minimum requirements of the Groundwater Directive 2006/118/EC, being an EU Member State) to 149 in the USA (**Figure 6**).

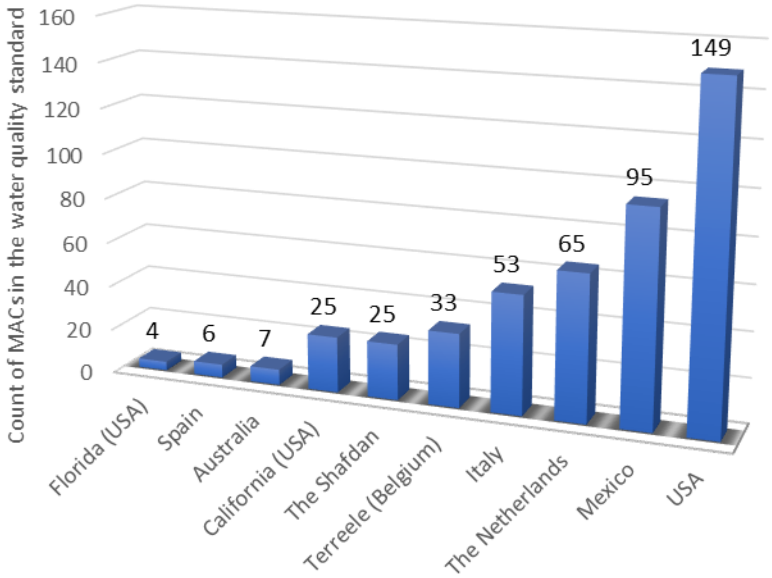


Figure 6. *Number of parameters per legislation with water quality standards analysed. In the case of the regulations with more than one quality standards, the most stringent one has been considered. From Fernández Escalante et al. (2020).*

The total number of parameters included in the ten reported water quality standards is 255. Four more are listed in the Australian Guidelines as an ongoing proposal, but they are not normalised yet. These parameters are: biodegradable dissolved organic carbon (BCOD), dissolved organic carbon (DOC), membrane filtration index (MFI), and UV254 abs.

In water quality standards such as the ones from California, Mexico, and Spain, a distinction is made depending on the type of recharge, either direct injection, percolation, infiltration through ponds or wells, with different limits for each case. For instance, in the Mexican standard, total organic carbon (TOC) must have a value equal or less than 1 mg/l, when water injection is direct, while there is a limit of 16 mg/l for percolation. In the state of Florida (USA) the legislation goes further and makes four standards based on the sort of recharge and in the receiving medium conditions. Italy categorises the water quality limits for the source water body in two groups, one for the surface water bodies, with standards defined in Table 1 and 2 according to the implementation of the WFD into the Italian regulations (D.Lgs. 152/2006), and the second for the quality of groundwater bodies (including the product of the interaction between groundwater and the water-associated ecosystem; Table 3 in DM 100/2016).

There are two parameters which considerably vary among water quality standards: TOC (x16, which means that the maximum concentration is the minimum multiplied by 16), and Total Suspended Solids (TSS). In Florida, TSS must be below 5 mg/l while in Mexico, 150 mg/l (x10) are permitted. There is a series of parameters which are regulated by most of the standards explored. In general, the Mexican legislation shows the most permissive values, while the strictest ones are found in different standards, but especially in Spain and California. For instance, the total nitrogen has the highest allowed value in Mexico (40 mg/l) and the lowest in California and Spain (10 mg/l) (x4). The total phosphorus limit in the Mexican standard is the highest, 20 mg/l, while Belgium has the lowest, namely 0.4 mg/l (x100). The chloride limit in Mexico is 300 mg/l and the lowest value is found in the Californian legislation, with 120 mg/l (x2.5). In the case of sulphates, Mexico shows the highest value again, which is, 300 mg/l, and California the lowest (125 mg/l). An exception is the turbidity, which shows its highest MAC in Israel's standard (10 NTU) and the lowest and most strict in Spain (2 NTU for the direct injection case) (x5).

Among major ions, nitrate (NO_3^-) is the most frequently regulated parameter and is regulated in the standards from The Netherlands, Torreele (Belgium), Spain, Italy, Mexico and the State of Florida (USA). After nitrate, total nitrogen (TN) and total dissolved solids (TSS) are the parameters most frequently regarded in the analysed quality standards.

Regarding (heavy) metal(oid)s, there are substantial differences among the standards. Torreele (Belgium) and the Netherlands are the strictest. For example, the maximum allowable concentration of zinc is 200 µg/l in Torreele and 65 µg/l in The Netherlands (x1/3). On the other hand, California and Mexico propose a lower value of 5 mg/l (x77). The most regulated heavy metals are arsenic, cadmium, lead and mercury, with their MACs reported in seven water quality standards.

An important group of contaminants to consider are the emergent pollutants, which pose a major concern in the reuse of reclaimed water (WHO 2003; Silver et al. 2018; Valhondo et al. 2020). The water quality standards from the USA, Italy, México, The Netherlands, Shafdan and Torreele take into account these sorts of pollutants. USA, Mexico and The Netherlands stand out for comprehensive regulation of herbicides (e.g. Mecoprop), insecticides (e.g. Mevinphos), and pesticides (e.g. Heptachlor), among other organic compounds. Italy has included in its MAR water quality standard a pioneer methodological approach and recommendations to achieve a "monitored recharge". This approach comprises controls on water quality through continuous high-frequency monitoring, and the proposal of a list of emergent pollutants which must be controlled.

Some major ions such as (bi)carbonates, potassium and calcium (the latter is often determined by means of the water hardness) are missing in most of the standards reported here. The authors propose a set of generic water quality parameters to be taken into account in MAR projects. These parameters are selected in the face of two factors: 1) the frequency in which they are requested as per the water quality standards reviewed, and 2) their usefulness in hydrogeological tools and hydrochemical calculation (Table 2). This table would constitute a list of essential parameters for MAR. Six of the recommended parameters pertain specifically to SAT-MAR (i.e. MAR with reclaimed water).

On the basis of the results of local risk assessment, additional parameters should be added to ensure safe MAR, taking into consideration the origin of water, MAR technology and use, and, of course, the experts´ criteria."

For more information on guidelines regarding implementation of MAR, please also see MARSoluT project deliverable D2.2 (MARSoluT 2023a).

4. Modern Water Quality Challenges for Managed Aquifer Recharge

4.1 Current context for MAR water quality issues

Managed Aquifer Recharge (MAR) is the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit, according to the International Association of Hydrogeologists, Commission on Managing Aquifer Recharge (https://recharge.iah.org).

Some of the opportunities and challenges related to Managed Aquifer Recharge (MAR) water quality for the current circumstances and international level, have been described in the article published in 2022 by Springer, in open access available since February 2023: "The 21st Century Water Quality Challenges for Managed Aquifer Recharge: Towards a Risk-Based Approach" (Zheng at al. 2023). One of the co-author´s contributions rose from the MARSoluT consortium's work, and some of the most important content has been extracted into this chapter. The herein information may be complemented consulting the mentioned publication (Zheng at al. 2023).

The article introduces some figures, such as the number of substances threatening the environmental and human health protection, estimated about 350,000 chemicals in global markets, plus new biological entities including coronaviruses. These new water quality hazards challenge proponents of MAR to ensure the integrity of the aquifer. The risk management approach increases due to the release of tens of thousands synthetic chemicals are increasing at a pace that outstrips the global capacity for assessment and monitoring (Persson et al. 2022).

As a response to these global threats, the authors have proposed a risk-based approach and management framework accounting for water quality changes in the subsurface, adoption of attenuation zones for future regulation of MAR and guidelines drafting, and enhancing the importance of advanced monitoring. Translated into MARSoluT terms, hydro-dynamic monitoring methods to give confidence in the sustainability of subsurface treatment as a post-treatment process, counting on a previous pre-treatment as a general rule.

4.2 Towards a risk-based approach

The starting point is the publication from UNESCO, 2021, in which 28 exemplary MAR schemes from 21 countries were gathered (two of them being MARSoluT case study sites), relying on a wide range of techniques to recharge, store and treat water in aquifers, or to induce recharge by river bank filtration. The annual recharge ranges from micro (640 m^3/yr) to giga (250,000,000 m^3/yr), and these figures have firmly established that MAR is a sustainable technology (Zheng et al. 2021).

MAR schemes, as nature-based engineering infrastructure built to augment water supply and environmental flow, including recycling treated wastewater, are poised to play increasingly significant roles in climate change adaptation.

Considering "novel entities" means that proponents of MAR must continue to manage risks associated with known, legacy pollutants such as chlorinated solvents, mineral oil components and metals, exemplified by regulated water quality parameters usually amounting to several hundred (Fernández

Escalante et al. 2020). It also means that they need to be equipped to address not (yet) regulated, and sometimes novel (unknown) water quality threats exemplified by "novel entities".

Clearly the capacity to manage current, emerging and unforeseen water quality risks is more important than ever. This is because we rely not only on chemical reactions but also on subsurface microorganisms to perform biogeochemical reactions to "purify" any purposefully recharged water. Especially noteworthy is the attenuation zone concept.

MAR practitioners have had to produce laboratory and field monitoring evidence that MAR operations are environmentally benign to gain regulatory approval for full scale schemes. However, some sceptical regulators are inclined to regard the subsurface environment as "pristine" and should not be "disturbed" by any means. In reality, "unmanaged" recharge from a wide range of anthropogenic activities has led to groundwater quality disturbance, frequently more pronounced at smaller depths than at greater depths, with pendant to be discovered consequences (IAH-MAR, Dillon et al. 2022).

The authors of the article posed a binomial on water quality issues frequently encountered in MAR implementation. Firstly, the way forward to resolve the contradiction, i.e., treating aquifer as a passive subject needing blind protection, versus allowing aquifers to contribute to sustainable fresh water availability as an active part of the earth system. This topic has also been discussed extensively within the framework of MARSoluT project.

Figure 7. *Global inventory of MAR schemes presented as online portal with the database being continuously updated (source: https://ggis.un-igrac.org/view/marportal; accessed January 20, 2023).*

4.3 Historical background

An account of 60 years of global progress of MAR estimates that the purposefully recharged water quantity has reached an estimated 10 km^3/year, ~2.4% of groundwater extraction in countries reporting MAR, or ~1.0% of global groundwater extraction (Dillon et al. 2019). A global inventory of MAR practices included 1,136 pilot and full-scale MAR schemes from 60 countries (**Figure 7**). The inventory was initiated by members of the IAH-MAR Commission and was based on an extensive literature analysis and direct stakeholders' interviews conducted in several international languages up to 2015 (Stefan & Ansems 2018). In total, 47 parameters were analysed and clustered in four categories: general information, operational parameters, aquifer properties and water quality parameters. While information such as influent water source, main objective or final use of recovered water was well-reported (96%, 82% and 73% of the total number of cases, respectively), detailed description of water quality parameters (over 100 considered) was mentioned in less than 5% of the studies. Nevertheless, water quality changes were mentioned in many papers, especially in conference papers and specific technical reports.

Water quality investigations are an integral part of any successful MAR project. We searched the expanded science citation index database for the time period of 1900 to present. Just above one third of the MAR publications, or 118 out of 391 papers, included water quality. The proportion remained constant through the years.

Water quality investigations during MAR projects serve many different aims, with monitoring for regulatory compliance as a basic starting point. Also, risk-based management is essential for the future of MAR (Imig et al., 2022), to ensure that we protect public and environment health, whilst also fully utilizing the potential of MAR to provide natural treatment and to facilitate recycling and reuse (**Figure 8**).

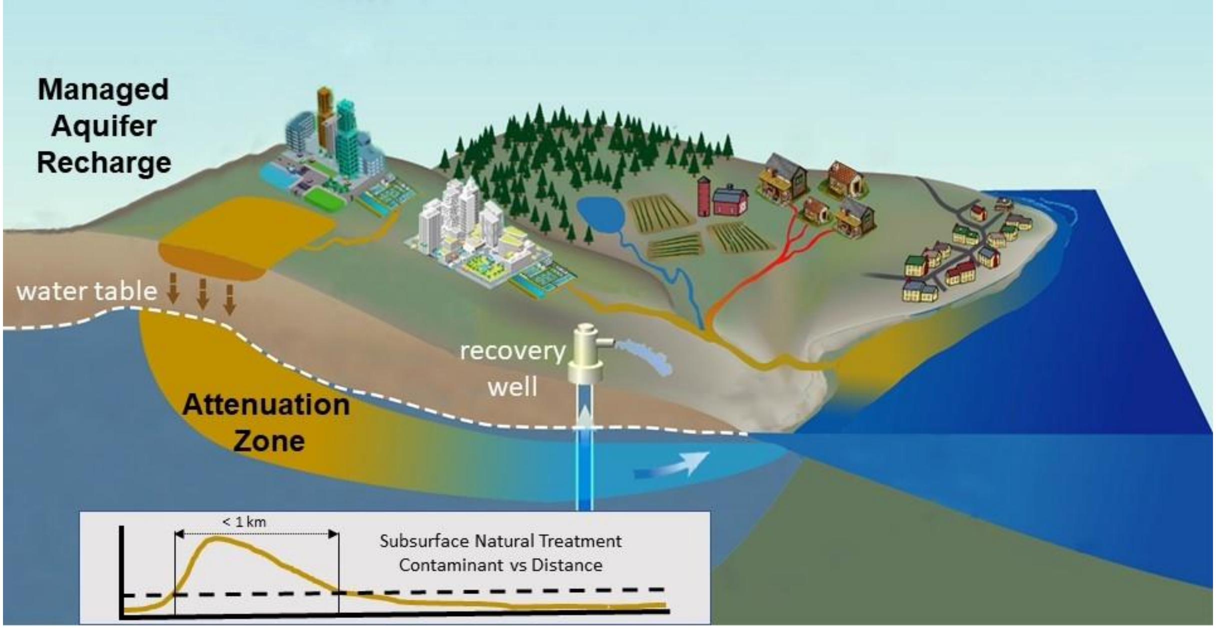


Figure 8. *Schematic diagram illustrating how MAR has been used to purify purposefully recharged water such as an infiltration pond through a series of natural treatment processes occurring in the unsaturated and saturated zones of an aquifer that facilitates the removal of organic pollutants and pathogenic microbes. Taken from Zheng et al. (2023).*

Complex and uncertain risks can be dealt with, hopefully, with decades of experience in water quality improvement and management in MAR, plus further research. Considering MAR as a step in a treatment train enables us to manage the complex topic of water quality when MAR alone cannot provide sufficient treatment, fate cannot be predicted, or where water quality degradation may occur.

We should continue developing approaches to assess aquifer microbial communities, their potential to augment treatment, response to changing geochemical conditions and ultimately the sustainability of treatment. Leveraging the natural treatment capacity, where available, allows for design of a sustainable treatment train and avoids overuse of energy intensive engineered pre-treatment without over treating water prior to MAR.

All uncertainties of regulated and unregulated water quality threats, the assumption that storage time mitigates risks especially of pathogens, biodegradable organic matter, and trace organic chemicals is likely to hold, although more research is warranted to determine the time scale for complete mineralization including mostly unknown biotransformation byproducts (Zheng et al. 2023).

4.4 The way forward

To enhance climate resilience and other social, economic and environmental benefits of groundwater through implementing MAR projects, water quality threats from novel entities need to be addressed to maintain resource integrity and to keep target aquifers within the safe operating space.

Modern water quality challenges can be approached from a risk-based perspective grounded by precautionary principles, developed over time through practice to solve clogging issues, and to overcome economics and policy barriers.

It is worth noting that, when it comes to groundwater recharge laws in the United States, a communitarian ethics has been suggested to underpin regulatory processes (Owen 2021). Authors encourage debate on how to arrive at a sensible regulatory framework to manage water quality risks for the European Union, with the precautionary principle as a starting point.

The Australian risk-based approach to MAR (NRMMC et al. 2009) is a model that sustainably protects groundwater quality, accounting for water quality changes, both improvements and deteriorations, in the subsurface. But it can be further expanded geographically because many countries in the world are still taking a highly prescriptive approach to measure compliance against a list of water quality parameters. These guidelines have been the base for two publications developed by MARSoluT. The first about water quality regulations all around the world (Fernández-Escalante et al. 2019); and the second being a proposal for a new concept called "Monitored and intentional Recharge" (MIR), which is, according to a summarized description posed by the authors, "*a conceptual model for drafting MAR and water reuse guidelines documents*" (Fernández-Escalante et al. 2022).

In Europe both the development of application and legislative framework for MAR has varied among different countries (Sprenger et al. 2017), with current legislation ranging from strict and uniform water quality requirements versus site-specific evaluation with respect to the water quality in the receiving aquifer such as in the Netherlands, similar to Australia. A European Union Directive on MAR water quality for different uses would be a very useful development.

The way forward clearly depends on regulations that value and enable sustained use of natural treatment capacity provided by MAR, seamlessly integrated to a treatment train with pre-treatment or post-treatment technologies.

There is also a need for advanced tools, including but not limited to real-time monitoring, data assimilation, and reactive-transport modeling to predict fate of chemicals and pathogens and to assess risks to human health and aquifer integrity. Special attention should be paid on the "attenuation zone" (an attenuation zone (after NRMMC, EPHC, NHMRC, 2009), is defined as an independent regulatory unit so that groundwater quality beyond this zone is sustainably protected), a subsurface natural treatment zone with a finite hydraulic retention time. The understanding of the fate of pathogenic organisms is necessary, including laboratory and field verification. Subsurface microbial communities are also providing a broader perspective on the sustainability of microbial and trace organic removal processes.

The referenced essay includes a call on hydrogeologists worldwide to rise to the 21st century water quality challenges using MAR, in order to maintain the integrity of groundwater resources and in turn, to meet humanity’s demand for good quality fresh water.

Both, the IAH-MAR Commission and the MARSoluT consortium strive to develop the body of scientific knowledge needed to have confidence in enhancing the sustainable and beneficial use of aquifers for people.

5. Recommendations and Conceptual Models to Regulate Water Quality for MAR

This chapter deals with the recommendations derived from the analysis of existing MAR guiding and regulating documents and the presentation of the Monitored and Intentional Recharge conceptual models, which provides a framework with the most relevant aspects to consider when drafting documents aiming at regulating MAR.

5.1 Considerations on the removal of organic pollutants from water during MAR

The water used for MAR is usually taken from surface waters or treated wastewater. Even if a high-quality standard exists, depending on the origin and degree of prior treatment, the water for MAR contains concentrations of emerging organic compounds (EOCs), such as pharmaceuticals and personal care products. Understanding the processes that influence the fate of EOCs in the aquifer is, therefore, a key point for evaluating and predicting contaminant plumes and risk assessment. Various processes influence this fate of EOCs, ranging from a delayed spread to complete degradation of the substance. These processes depend to a greater or lesser extent on the local conditions, composition of infiltration water and the type of MAR facility, such as materials used, organic content, pH value, the structure of the EOC, local microbiology and, in some cases, are not yet fully reproducible.

The two driving forces regarding the fate of EOCs are sorption and degradation. Sorption is the term used to describe all processes in which a substance accumulates within a phase or at the interface between two phases. Sorption is a crucial process when it comes to the fate of EOCs, as it leads to retardation in the spread of pollutants. At equilibrium, sorption and desorption rates are the same.

Solution ionic strength and composition affect the sorption of charged organic chemicals, especially if inorganic and organic ions compete for the binding sites. The mineral surface composition of the sorbent is also key; for example, oxides and hydroxides - like quartz or goethite mineral surfaces - present ionic radicals on their surfaces. Besides this, the age of organic matter also plays an essential role in sorption properties, implying a distributed reactivity and increasing the heterogeneity of the environment (Weber et al. 1992; Kleineidam et al. 2002).

In general, sorption is a more dominant process if the compounds have a hydrophobic behaviour with a tendency to bioaccumulation and high sorption capacity. Examples of these could be β-blockers (e.g., propranolol), and a few pharmaceuticals (e.g., ketoprofen) or illicit drugs (e.g., THC from cannabis). On the other hand, substances that present a hydrophilic behavioural are more frequently detected in groundwater. Indeed some pharmaceuticals and, in particular, carbamazepine, have been used as anthropogenic markers in the aquatic environment (e.g. Müller et al. 2013). An example of riverbank filtration analysis, Henzler et al. (2014) emphasized adsorption as a critical process influencing the transport of multiple EOCs, mostly MTBE (methyl tertiary-butyl ether) and carbamazepine. Ying et al. (2005) found strong adsorption of beta-estradiol to the local aquifer material under aerobic conditions.

Natural organic material can be a sorbent for nonpolar organic chemicals because they offer a relatively nonpolar environment into which hydrophobic organic compounds may abscond (Appelo & Postma 2013; Schwarzenbach et al. 2017). Investigations have shown that sorption can be increased by adding organic compounds, like compost (Rauch-Williams et al. 2010; Valhondo et al. 2018) or palm leaves (Grau-Martínez et al. 2017).

Besides sedimentary organic material, biomass can also act as a sorbent of organic compounds (Torresi et al. 2017). The sorption of organic compounds into biomass has been only related to ionic compounds (Flemming 1995; Franco et al. 2009; Torresi et al. 2017). In porous media, biomass is organized in biofilms, containing living organisms and other biological materials such as extracellular polymeric substance (EPS). The literature on the sorption of organic compounds in biofilms is poor and contradictory; for example, Torresi et al. (2017) only observed sorption into biofilm of 9 of 23 compounds, the cationic ones. On the other hand, Späth et al. (1998) observed that BTEX sorbed to biomass, mainly to EPS. Even for the authors, this was surprising because biofilm usually has a high water content (Brangarí et al. 2018), and sorption should be preferentially for polar compounds.

Lastly, mineral surfaces can also interact with organic compounds. In some environments with low organic matter concentrations, sorption into mineral surfaces of hydrophobic compounds has been observed. The sorption mechanism is through van der Waals or dipole-dipole energies and H-bonds. Although this mechanism is plausible and occurs, it is not dominant in most porous media. On the other hand, mineral surfaces can also serve as sorbents if they are ionic, which occurs specially with clays, oxides, and hydro-oxides.

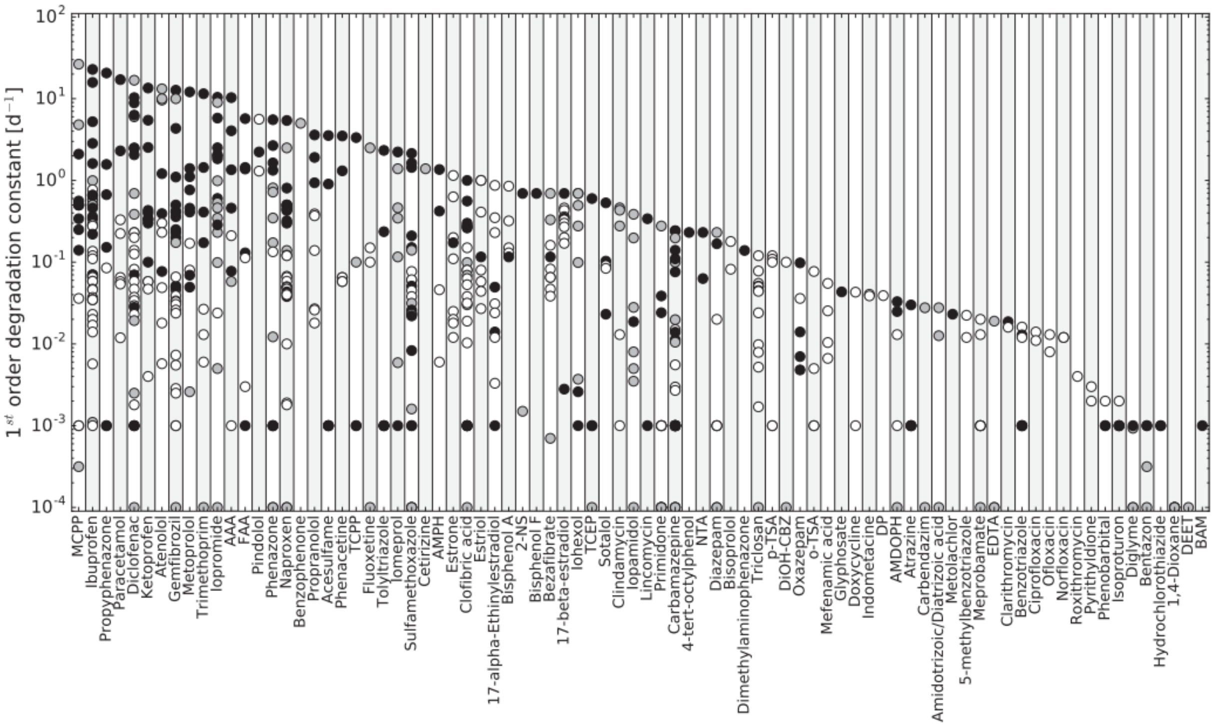


Figure 9. *Compilation of 1st order degradation rate constants for 82 compounds, including batch (indicated by white circles), column (black circles), and field (gray circles) studies. Taken from Greskowiak et al. (2017).*

Although sorption is a key process in the fate of EOCs, it is reversible and only increases the retardation of the compound transport. Greskowiak et al. (2017) investigated the degradation behaviour of 82 different substances, taking data from field, column, and batch studies. **Figure 9** shows a compilation of the 1st order degradation rate constants of this investigation. Among other things, they found with their study that the most important process for the removal of EOC in MAR is microbial degradation. Degradation of the EOCs depends on several factors like microbial activity, temperature, redox conditions or the recalcitrant behaviour of the contaminant. Other site characteristic parameters also influence the overall biodegradation rates of organic contaminants, such as microbial abundances/ diversity (Alidina et al. 2014).

Tran et al. (2013) studied the activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging organic contaminants and concluded that this degradation can be attributed to cometabolic and/or metabolic activities. **Figure 10** shows the biodegradation of EOCs via (a) metabolism and (b) cometabolism. Cometabolism occurs when the microorganisms involved do not produce energy or assimilable carbon when the substance is degraded. Autotrophic microorganisms show cometabolic activities, while heterotrophic organisms degrade EOCs via cometabolism and/or metabolic mechanisms, depending upon the nature of target EOCs and their bioavailability in the environment (Tran et al. 2013). In order to strengthen the degradation by cometabolism, conditions must therefore be created according to the contaminants present. Studies have shown that autotrophic ammonia oxidizers and nitrification play key roles in cometabolizing EOCs, particularly for slowly biodegradable compounds (Tran et al. 2013).

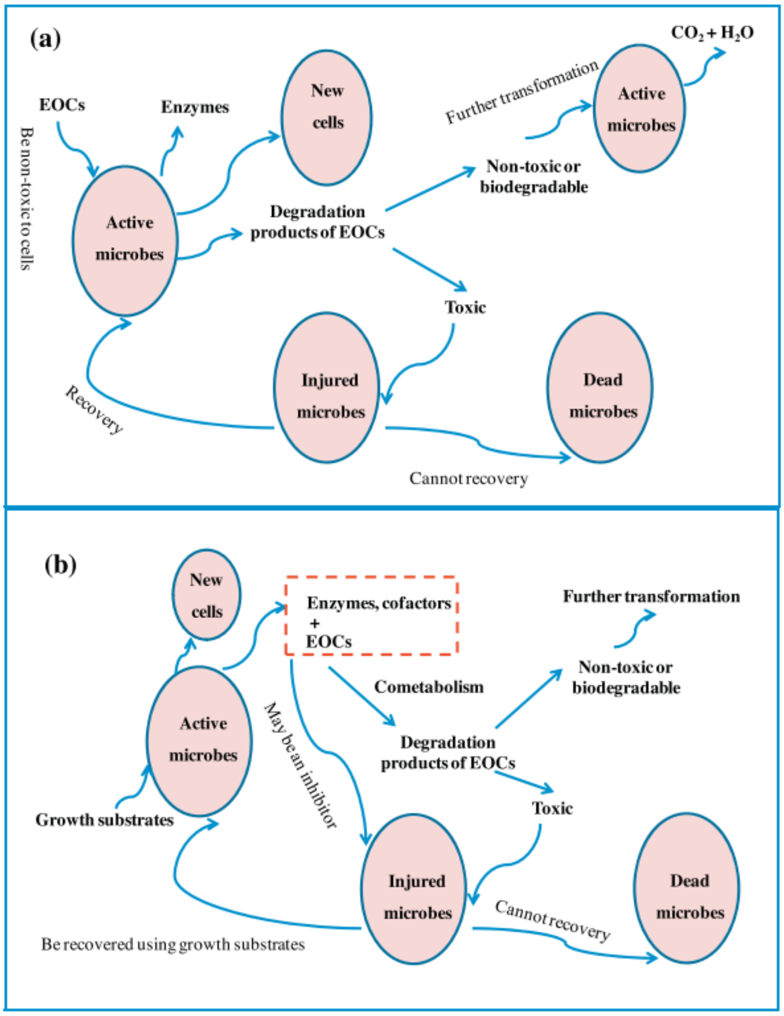


Figure 10. *Schematic of biodegradation of emerging trace organic contaminants (EOCs) via (a) metabolism and (b) cometabolism. Taken from Tran et al. (2013).*

An important factor controlling hydrogeochemical bacterially mediated reactions is the redox potential, which governs a system's reducing or oxidizing capacity. If organic substances are present, the formation of a steep redox potential gradient due to the utilization of different electron acceptors is typical for the sediment-water interface. The spatial distribution into different redox zones significantly affects the degradation of EOCs, as different reactions occur in these zones. The effect of aerobic/anaerobic conditions is observed from several examples of specific compounds. Under aerobic conditions, dissolved oxygen serves as an oxidant. Under anaerobic and anoxic conditions, other dissolved oxidants, like nitrate and sulfate, take over the role of electron acceptor. In general, EOC degradation is faster under aerobic than anaerobic conditions (Watanabe et al. 2010). Thus, the impact of reduction-oxidation conditions in EOC degradation is compound specific. For instance, the natural attenuation of three β-blockers (atenolol, metoprolol, and propranolol) was investigated under denitrifying conditions by Barbieri et al. (2012). Atenolol was removed (about 65%) via abiotic and biotic processes, whereas metoprolol and propranolol were not biotransformed.

However, these reactions and thus the degradation reactions are generally carbon limited and thus depend on the Dissolved Organic Carbon (DOC) content. Investigations have shown that using a reactive barrier succeeds in releasing DOC and increasing the removal of the contaminants investigated (Valhondo et al. 2015). The increase in removal may partly be caused by sorption or biodegradation under the various redox conditions supported by the released DOC (Valhondo et al. 2015; Schaffer et al. 2015). A barrier made of equal volumetric proportions of coarse sand and gravel, and vegetable compost from gardens and wood, supplemented with clay, was used in the examination (Valhondo et al. 2015). Vegetable compost and wood served as suppliers of organic sorption sites and for deriving easily degradable organic carbon (Valhondo et al. 2015).

In conclusion, depending on the source and the degree of pretreatment, recharging water may have undesirable concentrations of EOC, aside from other potentially hazardous substances and pathogens. Thus, for the implementation and successful execution of MAR, a wide-ranging knowledge of the local conditions and the composition of the soil and water used is necessary to make statements about what happens to the pollutants. If there is not enough natural organic matter, additional reactive barriers can be used to increase sorption. If this external addition of organic matter occurs, it can be assumed that biodegradation will also be improved by the longer residence time due to sorption (Valhondo et al. 2018) and due to the release of DOC into the system.

5.2 Recommendations

A large set of recommendations has been posed as bullet points divided according to the regulations approach, and water quality standards.

5.2.1 Regulatory framework

- "*Developing a common terminology agreement, with legal implications*. A homogeneous definition of Artificial Recharge or Managed Aquifer Recharge is thoroughly demanded, at least for the geographical areas which have a common regulation (e.g. the EU). The regulation reviewed hint that there is a shared idea about the MAR concept. Still, the precise meanings are missing in some of them, driving, in case of conflict, to judge’s decisions in the absence of widely approved common legal definitions. Such definitions should be compulsory, at least at the European level. In this sense, the WFD should include a legal definition of MAR far from ambiguities (Fernández Escalante & García-Rodríguez 2004). Another practical alternative at the European level would be the development of a Common Understanding between the Member States, such as in a CIS Guidance Document."

- "*Including a permitting process*. Water allocation permits and water extraction rights ownerships must be considered in all regulations and established well in advance, including the simple right of use. At the European level, an authorisation is a requirement of the WFD. What is needed is a risk-based approach to develop the conditions of the permit. This approach could be replicated in other countries. Some national laws still leave the governments the right to grant permits to regional authorities, as is the case in Spain, while the fundamental right must be the same for all applicants. This aspect of the regulatory framework is especially relevant in the face of pressure on water resources, such as over-exploitation of aquifers or climate change impacts, which can exacerbate water ownership conflicts (Rodríguez-Escales et al. 2018)."
- "*Legal development*. There is an insufficient theoretical background on legal aspects of MAR. Furthermore, there are very few countries with a specific regulation on MAR and SAT-MAT. From these, some do not explore in detail the water quality standards, the type of infiltration system or the final use, making difficult for the authorities to grant permits (Sastre-Beceiro 2009)."
- "*Independent control and surveillance*. Once an authorisation has been granted, there is a general failure in the mechanisms of control and oversight of the operations. Furthermore, the water-right holder usually provides most of the information and, only in singular cases, the operators, river basin authorities or civil servants taking care of the water quality. A "structured reporting process" should be developed."
- "*Time continuity*. Many experiences have been related to research and development projects. Once such projects come to an end either for budgetary or planning reasons, they are abandoned, and the continuity is, generally, uncertain. The Administration and the Water Basin Authorities should study continuity mechanisms to allow assessing the long-term effects of MAR."
- "*Inclusion of Budgetary aspects*. The financial aspects of MAR projects are frequently excluded in both, the regulations and the granting of authorisations. The Water Authorities might request detailed budgets and a certain guarantee of continuity. These demands do not appear in the analysed regulations and guidelines. A certain consideration could be given to positive economic externalities of MAR, e.g. increased water availability, reduction of pumping cost due to a higher water table and blue environmental values. In this way, the unmonetised benefits of MAR would be included in the equation, and a net positive effect of MAR systems would be guaranteed."
- "*Including the technical background for authorisations*. In cases in which local water authorities implement regulations (i.e. implemented at the regional level), there might be slight differences in the monitoring and permission approaches with respect to the national law. Concessions to grant a MAR implementation must take into account the specific water quality standard for an area. It should also require specific studies for the endorsed area duly signed by a competent technician. Some points of concern are the construction of the MAR

facilities, operation and monitoring. The compliance of regulation is in state or operator´s control, however, often not fully implemented. It is essential to study whether the technical solutions proposed to improve the efficiency of any MAR scheme are legal, in accordance with the applicable laws. This aspect could be particularly relevant when dealing with the potential beneficial impact of the unsaturated zone, so important in the final groundwater quality due to interaction processes."

- "*Moving forward with the WFD*. The implementation of MAR and SAT-MAR in the EU may be facilitated by taking the following measures: 1) Establishing a framework of permit or authorisations (EC 2006); 2) Establishing control and surveillance mechanisms to ensure the implementation of the permit conditions; and 3) Undertaking the necessary oversight of MAR systems to renew any permission or concession (EC 2007)."

5.2.2 Water quality standards

- "*Tailoring water quality guidelines based on aquifers and source water*. Water standards for MAR must be designed at the aquifer level and taking into account the interactions between the source water and the aquifer. This involves studying the aquifer in-depth and considering the possible sources of water. In this sense, it might be feasible to extend water quality standards across aquifers with similar characteristics. The nation-wide standards seem to be the most straightforward approach, and the aquifer-wide standards would be the safest."
- "*High number of pollutants to be regulated.* MAR possesses great potential in the face of multiple water-related challenges, as long as contamination is minimised. There are scientific uncertainties related to water quality processes and water-mineral interactions. The number of potential pollutants to be analysed may be too large, and their chemical interactions too complex to be demanded by any regulation (Silver et al. 2016). This situation urges an integrated approach considering water origin (with different degrees of potential pollution), MAR technology and final uses. The WFD allows this flexibility, with threshold values for groundwater being established at the groundwater body level; hence the relevance of the risk-based approach: The more stringent the controls on the quality of the source of water, the fewer parameters would need to be taken into consideration at the end."
- "*MAR sources and receiving medium considerations.* During MAR activities, the receiving medium has a certain capability to remove pollutants, even though the donor water body must be in good chemical status, as appointed in the WFD. A risk analysis approach usually counts on this capability, while water quality standards consider, to a limited extent the aquifer´s purification capacity."
- "*Water quality standards* should be differentiated according to the MAR technology involved to minimise the impact of the previous points exposed, as it has been done for instance in Spain, Mexico, and the GWD. In these regulations, direct and indirect inputs are taken into consideration following different MAR techniques. It is also important to consider how the impact of the unsaturated zone (not just the aquifer) is taken into account in the legislation."
- "*Updating some water quality standards.* Some pollutants with proved adverse effects on health and the environment are challenging to determine due to high detection limits in laboratories or analytical costs, e.g. NDAs (Fernández Escalante 2005). In this sense, some specific water quality standards should be reviewed and updated periodically according to the

state-of-the-art´s progress and the instrumental measuring capabilities (for "aquifer-wide" standards)."

- "*Considering the monitoring cost.* Guidelines must consider the cost of analysis, especially in developing countries and when the monitoring frequencies are compulsory by law. International institutions such as the IAH-MAR Commission should provide technical support when tailoring MAR regulations and water quality standards."
- "*Considering monitoring frequencies for each parameter.* Water quality guidelines might include additional columns specifying the frequency of monitoring for each parameter and the exact point to collect the samples, e.g. infiltration basin, extraction well, etc."
- "*Including common parameters.* It is advisable to measure major ions such as bicarbonate, calcium and potassium. They are not considered in most of the reviewed regulations, and they are essential in relation to calcite precipitation (chemical clogging) and water processes involved in the hydrogeological methods employed to study groundwater quality and evolution (e.g. hydrograms, ionic relations, and models). The sets of parameters and compounds exposed in **Table 2** cover most of the regulated necessities, except for highly polluted environments, in which specific and adapted analyses should be requested."
- "*Considering the final use.* Water quality standards should also consider the final use of the water for which MAR has been implemented. Domestic water supply is more demanding in terms of water quality than irrigation or industrial uses. Thus, the purification process must be adapted to the final use. Differentiating water quality standards depending on the water needs to be covered (e.g. the 2020/741 Regulation on water reuse (European Parliament 2020)), is controversial. Setting permissive limits for uses which require low water quality (e.g. irrigation) might jeopardise other potential uses (e.g. urban water supply). Even MAR in cities entails certain risks, reduced by means of a proper monitoring, as it is the case of the Shafdan MAR scheme in Israel (**Figure 11**).”

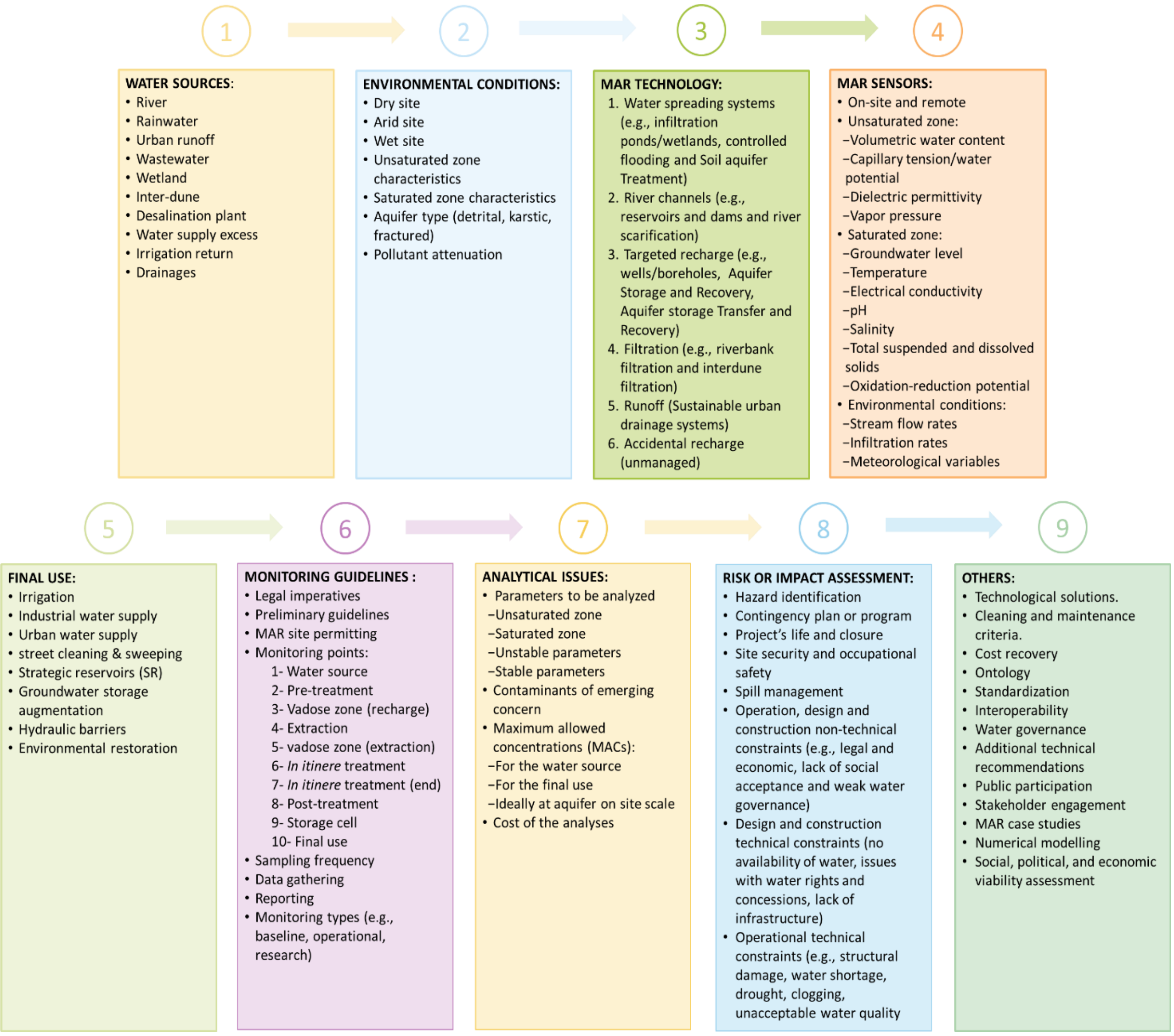
Figure 11. *MAR regulated system in Shafdan, Israel. Sensors inside the infiltration basins allow the water quality monitoring in real time, in order to attain the standards of quality. From Fernández Escalante et al. (2020).*

Table 2. *Proposal of a general list of parameters to be determined in laboratory and field for a MAR-related water sample. Modified from Fernández Escalante et al. (2020).*

PARAMETERS (MAR water)	EXPLANATION
E.coli	Ecotoxicological aspects. Demanded in most of the regulations (SAT-MAR)
Nematodes	Ecotoxicological aspects. Demanded in most of the regulations (SAT-MAR)
pH	Influence on REDOX conditions
Temperature	Environmental conditions. Product of solubility, stoichiometry
Conductivity	Parameter related to salinization and the total amount of compounds
Chemical Oxygen Demand (COD)	Specific parameter for water reuse, to be removed in case of natural water origin (SAT-MAR)
Biochemical Oxygen Demand in 5 days (BOD_5)	Specific parameter water reuse, to be removed in case of natural water origin (SAT MAR)
Total Dissolved oxygen (TDO)	Potential hyper-oxidation conditions and gas clogging creation in the receiving medium
Total Organic Carbon (TOC)	Indicator of biological clogging potential and buffer for chemical reactions
Total nitrogen (N)	Residual product after nitrogenised molecules breakdown, e.g. product of diffuse contamination decomposition
Total phosphorus (P)	Indicator of biological clogging potential and buffer for chemical reactions
Total suspended solids (TSS)	Parameter related to turbidity and demanded in most of the regulations
Total Dissolved Solids (TDS)	Parameter related to turbidity and demanded in most of the regulations
Turbidity	Parameter requested in most of the regulations
Ammonium (NH_4)	Residual product after nitrogenised molecules breakdown
Nitrates (NO_3^-)	Thick molecules usually trapped in the receiving mediums in which MAR projects take place
Sulphates ($SO_{4)}$	Macroconstituents, chemical attack on materials
Chloride	Macro, chemical attack on materials, salinity indicator
Bicarbonates	Parameter not requested in the regulations but fundamental for hydrochemical calculations
Sodium (Na)	Macro, chemical attack on materials, salinity indicator
Potassium (K)	Parameter not requested in the regulations but fundamental for hydrochemical calculations
Calcium (Ca)	Parameter not requested in the regulations but fundamental for hydrochemical calculations, hardness, etc.
Magnesium (Mg)	Parameter not requested in some regulations but fundamental for hydrochemical calculations, hardness, etc.
Boron (B)	Phytotoxic ion par excellence
Silica (Si)	Determines geochemical environments and biological/chemical reactions. Potential quartz precipitation
Arsenic (As)	Ecotoxicological ion par excellence
Iron (Fe)	Metal with high effect on physical, chemical and biological clogging generation
Manganese (Mn)	Physical, chemical, biological clogging determinant parameter
Chromium (Cr)	Physical, chemical, biological clogging determinant parameter. Requested in most of the regulations
Copper (Cu)	Special effect on crops. Usual spill from agro-industrial activities
Zinc (Zn)	Special effect on crops
Fats and oils	Specially for urban areas runoff and SAT-MAR (can be removed for natural river / rain water

5.3 Monitored and Intentional Recharge (MIR)

The review of MAR regulations and guidelines and the experience of several years with projects for artificially recharging aquifers have led to the development of the Monitored and intentional recharge (MIR) conceptual model. This model's goal is to provide a framework with the minimum factors that any regulation or guideline on MAR should consider and develop. These factors have been grouped into nine blocks based on their main topic. The proposed blocks are the following (**Figure 12**): i) water sources, ii) environmental conditions, iii) MAR technology, iv) MAR sensors, v) final use, vi) monitoring guidelines, vii) analytical issues, viii) risk or impacts assessment, and ix) others.



1

WATER SOURCES:
- River
- Rainwater
- Urban runoff
- Wastewater
- Wetland
- Inter-dune
- Desalination plant
- Water supply excess
- Irrigation return
- Drainages

2

ENVIRONMENTAL CONDITIONS:
- Dry site
- Arid site
- Wet site
- Unsaturated zone characteristics
- Saturated zone characteristics
- Aquifer type (detrital, karstic, fractured)
- Pollutant attenuation

3

MAR TECHNOLOGY:
1. Water spreading systems (e.g., infiltration ponds/wetlands, controlled flooding and Soil aquifer Treatment)
2. River channels (e.g., reservoirs and dams and river scarification)
3. Targeted recharge (e.g., wells/boreholes, Aquifer Storage and Recovery, Aquifer storage Transfer and Recovery)
4. Filtration (e.g., riverbank filtration and interdune filtration)
5. Runoff (Sustainable urban drainage systems)
6. Accidental recharge (unmanaged)

4

MAR SENSORS:
- On-site and remote
- Unsaturated zone:
  –Volumetric water content
  –Capillary tension/water potential
  –Dielectric permittivity
  –Vapor pressure
- Saturated zone:
  –Groundwater level
  –Temperature
  –Electrical conductivity
  –pH
  –Salinity
  –Total suspended and dissolved solids
  –Oxidation-reduction potential
- Environmental conditions:
  –Stream flow rates
  –Infiltration rates
  –Meteorological variables

5

FINAL USE:
- Irrigation
- Industrial water supply
- Urban water supply
- street cleaning & sweeping
- Strategic reservoirs (SR)
- Groundwater storage augmentation
- Hydraulic barriers
- Environmental restoration

6

MONITORING GUIDELINES :
- Legal imperatives
- Preliminary guidelines
- MAR site permitting
- Monitoring points:
  1- Water source
  2- Pre-treatment
  3- Vadose zone (recharge)
  4- Extraction
  5- vadose zone (extraction)
  6- *In itinere* treatment
  7- *In itinere* treatment (end)
  8- Post-treatment
  9- Storage cell
  10- Final use
- Sampling frequency
- Data gathering
- Reporting
- Monitoring types (e.g., baseline, operational, research)

7

ANALYTICAL ISSUES:
- Parameters to be analyzed
  –Unsaturated zone
  –Saturated zone
  –Unstable parameters
  –Stable parameters
- Contaminants of emerging concern
- Maximum allowed concentrations (MACs):
  –For the water source
  –For the final use
  –Ideally at aquifer on site scale
- Cost of the analyses

8

RISK OR IMPACT ASSESSMENT:
- Hazard identification
- Contingency plan or program
- Project's life and closure
- Site security and occupational safety
- Spill management
- Operation, design and construction non-technical constraints (e.g., legal and economic, lack of social acceptance and weak water governance)
- Design and construction technical constraints (no availability of water, issues with water rights and concessions, lack of infrastructure)
- Operational technical constraints (e.g., structural damage, water shortage, drought, clogging, unacceptable water quality

9

OTHERS:
- Technological solutions.
- Cleaning and maintenance criteria.
- Cost recovery
- Ontology
- Standardization
- Interoperability
- Water governance
- Additional technical recommendations
- Public participation
- Stakeholder engagement
- MAR case studies
- Numerical modelling
- Social, political, and economic viability assessment

Figure 12. *The nine blocks comprised in the Monitored and Intentional Recharge (MIR) conceptual model and some of the aspects each one develops. From Fernández Escalante et al. (2022).*

Two main approaches were used to arrive at this conceptual model: i) critically reviewing the existing documents that regulate or guide MAR projects, and ii) using a scoring system to determine the most critical factors discussed in the documents.

The following documents were reviewed: the WHO guidelines for water recycling, the Australian guidelines on MAR, the USA regulatory body on MAR, including rules scoped at the state level, the MAR guidelines of the American Society of Civil Engineers (ASCE), the European guideline on waste-water reuse for irrigation, and MAR regulatory or guiding documents for Chile, India, and Mexico.

The scoring system consisted of the following: the main aspects elaborated in the documents reviewed were listed. Subsequently, the level of development of each of these aspects in the MAR documents was assessed with a score from zero to four, where zero corresponds to no mention and four to a detailed discussion on the topic. The scores for each main aspect were added, ranked and included in the most appropriate MIR block. The final ranking can be found in Fernández Escalante et al. (2022).

One of the strengths of the MIR concept is that it provides a series of graphical illustrations of the blocks' key aspects that ease understanding of the main concepts. **Figure 13** is one of these illustrations and visually summarises the blocks that are part of MIR.

Next, a brief discussion of the MIR blocks and the appropriate figures or tables are provided. More details can be found in Fernández Escalante et al. (2022).

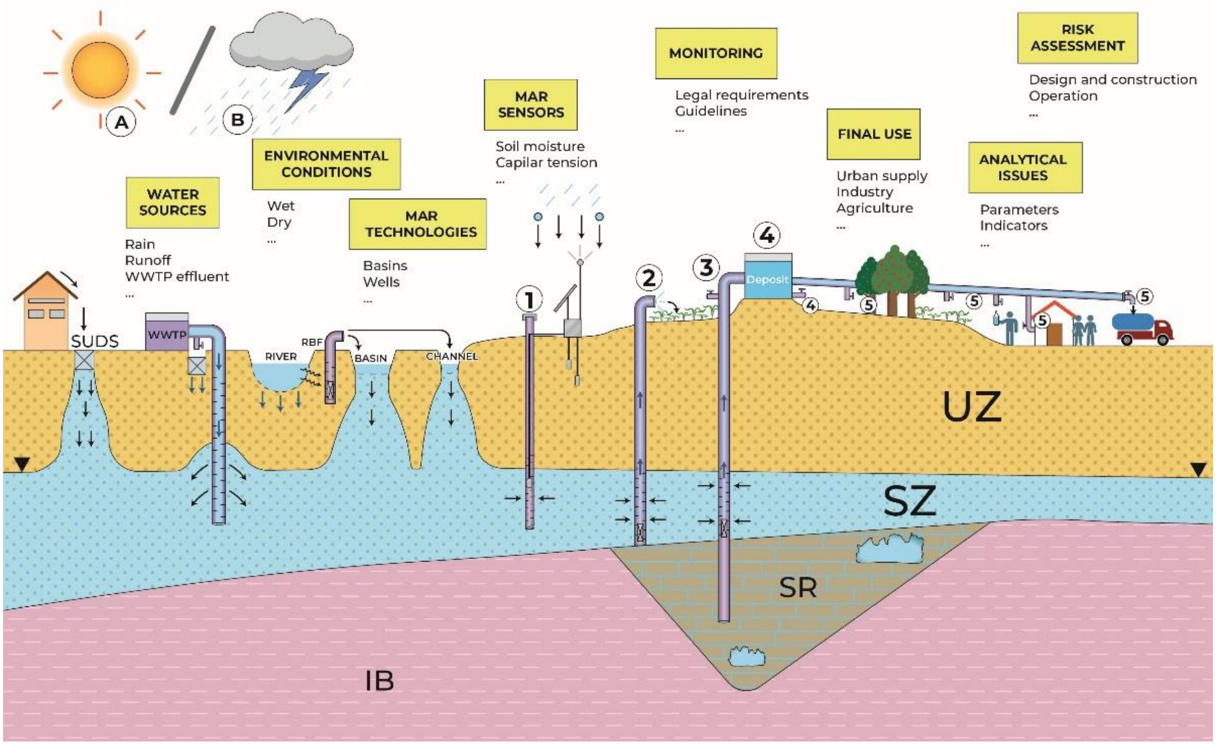


__Figure 13.__ Summary of the main block comprised in the Monitored and Intentional Recharge (MIR) conceptual model. From Fernández Escalante et al. (2022).

5.3.1 Water sources

The main water sources often found among MAR projects are surface water bodies (rivers and lakes, predominantly), rainwater, and reclaimed wastewater. This block of MIR discusses essential matters. For instance, it recommends considering any surface water surplus (after all water demands have been met, including ecological volumes) as potentially usable for MAR since valuable water can be lost to evaporation or the sea. Furthermore, the promising role of wastewater in closing the water cycle is highlighted and the quality issues that must be faced when using urban runoff. **Figure 14** depicts the most common water sources for MAR.

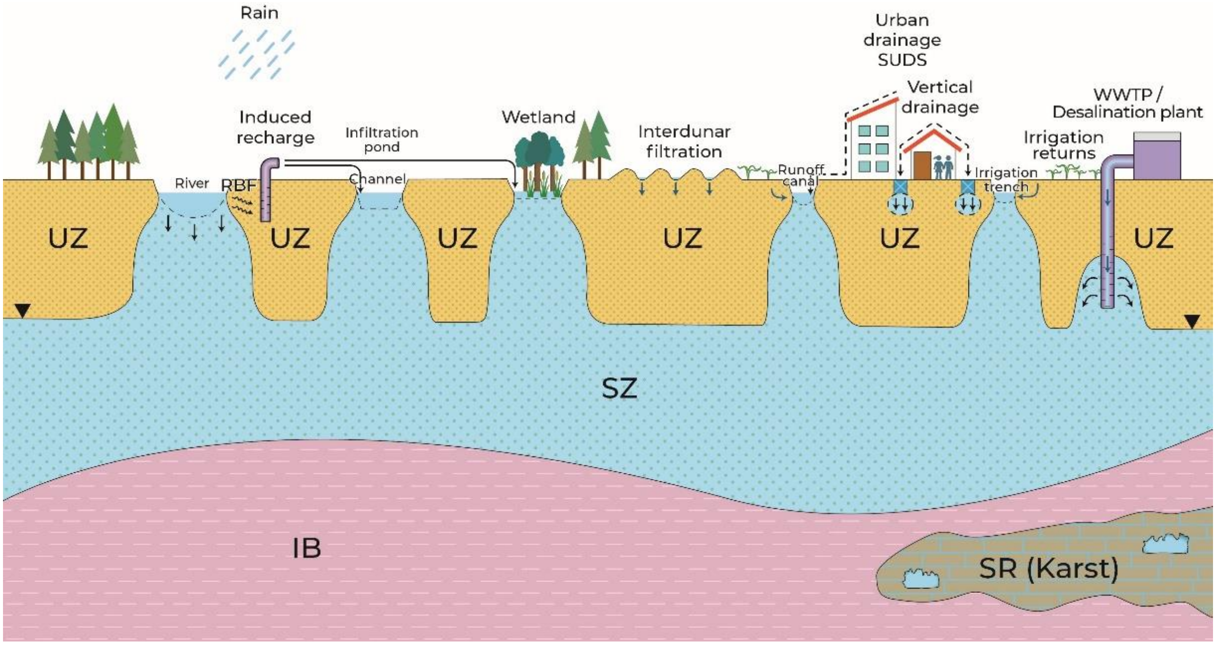


Figure 14. *Main water sources considered by the Monitored and Intentional Recharge (MIR) conceptual model. From Fernández Escalante et al. (2022).*

5.3.2 Hydrogeological and environmental conditions

MIR also recommends a careful evaluation of the hydrogeological and environmental conditions. These conditions will determine the feasibility of underground storage and the availability of water resources for MAR. Key aspects to consider in relation to this block include the aquifer's characteristics (hydraulic conductivity, transmissivity, storability, etc.) and type (karstic, detrital, fractured hard-rock) and the magnitude and distribution of hydrological variables such as precipitation, runoff, river flows, etc.

This block also introduces crucial and contemporary topics such as the need to characterise long-term performance under climate change, the contaminant attenuation potential of the saturated and unsaturated zones, and the evaluation of impacts on dependant ecosystems. **Figure 15** shows some of the most usual hydro(geo)logical settings where MAR projects are developed.

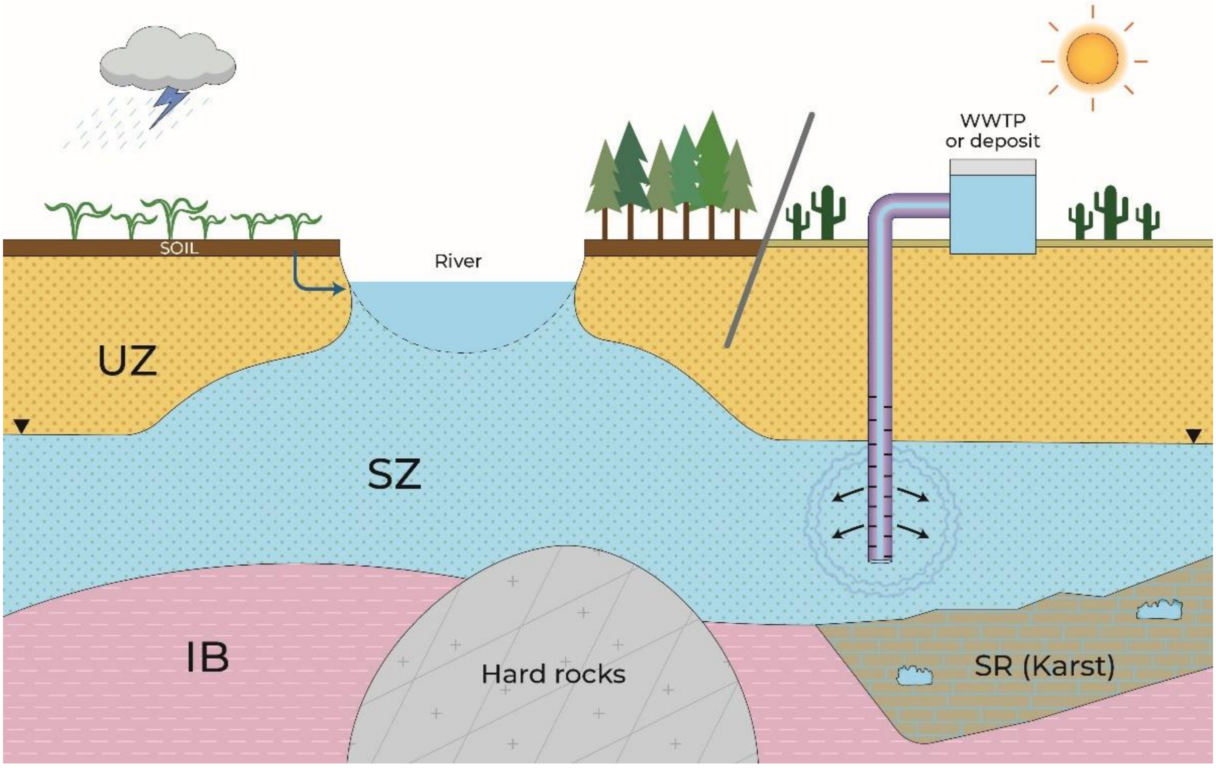


Figure 15. *Possible hydro(geo)logical conditions to consider when drafting MAR regulations and guidelines. From Fernández Escalante et al. (2022).*

5.3.3 MAR Technology

There is great diversity in MAR methods that can address a wide range of water-related issues. Consequently, the third block of the MIR concept suggests evaluating the existing technologies under the lens of the particular conditions of the intended MAR project. To ease this task, MIR provides a list of MAR technologies that include pictures, diagrams, the spatial distribution of the solution, and some examples in Spain. **Table 3** is a simplified version of the full list, both available in the article by Fernández Escalante et al. (2022).

Table 3. *Compilation of main MAR technologies categorised into five main groups. An additional group, including sources of unintentional recharge, is included for reference. From Fernández Escalante et al. (2022).*

MAR category	MAR type
Water spreading	- Infiltration ponds/ wetlands - Channels and infiltration ditches - Ridges/ soil and aquifer treatment techniques - Infiltration fields (controlled flooding)
River channels	- Reservoir dams and dams - Permeable dams - Levees - Riverbed scarification - Sub-surface/ underground dams - Drilled dams
Targeted recharge	- Qanats (underground galleries) - Open infiltration wells, shafts - Deep wells and boreholes - Boreholes - Sinkholes, collapses - Aquifer Storage and Recovery (ASR) - Aquifer Storage, Transfer and Recovery (ASTR)
Filtration	- River Bank Filtration (RBF) - Interdune filtration - Underground irrigation
Rain based systems	- Rainwater harvesting systems - Sustainable Urban Drainage Systems (SUDS)
Accidental recharge	- Accidental recharge from pipes and sewer systems - Accidental recharge by irrigation return

5.3.4 MAR Sensors for data gathering

This block elaborates on the sensors used to monitor environmental variables when conducting MAR. It introduces the issue of data interoperability through the review by Henao Casas et al. (2022a), who point out that data gathered by data loggers from different manufacturers store and retrieve information in various formats that can differ considerably. This situation requires additional efforts to integrate and analyse the data. A sound way to circumvent this issue is by arriving at a data storage standard, enhancing interoperability. **Table 4** lists properties commonly measured in MAR projects.

Table 4. *Environmental variables commonly measured during MAR operations. These variables have been categorised as a function of the realm involved: the atmosphere, the hydrosphere, the pedosphere and the lithosphere. From Fernández Escalante et al. (2022).*

Realm (earth-sphere)	Property
Environmental conditions (atmosphere and hydrosphere)	- Flow rates and discharge - Soil infiltration /seepage rates - Precipitation - Solar radiation - Wind speed and direction - Relative humidity - Other meteorological variables
Unsaturated zone (pedosphere)	- Volumetric Water Content (VWC) - Soil electrical properties (dielectric permittivity, resistivity, and conductivity) - Water potential - Vapour pressure - Conductivity - Temperature
Saturated zone (lithosphere)	- Water level - Temperature - Conductivity - pH - Oxidation-reduction potential (ORP) - Turbidity - Total Dissolved Solids (TDS) - Total Suspended Solids (TSS) - Other physic-chemical properties - Salinity - Hydrogeochemical parameters

5.3.5 Monitoring guidelines

This MIR block emphasises the importance of clear guidelines to monitor water quality and quantity variables. Ten key water sampling points are proposed (**Figure 16**). These points are determined as a function of the location in the MAR water production process (e.g., source water treatment, passage through the unsaturated/saturated zone, extraction, post-treatment, etc.). The block also shows some of the most common sampling/measuring frequencies and how information is retrieved: on-site or remotely (**Figure 16**).

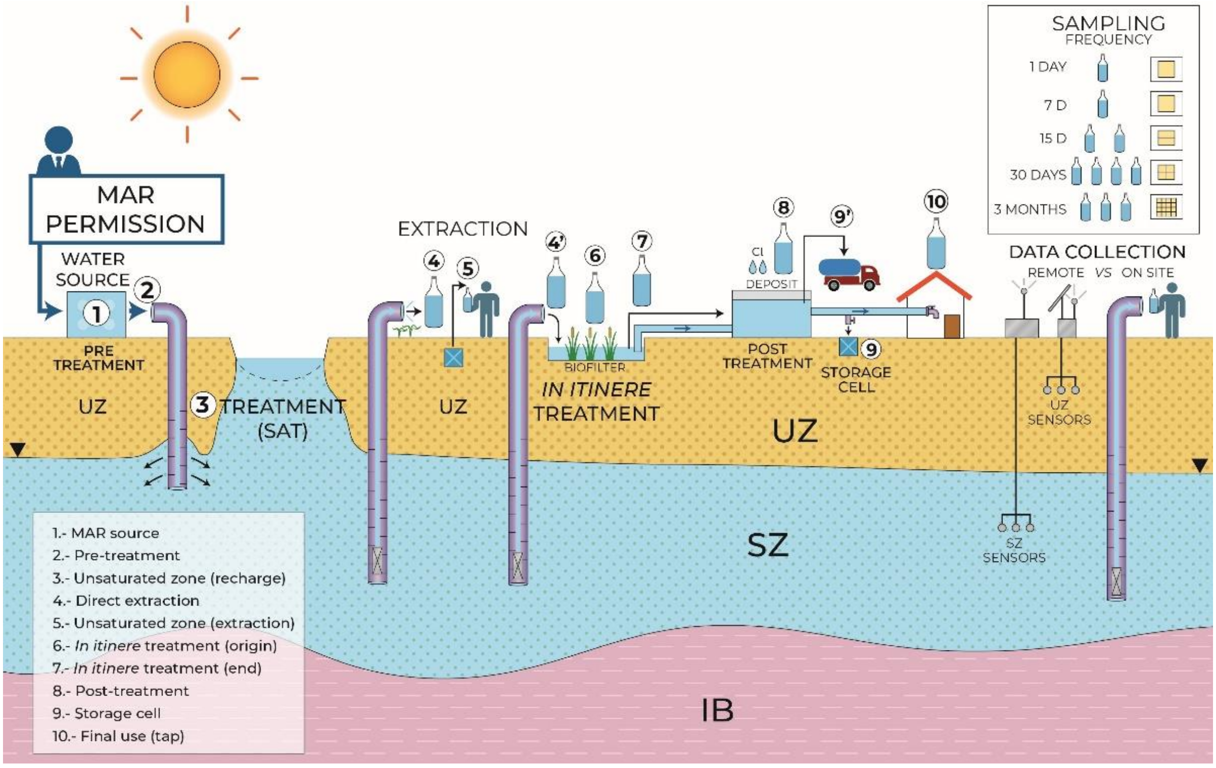


Figure 16. *Fundamental monitoring aspects to consider when drafting MAR guidelines, including sampling point's frequency and sensors. From Fernández Escalante et al. (2022).*

A great part of the monitoring chapter is based on experiences on modeling from MARSoluT members (Malta, Spain, and Italy). The modeling results from Malta have already been published and are accessible in MARSoluT Deliverable D4.1 (MARSoluT 2023b). These findings were observed within the MARSoluT individual research project (IRP) "*Hydrogeological and geochemical modelling of a seawater intrusion barrier in an island/coastal groundwater body*".

5.3.6 Final use of the intentionally recharged water

This block showcases the most common uses for the water stored underground through MAR, which include irrigation, drinking water supply, industrial water supply and strategic storage, among others (**Figure 17**). This block also points out the importance of involving water user organisations in managing water resources to enhance governance.

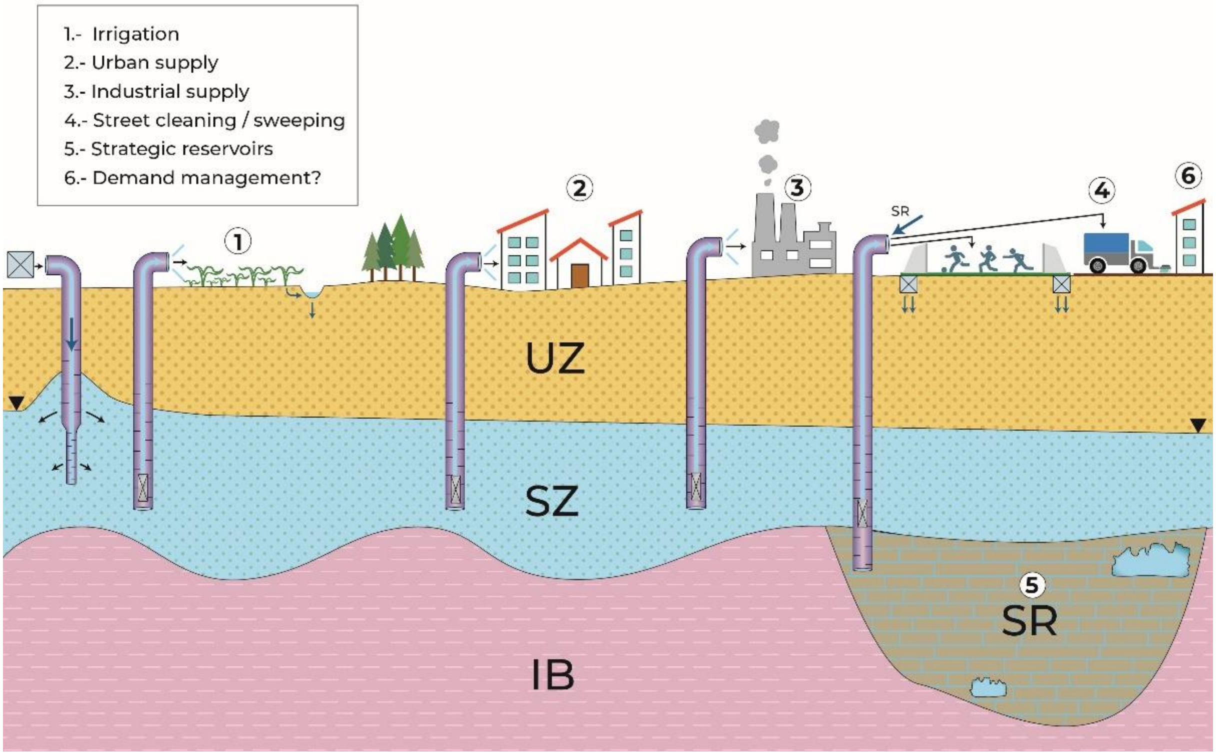


Figure 17. *Final use of MAR water. From Fernández Escalante et al. (2022).*

5.3.7 Analytical aspects

This block entails concepts related to the parameters that determine water quality. It presents the minimum parameters that should be included in any water quality monitoring program for MAR (**Table 2**). It also elaborates on hot topics, including the need for increasing surveillance of pollutants of emerging interest, the scope of maximum allowable concentrations (MACs), the dimension of the regions to which they should be applicable, and the lack of water quality data monitoring found across many regions.

5.3.8 Risk and/or impact assessment

MIR proposes adopting a risk approach in which risks are identified, and multiple barriers are setup so that the residual risk is acceptable. Two main blocks of risks are presented to help in their identification (**Table 5**).

Table 5. *Main risk to bear into consideration concerning MAR operations. From Fernández Escalante et al. (2022).*

	Technical aspects	**"Non-technical" aspects**
Design and construction	- Legal constraints - Economic constraints - Lack of social acceptance - Weak water governance	- Availability of water source - Concessions or water rights constraints - Water scarcity - Hydrogeological assessment - Lack of infrastructure. - Dependence of valuable habitats
Operation (and management)	- Legal constraints - Economic constraints - Lack of social acceptance - Weak water governance	- Structural damage - Water shortage and volume constraints at the source - Drought - Clogging - Unacceptable water quality in a sensitive location - Specific objectives - Distortion of local ecological relations

5.3.9 Other aspects and general recommendations

The final block is open to new aspects. It also discusses some topics that were not suited to any of the other blocks, such as the importance of stakeholder engagement, the principle of the recovery of costs, and considering collateral benefits and interoperability.

6. Water Quality Characterization in MAR and SAT-MAR Sites in Spain

There are relatively few regulations on MAR worldwide. Some use maximum allowable concentration (MAC) standards for MAR source water to control pollution, including the USA, Mexico, Spain, Italy, and The Netherlands (Fernández Escalante et al. 2020, 2022). Some regulations and studies suggest a risk approach which is probably more adequate to prevent water pollution when realising MAR (NRMMC et al. 2009; Zheng et al. 2023).

The current analysis explores whether using MACs would be a convenient approach to reducing the risk of aquifer contamination when artificially recharging aquifers in Spain. In the following, water quality issues of 11 MAR sites in Spain are presented, with Los Arenales being the main test site.

6.1 Methodology

A sound MAC standard to control water contamination during MAR should be able to consider the water quality variability of water sources for MAR within its jurisdiction and don't pose too stringent limits that could deter the implementation of MAR. Consequently, this analysis focuses on two main aspects: an exploration of MAR water quality at MAR sites in Spain and a comparison between several quality parameters in these sites and some MAC-based water quality control standards.

6.1.1 Evaluation of water quality at Spanish MAR sites

The evaluation of the hydrochemistry of water sources for MAR at several Spanish MAR sites is based on reported values for multiple water quality parameters. This evaluation also entails an analysis of the main hydrofacies and the principal water quality issues that every MAR site faces.

The collection of Spanish MAR sites was established based on the availability of water quality data, which was gathered either from the literature or through direct requests to institutions involved at any stage of a MAR project implementation. The geographical location and general characteristics of the selected MAR sites are shown in **Figure 18** and **Table 6**.

6.1.2 Comparison of MAR water sources with MAC-based standards

Hydrochemical parameters of MAR water sources from multiple Spanish MAR sites were compared to the corresponding maximum allowable concentrations established by European countries for artificial recharge (= Managed Aquifer recharge). This analysis aims to elucidate whether Spanish MAR sites would comply with existing regulations and, consequently, whether a MACs approach would satisfactorily prevent groundwater contamination, increase the water and food security, and simultaneously, give room for further MAR implementation.

Each water quality parameter from MAR water sources was compared to the corresponding limit in the MAC standards. The total number of times the parameter is above the standard was counted. MAR sites that are uncompliant with a given regulation due to a breach in the MAC standard were also tracked. The water quality parameters available for each MAR site are shown in **Table 7**. The number of water quality analysis considered for each site are presented in **Table 8**.

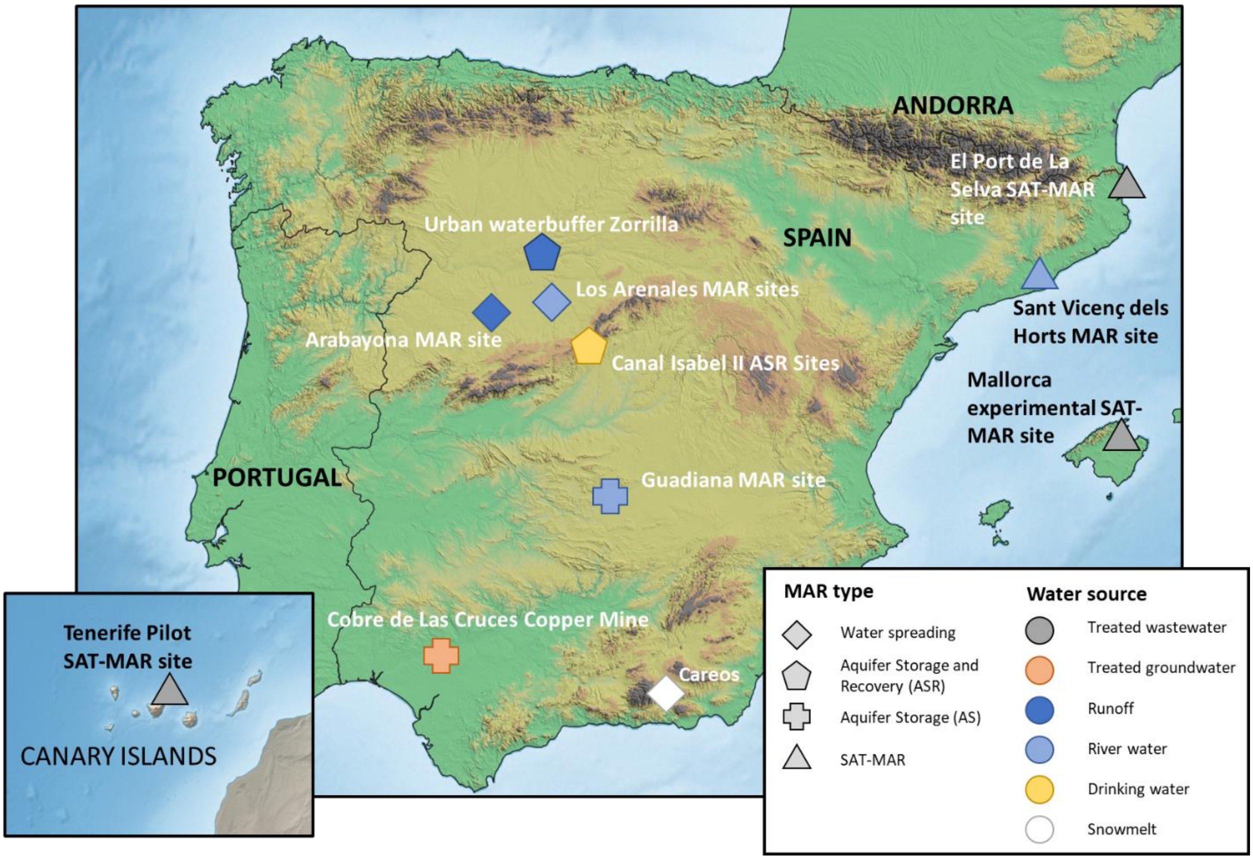


Figure 18. *Evaluated MAR sites in Spain.*

Table 6. *Characteristics of the Spanish MAR sites evaluated.*

MAR site	**Location**	**Source water type**	**Objective**	**MAR type**
Arabayona MAR site	Arabayona de Mógica, Castilla y León	Runoff	Evacuation of flooding water to a neighbour aquifer	Rainwater harvesting
Canal Isabel II ASR Sites	Region of Madrid	Treated water	Strategically store water in case of need	ASR
Careos	Granada and Almería provinces	Snowmelt	Improve water supply for agriculture and villages during the dry season	Water spreading
Cobre de las Cruces Copper Mine	Province of Sevilla, Sevilla	Treated wastewater	Drain the open-pit area	AS
El Port de La Selva SAT-MAR site	El Port de la Selva, Catalunya	Treated wastewater	Water reuse to cover peak demands	SAT
Guadiana MAR site	Ciudad Real province, Castilla La Mancha	River water	Recover environmental assets and agriculture	AS
Los Arenales MAR sites	Segovia and Valladolid Provinces, Castilla y Leon	River water	Reverse groundwater depletion and sustain irrigation	Water spreading
Mallorca experimental SAT-MAR site	Mallorca, Islas Baleares	Treated wastewater	Strategic reservoir for peak demands	SAT
Sant Vicenç dels Horts MAR site	Sant Vicenç dels Horts, Catalunya	Treated wastewater	Increase the irrigation guarantee	SAT
Tenerife Pilot SAT-MAR site	Tenerife Island, Canary Islands	Treated wastewater	Incipient experiment to diversify water supply systems	SAT
Urban Water buffer Zorrilla	Valladolid, Valladolid	Rainwater	Experiment to use urban runoff for irrigation of city gardens	ASR

Table 7. *Parameters considered for each MAR site in the water quality standard analysis. This table did not include parameters that were measured as part of the water quality analysis and did not yield a value above the detection limit.*

PARAMETER	Arabayona	Canal Isabel II	Careos	Cobre de las Cruces	El Port de La Selva	Guadiana	Los Arenales	Urban Water buffer	Tenerife	Mallorca	Sant Vicenç dels Horts
Alkalinity, total	-	-	X	X	X	-	X	-	-	-	X
Chemical Oxygene Demand (COD)	-	-	-	-	-	-	-	-	X	-	-
Conductivity (µS/cm)	X	X	X	X	X	X	X	X	X	-	X
Dissolved Organic Carbon (DOC)	-	=	-	-	-	-	-	-	-	-	-
Max. pH	X	X	X	X	X	X	X	X	X	-	X
Temperature (ºC)	-	-	X	-	X	-	X	X	-	-	-
Total Dissolved Solids (TDS)	-	-	-	X	-	-	X	-	-	-	-
Total nitrogen (N)	-	-	-	-	-	-	-	-	X	-	-
Total Organic Carbon (TOC)	-	-	X	-	X	-	-	-	-	-	X
Total phosphorus (P)	X	-	-	-	-	-	-	X	X	-	X
Total Suspended Solids (TSS)	-	-	-	-	-	-	X	X	-	-	-
Turbidity (NTU)	-	-	-	-	X	-	X	-	-	-	-
Calcium (Ca) hardness in ºF or	-	-	X	-	-	X	X	X	-	X	X
Magnesium (Mg)	-	-	X	-	-	X	X	X	X	X	X
Sodium (Na)	-	-	X	X	X	X	X	X	-	X	X
Chloride (Cl^-)	-	-	X	X	X	X	X	-	-	X	X
Sulphate (SO_4^{2-})	-	-	X	-	X	X	X	X	-	X	X
Fluoride	-	-	-	X	-	-	-	-	-	-	-
Nitrite-Nitrate (both as N)	-	-	-	-	X	-	-	-	-	-	-
Nitrate (NO_3^-)	X	X	X	-	X	X	X	X	X	X	X
Nitrite (NO_2^-)	X	-	-	-	-	X	X	-	-	-	X
Ammonia (NH_4^+)	-	-	-	-	X	-	X	X	X	-	X
Phosphates	-	-	-	-	-	X	X	-	X	-	-
Boron (B)	-	-	-	X	X	X	-	-	-	-	-
Cyanide (CN^-)	-	-	-	-	X	-	-	-	-	-	-
Faecal Coliforms (f.c /100 ml)	-	-	-	-	X	-	-	-	-	-	-
E.coli (UFC/100 mL)	-	-	-	-	-	-	-	X	-	-	-
Aluminium (Al)	-	-	-	-	-	-	-	-	-	-	X
Antimony (Sb)	-	-	-	-	-	-	-	-	-	-	-
Arsenic (As) VI	-	X	-	X	-	-	-	-	-	-	-
Barium (Ba)	-	-	-	X	-	-	-	-	-	-	-
Cadmium (Cd)	-	-	-	-	-	-	-	-	-	-	-
Chromium total (Cr)	-	-	-	-	-	-	-	-	-	-	-
Copper (Cu)	-	-	-	X	X	-	-	-	-	-	-
Iron (Fe)	-	-	-	-	-	-	X	X	X	-	X
Lead (Pb)	-	-	-	-	X	-	-	-	-	-	-
Manganese (Mn)	-	-	-	-	X	-	-	-	-	-	X
Mercury (Hg)	-	-	-	-	-	-	-	-	-	-	-
Nickel (Ni)	-	-	-	-	-	-	-	-	-	-	X
Zinc (Zn)	-	-	-	-	-	-	-	X	-	-	-
Fats and oils	-	-	-	-	-	-	-	X	-	-	-
Naphthalene	-	-	-	-	X	-	-	-	-	-	-

Table 8. *Number of water quality analyses of the MAR water source for all MAR sites analysed.*

MAR site	Number of water quality analysis	Source
Arabayona MAR site	1	Provided by an involved party
Canal Isabel II ASR Sites	2	Nogueras et al. (2019)
Careos	12	Barberá et al. (2018)
Cobre de las Cruces Copper Mine	1	Baquero et al. (2016)
El Port de La Selva SAT-MAR site	1	Amphos 21 (2016)
Guadiana MAR site	1	Fernández Escalante (2015)
Los Arenales MAR sites	5	Fernández Escalante et al., in MARSOL (2016b)
Mallorca experimental SAT-MAR site	3	Provided by an involved party
Sant Vicenç dels Horts MAR site	4	Provided by an involved party and the Dessin project (https://dessin-project.eu/)
Tenerife pilot SAT-MAR site	1	Provided by an involved party
Urban Waterbuffer Zorrilla	3	Provided by an involved party and www.fieldfactors.com

For the current analysis, the MAC standards of Italy, the Netherlands and Spain (which has two standards as it differentiates between direct injection and percolation) were considered because they are member states of the European Union and consequently share some geographical and regulatory characteristics with Spain. Other MAC standards, such as those of Mexico and the USA, imply a different context and were consequently not considered.

The analysis has not been restricted to the MACs for Spain, since the number of parameters it entails is very limited (i.e., six) and the thresholds very restrictive. Furthermore, the current Spanish regulatory framework does not address MAR adequately, considering this technology a mechanism for water disposal. This situation might change soon as amendments are being made to the national water law. The value of the MACs in these four MAC standards are presented in **Table 9**. More information about the standards considered has been provided in sections MAR in Spain and Wastewater reuse in Spain.

Table 9. *Maximum allowable concentration (MAC) for MAR source water in Italy, Spain, and the Netherlands legislation. All parameters are in mg/L unless otherwise noted.*

Country	Italy	Spain (percolation)	Spain (direct injection)	The Netherlands
Conductivity (µS/cm)	2500	-	-	-
Total nitrogen (N)	-	10	10	-
Total Suspended Solids (TSS)	-	35	10	-
Turbidity (NTU)	-	-	2	-
Sodium (Na)	-	-	-	120
Chloride (Cl^-)	250	-	-	200
Sulphate (SO_4^{2-})	250	-	-	150
Fluoride	1.5	-	-	1
Nitrate (NO_3-)	50	25	10	5.6
Nitrite (NO_2^-)	0.5	-	-	-
Ammonia (NH_4^+)	0.5	-	-	2.5
Phosphates	-	-	-	0.4
Halogenated organic compounds (AOX)	-	-	-	0.03
Boron (B)	1	-	-	-
Cyanide (CN^-)	-	-	-	0.01
Free Cianide (CN)	0.05	-	-	-
E.coli (UFC/100 mL)	-	1000	0	-
Nematodes (egg/10 L)	-	-	1	-
Antimony (Sb)	0.005	-	-	-
Arsenic (As)	0.01	-	-	0.01
Barium (Ba)	-	-	-	0.2
Cadmium (Cd)	0.005	-	-	0.0004
Chromium total (Cr)	0.05	-	-	0.002
Chromium VI (Cr VI)	0.005	-	-	-
Cobalt (Co)	-	-	-	0.02
Copper (Cu)	-	-	-	0.015
Lead (Pb)	0.01	-	-	0.015
Mercury (Hg)	0.001	-	-	0.00005
Nickel (Ni)	0.02	-	-	0.015
Selenium (Se)	0.01	-	-	-
Vanadium (V)	0.05	-	-	-
Zinc (Zn)	-	-	-	0.065
Mineral oils	-	-	-	0.2
Aldrin	0.03	-	-	0.00005
Alpha-HCH	-	-	-	0.00005
Anthracene	-	-	-	0.00002
Atrazine	-	-	-	0.0001
Azinphos-methyl	-	-	-	0.0001
Bentazon	-	-	-	0.0001
Benzene	0.001	-	-	-
Benzo (a) pyrene (PAHs)	0.00001	-	-	0.0001
Benzo (b) fuorantene	0.0001	-	-	-
Benzo (g,h,i) perilene	0.00001	-	-	-
Benzo (k) fuorantene	0.00005	-	-	-
Beta-esaclorocicloesano	0.0001	-	-	-
Bromodiclorometano	0.00017	-	-	-
Chlorobenzene (mono)	0.04	-	-	-
Chlorotoluron	-	-	-	0.0001
Crysen	-	-	-	0.00002
DDT (DDD,DDE)	0.0001	-	-	0.00005
Dibenzo-antraceno	0.00001	-	-	-
Dibromoclorometane	0.00013	-	-	-
Dichlorobenzene 1,4	0.0005	-	-	-
Dichloroethane 1,2	0.003	-	-	-

Country	Italy	Spain (percolation)	Spain (direct injection)	The Netherlands
Dichloroethylene Trans-1,2	0.06	-	-	-
Dichlorophenol	-	-	-	0.0005
Dichlorophenoxyacetic acid (2,4D)	-	-	-	0.0001
Dichloropropane 1,2	-	-	-	0.00005
Dichlorvos (DDVP)	-	-	-	0.0001
Dieldrin	0.03	-	-	0.00005
Dimethoate	-	-	-	0.0001
Dinitrophenol 2,4	-	-	-	0.0001
Dinoseb	-	-	-	0.0001
Endosulfan	-	-	-	0.00005
Endrin	-	-	-	0.00005
Esachlorobenzene	0.00001	-	-	-
Esaclorebutadiene	0.00015	-	-	-
Ethyl-Benzene	0.05	-	-	-
Fluoranthene	-	-	-	0.0001
HC Total	0.35	-	-	-
Heptachlor and heptachlor epoxide	-	-	-	0.00005
Heptachlor epoxide	-	-	-	0.00005
Hexachlorabutadiene (mg/L)	-	-	-	0.00005
Hexachlorobenzene	-	-	-	0.00005
Hexachlorocyclohexane (HCH)	-	-	-	0.00005
Indeno (1,2,3, c-d) pirene	0.0001	-	-	-
Isoproturon	-	-	-	0.0001
Linuron	-	-	-	0.0001
Mecoprop (MCPP)	-	-	-	0.0001
Methyl 2 - chlorophenoxysacetic-4 acid (MCPA)	-	-	-	0.0001
Metolachlor	-	-	-	0.0001
Metoxuron	-	-	-	0.0001
Mevinphos	-	-	-	0.0001
Naphthalene	-	-	-	0.0001
Nitrobenzene	0.0035	-	-	-
Organoalogenates Total	0.01	-	-	-
Parathion	-	-	-	0.0001
Paraxileno	0.01	-	-	-
PCDD, PCDF	4E-09	-	-	-
Pentachlorobenzene	0.005	-	-	-
Pentachlorophenol	-	-	-	0.0001
Pesticides Active substances	0.0001	-	-	-
Pesticides- total	0.0005	-	-	-
Phenanthrene	-	-	-	0.00002
Plaguicides s.l.	-	-	-	0.5
Polychlorinated biphenyls (PCBs)	0.00001	-	-	-
Simazine	-	-	-	0.0001
Sum organochlorine pesticides	-	-	-	0.0001
Tetrachlorethylene	-	-	-	0.0005
Tetrachlorophenol	-	-	-	0.0001
Toluene	0.015	-	-	-
Trichlorobenzene 1,2,4	0.19	-	-	-
Trichloroethylene	0.0015	-	-	0.0005
Trichlorophenol	-	-	-	0.0001
Triclorometane	0.00015	-	-	-
Trihalomethanes (THMs)	-	-	-	0.002
Vinyl Chloride	0.0005	-	-	-

6.2 Evaluation of water quality at Spanish MAR sites

This section provides an overview of all MAR sites considered in this analysis. This overview includes a description of the site's objective, context, water sources, main hydrofacies and major water quality concerns. This section concludes with a general analysis considering all sites.

6.2.1 The Arabayona MAR site (Salamanca, Spain)

The Arabayona MAR site drains water from an area. It conducts it into a MAR canal where water infiltrates an underlying tertiary unconfined aquifer comprising conglomerates, sandstone, silt, and mud. This site seeks to decrease the impact of water logging. The Arabayona irrigation district was settled in a region that had various wetlands. These wetlands were dried up in the 80s to promote agriculture and give economic dynamism to a depressed area. Nonetheless, the area's topographic and environmental conditions favour inundation mainly due to precipitation, high groundwater tables, and irrigation, frequently resulting in crop damage (**Figure 19 a,b**). To deal with this issue, a series of main and secondary sewer systems collect excess water and convey it to the infiltration canal (**Figure 19 c**) (Fernández Escalante & Paredes Núñez 2022).

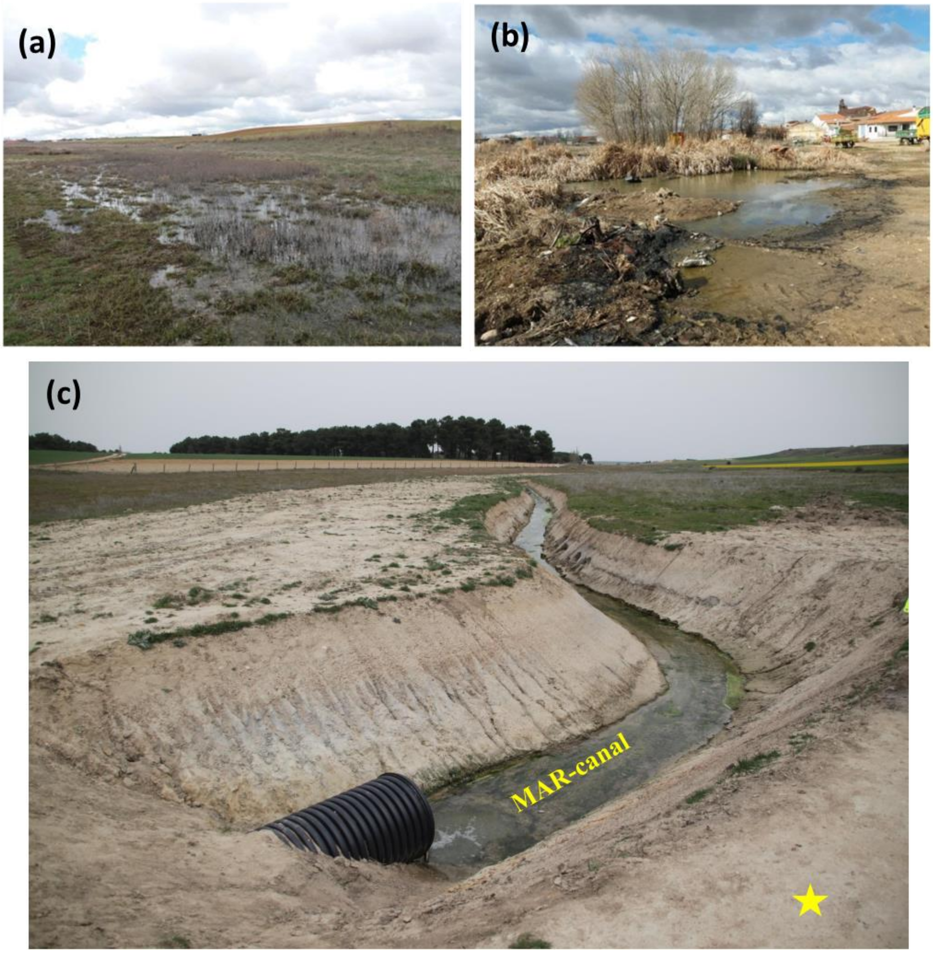


Figure 19. *The Arabayona MAR site: (a,b) examples of water logging issues experienced in the area due to poor drainage and (c) MAR-canal built to infiltrate excess water. Modified from Fernández Escalante & Paredes Nuñez (2022), which is available at https://dinamar.tragsa.es/file.axd?file=/PDFS/P-ISMAR-11.pdf (accessed 28/02/2023).*

The main issue of the source water involved in this MAR site is the high concentration of nitrates due to using fertilisers for agriculture.

6.2.2 The Canal Isabel II ASR Sites (Madrid, Spain)

Canal Isabel II (CYII) is the Madrid region's main water supply and wastewater treatment organisation. It relies predominantly on dam storage to meet water demand and can extract up to 70 Mm^3 of groundwater from the multi-layer Tertiary Detrital Aquifer of Madrid (TDAM) in case of emergency (e.g., prolongated drought). In this context, CYII has conducted Aquifer Storage Transfer and Recovery (ASTR) tests at three sites to replenish groundwater storage in the TDAM (Nogueras et al. 2019), namely, Casilla Valverde Bis, La Cabaña Bis, and FE-1 R.

The wells for extraction reach depths around 700 m while the MAR recharge infrastructure does not exceed 400 m. MAR trials have been conducted to assess the impact of ASR on water quality, quantity and some design criteria for optimal performance (Nogueras et al. 2019; Sánchez & Gutiérrez 2019).

One of the main analyses by Nogueras et al. (2019) about this trial site is the changes in the quality of the injected water as it travels between the injection and extraction wells. The injected water meets the Spanish criteria for drinking water set forth by Royal Decree 140/2003. Groundwater levels rise by about 8-10 m during recharge. The conductivity of groundwater (300 µS/cm) drops due to mixing with the recharged water (90-100 µS/cm) (Nogueras et al. 2019; Sánchez & Gutiérrez 2019). Trihalomethanes (THMs) can be found in the aquifer due to the injection of drinking water and show potential as a tracer to determine the distribution of MAR water in the aquifer (**Table 10**). However, significant changes in the quality of the native groundwater were not found due to the implementation of ASTR and the recovered water met Royal Decree 140/2003 drinking water standards (**Table 10**) (Nogueras et al. 2019).

Table 10. *Water quality during the main stages of the ASR trail schemes. Taken from Nogueras et al. (2019).*

	Casilla Valverde Bis			FE-1 R		
Parameter	**Before AR**	**Beginning of recovery pumps**	**At the end of recovery pumps**	**Before AR**	**Beginning of recovery pumps**	**At the end of recovery pumps**
Conductivity (µS/cm)	219	149	317	260	220	431
pH	7.8	8.78	8	7.49	7.26	8.15
As (µg/l)	7.5	< 2.5	17	7.2	< 2.5	36.1
THMs (µg/l)	0	35	1.7	0	11.9	2.1
Nitrate(mg/l)	2.8	0.3	3.4	4.8	5.6	2.6

The water quality of the TDAM shows spatial variation. It changes with depth from Ca-HCO3 to Na-HCO_3 hydrofacies (**Figure 20**) (Sánchez & Gutiérrez 2019).

In this case, water for MAR is of very good quality (urban supply´s surplus) and does not need any additional treatment prior to recharge.

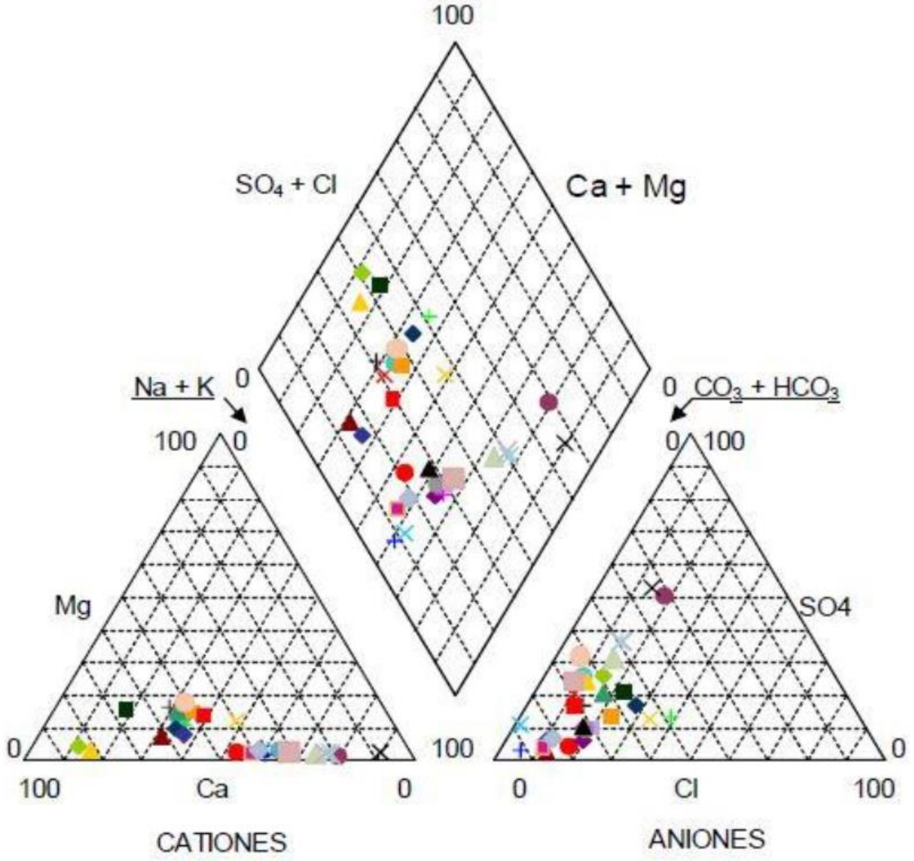


Figure 20. *Groundwater quality around ASTR trial site FE-1 R. Taken from Sánchez & Gutiérrez (2019).*

6.2.3 The Careos (Granada, Spain)

The "Acequias de Careo" are MAR channels of permeable bottom and water-spreading systems used in Sierra Nevada, Southern Spain, to increase water availability since the early Al-Andalus (8-10th century AD). They consist of dug canals at the headwater of the basins that collect, transport and enhance snowmelt and runoff recharge into the underlying fractured aquifer (**Figure 21**). This recharge occurs predominantly in spring and increases groundwater discharge into the lowlands during the dry season (Fernández Escalante et al. 2005).

Barberá et al. (2018) studied the role of the Careos in the hydrological cycle of the Bérchules River Watershed, which extends over an area of about 68 km^2 on the southern edge of Sierra Nevada. The authors integrated different approaches and focused on analysing the hydrochemistry of major ions, chemical components, and water isotopes. Water samples were collected from wells, springs and surface water points in two campaigns during the snowy (January-February) and the snowmelt (May-June) seasons of 2015. Snow samples were analysed in April 2015 (Barberá et al. 2018; Jódar et al. 2022).

Overall, water in Bérchules has calcium-bicarbonate and calcium-magnesium-bicarbonate type facies, with fewer occurrences of calcium-magnesium-bicarbonate-sulphate and sodium-calcium-bicarbonate types. Groundwater electric conductivities range between 19 and 1,188 µS/cm with an average of 111 µS/cm and show some mineralisation level concerning the uplands (≤ 36 µS/cm). The mineralisation of groundwater is due to two main processes: the concentration of solutes such as Na, Ca, Cl, and SO_4 due to evaporation and chemical reactions between the recharged water and the porous medium, namely hydrolysis (e.g., albite, anorthite, and K-feldspar) and dissolution (calcite and dolomite). There is also some input of CO_2 to water from biogenic sources in the soil and the atmosphere. The study of temperature gradients, isotopes and conservative chloride concentrations led to conclude that nearly 78% of basin discharge corresponds to groundwater and that 21% of annual precipitation results in recharge. MAR in these areas has considerably increased recharge since the characteristic steep slopes, and low-permeable lithologies could not account for the high percentage of precipitation converted into groundwater (Barberá et al. 2018; Jódar et al. 2022).

Figure 21. *Examples of Careos in the Bérchules River watershed, Sierra Nevada, Spain. Photos of the authors. https://dinamar.tragsa.es/post/Galeria-fotografica-de-los-Careos-de-las-Alpujarras.*

Snowmelt and groundwater are predominantly Ca-SO_4 and Ca-HCO_3 facies (**Figure 22**), although in some particular springs and wells different hydrofacies are observed.

The source water for MAR in this MAR scheme is high-quality and does not require any barrier to reduce the risk of water pollution. Also, the literature doesn't mention any geogenic contaminant that could be mobilised by MAR and pose a risk for later human use or the environment.

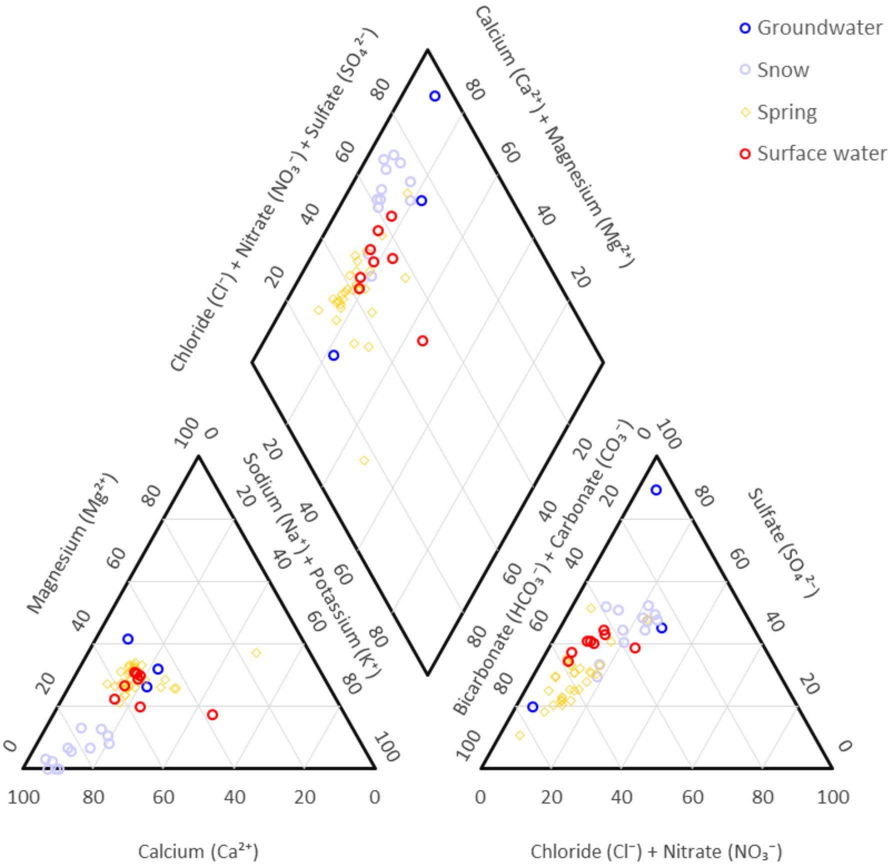


Figure 22. *Piper-Hill-Langelier diagram for various water points in the Bérchules watershed during the snowy season. Own elaboration with data taken from Barberá et al. (2018).*

6.2.4 The Cobre de Las Cruces Copper Mine (Seville, Spain)

The Cobre de Las Cruces Copper Mine is an open pit mine in Southwestern Spain. The mine has intersected the Niebla-Posadas aquifer and therefore requires complex drainage (**Figure 23 a**) and re-injection (**Figure 23 b**) system to dewater a large area. The drainage system comprises 32 active extraction wells. Before the re-injecting of the abstracted water by means of 28 injection wells in an outer ring, water is treated through reverse osmosis to remove metals and other water constituents (**Figure 24**). The drainage and re-injection system transports an annual volume of around 3.2 Mm^3 (Baquero et al. 2016).

At the mine site, the aquifer is confined by a marl layer whose thickness varies between 120-150 m. The native groundwater is almost not renewable and is a mix of two end-members, one of which is highly saline cognate water that probably remains since the transgression of the Tortonian Sea. Groundwater quality varies spatially. As it travels from the recharge zone in the northern fringe of the aquifers to the south, the concentration of As, NH_4, and B increase through natural processes predominantly that involve organic matter, minerals in the porous medium, and mixing of waters. In some parts of the aquifer, some constituents' concentration exceeds drinking and irrigation water quality (Baquero et al. 2016).

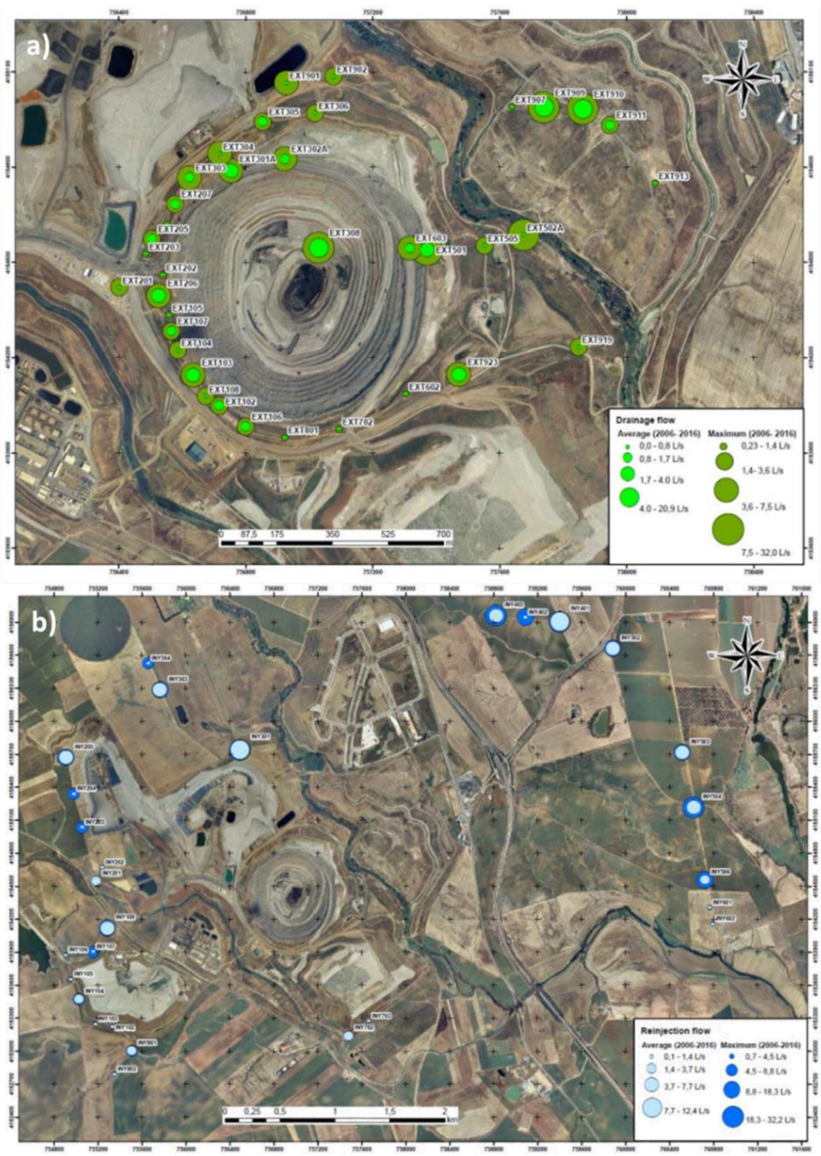


Figure 23. *The Cobre de Las Cruces mine: drainage well network (a), and re-injection well network (b). Taken from Baquero et al. (2016).*

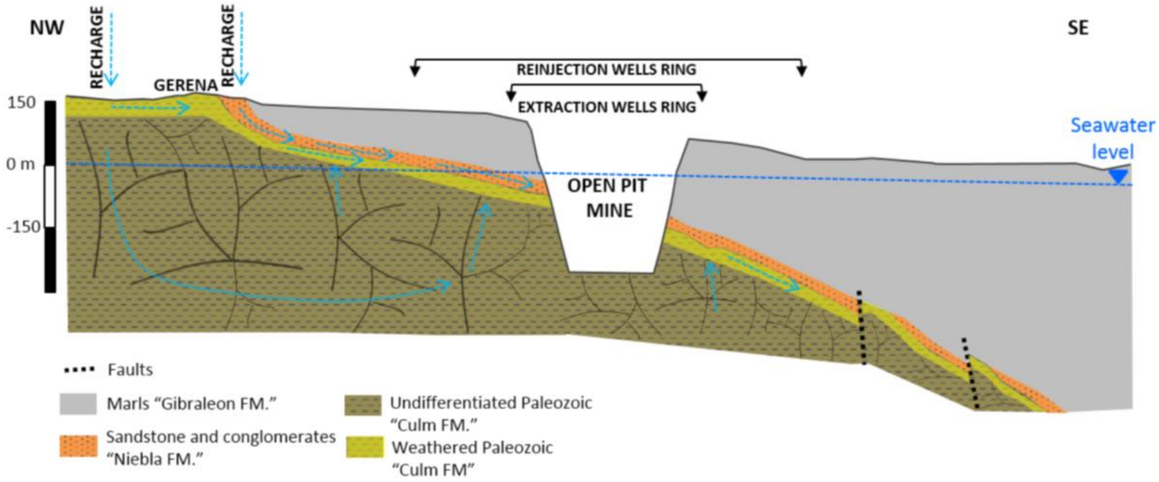


Figure 24. *Geological cross-section of the Cobre de Las Cruces mine. Taken from Baquero et al. (2016).*

In the recharge zones, nitrate concentration and sulphate are high due to agricultural activities and environmental enrichment, respectively. Nitrate concentrations decrease as groundwater travels southward and disappears once the aquifer becomes confined (Baquero et al. 2016). The re-injected water must be treated to comply with the water authority's requirements. This treatment takes place in a wastewater treatment plant. The resulting water also loses calcium and magnesium (**Figure 25**) (Baquero et al. 2016). Regarding hydrofacies, the native groundwater and the treated groundwater belong to the Na-Cl type (**Figure 25**).

In this site, the concentration of certain pollutants of natural origin is above desired levels. Consequently, water treatment is required before MAR to comply with environmental standards set by the regional water authority.

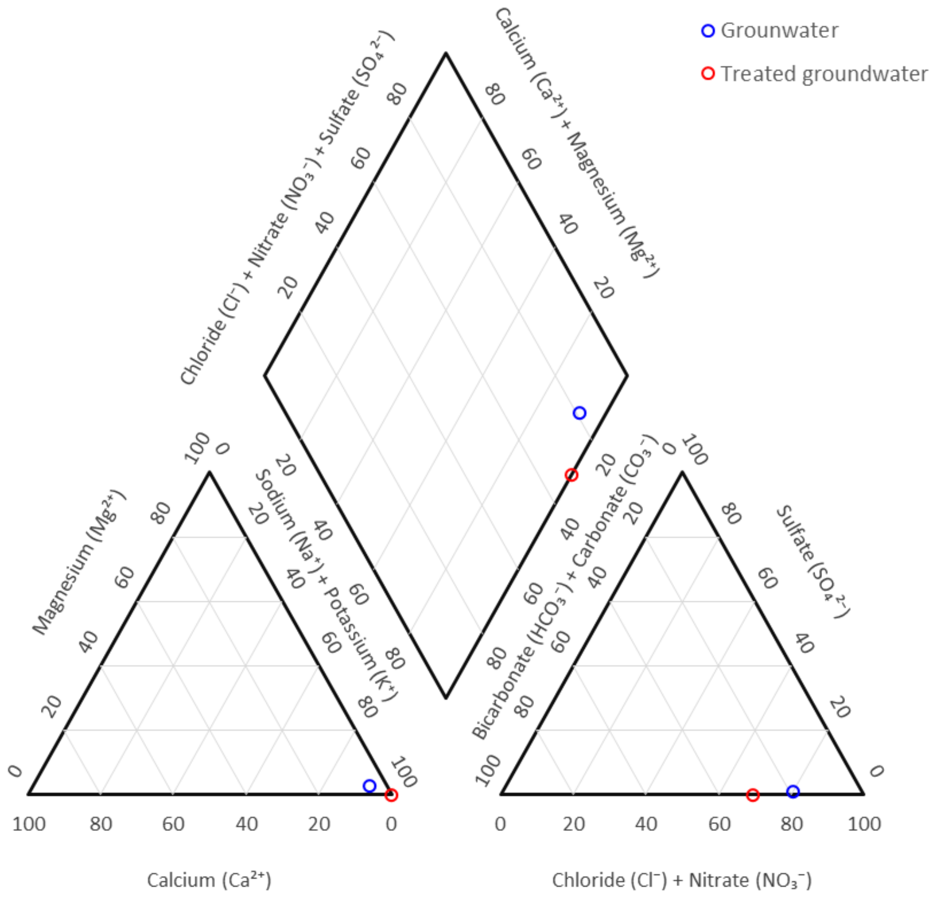


Figure 25. *Piper-Hill-Langelier hydrogram for the groundwater and treated groundwater at the Cobre de Las Cruces MAR scheme. Own elaboration with data taken from Baquero et al. (2016).*

6.2.5 The El Port de La Selva MAR site (Gerona, Spain)

In this site, tertiary-treated wastewater from the town of El Port de La Selva, Spain, is recharged into unconfined aquifers through three infiltration basins. Since this site relies on the unsaturated and saturated zones to improve the quality of the recharged water, it constitutes an example of a Soil Aquifer Treatment (SAT) scheme. The final use of the recharged water is potable water supply. Secondary effluent from the WWTP is directed to a tertiary treatment plant comprising a dual media filter, a granular activated carbon filter to reduce the concentration of certain emerging contaminants and a UV disinfection system. Tertiary effluent is finally conveyed to an elevated storage tank providing water to the infiltration basins (**Figure 26**). MAR takes place during winter when primary effluent can be treated to reduce total nitrogen to a concentration below 10 mg/l effectively (Fajnorová et al. 2021).

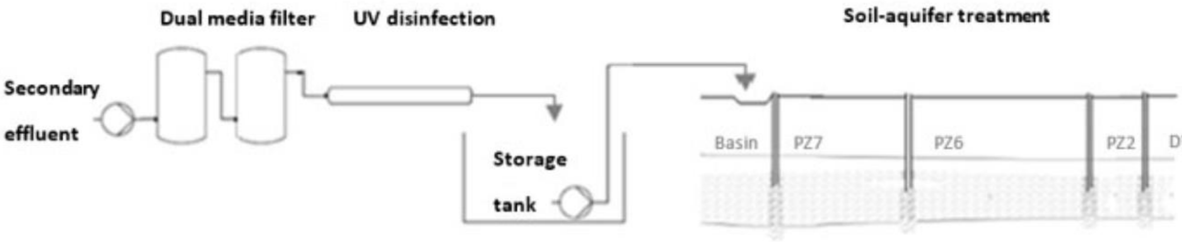


Figure 26. *Schematic representation of the El Port de La Selva MAR Site. PZ: groundwater monitoring piezometer; DW: drinking water well. Taken from Fajnorová et al. (2021).*

Operations started in 2015. Recharge is conducted by means of three infiltration basins with a combined area of 439 m^2 that operate following wet and dry cycles (**Figure 27**). Changes in groundwater quality are monitored through a small network of piezometers located nearby the infiltration facilities and down-gradient of the infiltration sites (PZ4, PZ6 and PZ7). Piezometer PZ3 is unaffected by recharge and monitors native groundwater quality (**Figure 27**). The aquifer consists of unconsolidated block and gravel deposits embedded in a sand and silt matrix. The total thickness is about 13-14 m (Amphos 21 2016, Fajnorová et al. 2021).

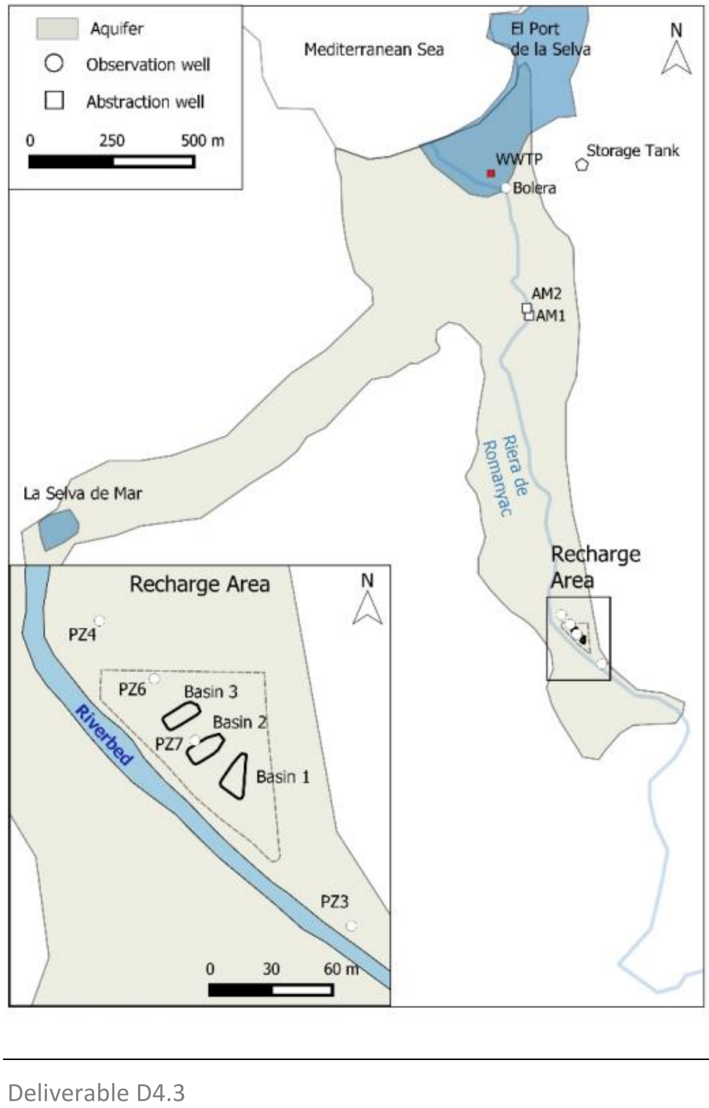


Figure 27. *Plan view of the El Port de La Selva MAR site. Taken from Fajnorová et al. (2021).*

The SAT system in El Port de La Selva combined with attenuation processes in the aquifer also helps to reduce the concentration of several water constituents (e.g., dissolved organic carbon, chloride, sulphate, and dissolved oxygen), which in many cases reach concentration below the ambient groundwater after travelling through the aquifer (**Figure 28**).

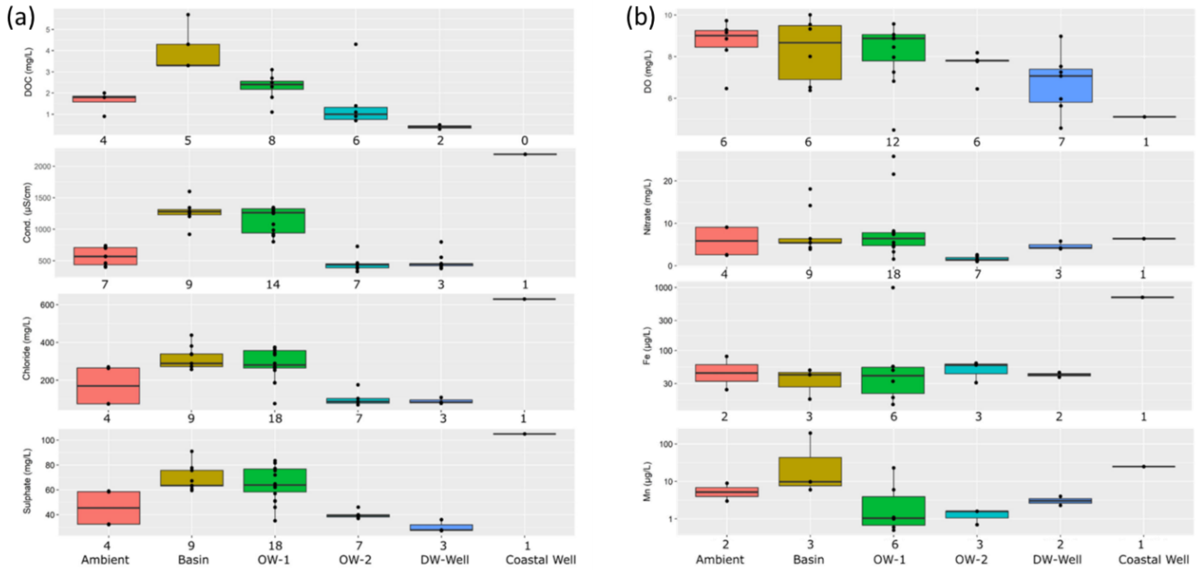
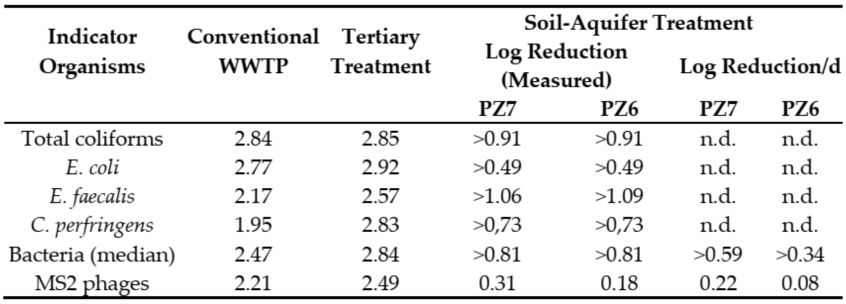


Figure 28. *Concentration of various groundwater constituents at multiple locations related to Port de La Selva MAR site. Modified from Fajnorová et al. (2021).*

SAT help to reduce the prevalence of indicator bacteria, enteric viruses and phages (**Figure 29**) and help to reduce antibiotic resistance to the levels found in the native groundwater (Fajnorová et al. 2021).



Indicator Organisms	Conventional WWTP	Tertiary Treatment	Soil-Aquifer Treatment Log Reduction (Measured)			
					Log Reduction/d	
			PZ7	PZ6	PZ7	PZ6
Total coliforms	2.84	2.85	>0.91	>0.91	n.d.	n.d.
E. coli	2.77	2.92	>0.49	>0.49	n.d.	n.d.
E. faecalis	2.17	2.57	>1.06	>1.09	n.d.	n.d.
C. perfringens	1.95	2.83	>0,73	>0,73	n.d.	n.d.
Bacteria (median)	2.47	2.84	>0.81	>0.81	>0.59	>0.34
MS2 phages	2.21	2.49	0.31	0.18	0.22	0.08

Figure 29. *Log-reduction of various microorganism indicators at multiple Port de La Selva MAR Site locations. Taken from Fajnorová et al. (2021).*

The main water quality concerns related to this site are the fate of microorganisms (bacteria and enteric viruses), antibiotic resistance, and contaminants of emerging concern (CEC). In fact, Fajnorová et al. (2021) found that despite SAT, which helped remove or decrease the concentration of many potential contaminants, 15 CECs were found in groundwater above health-based or drinking water thresholds.

6.2.6 The Guadiana MAR canal (Ciudad Real, Spain)

This MAR site utilises opportunistic river water surpluses to recharge it into an unconfined aquifer. It consists of a series of wells placed on the river bank of the Guadiana Canal that capture river water during high stages (especially in winter) and inject it (**Figure 31**) into a karstic aquifer comprising tertiary limestone and detrital plio-quaternary volcanic sediments. The aquifer is heterogeneous, with permeabilities that range between 50 and 20,000 m/day. Water tables are reached at a depth between 50 and 30 m. The final use of the water stored through MAR is irrigation demands along the Guadiana Canal and the restoration of degraded wetlands in the Daimiel National Park (**Figure 30**) (Fernández Escalante 2015).

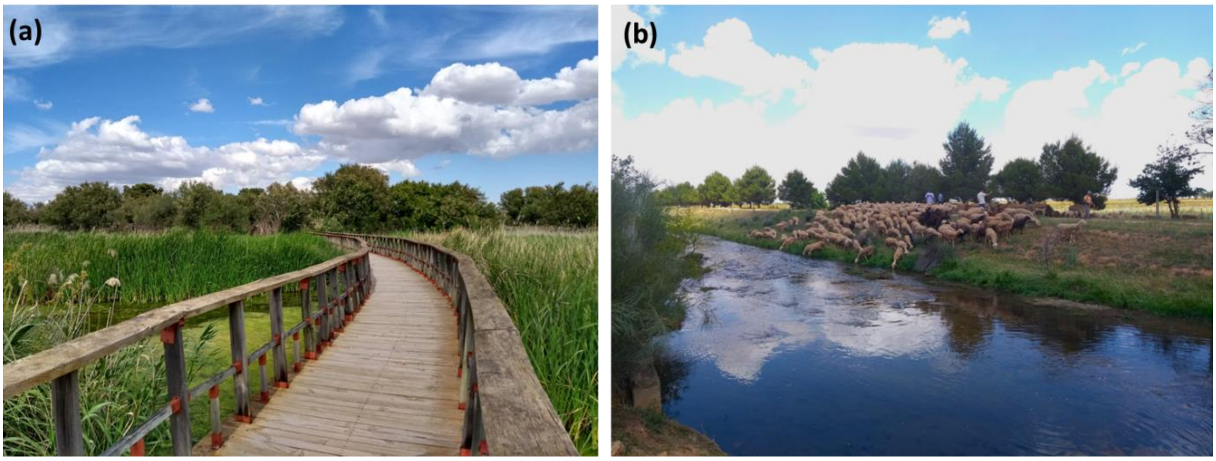


Figure 30. *Guadiana MAR site: (a) Daimiel National Park, and (b) Guadiana Canal.*

Figure 31. *The Guadiana MAR site: (a) Peñarroya dam heading the MAR canal), and (b) MAR well used to recharge river water into the mudstone aquifer. Photos of the authors.*

Water source hydrofacies correspond to $Na\text{-}CO_3$ while groundwater's to $Na\text{-}CO_3$, predominantly, and $Na\text{-}HCO_3$ in at least one well (**Figure 32**). Groundwater in the area can be of poor quality in some wells, especially in regard to nitrate and nitrite concentration, likely as a result of agriculture in the region. The main water quality issue in this site is the presence of nitrites above the Spanish regulation for MAR (Royal Decree 1620/2007), mainly due to the MAR water collecting method. Nonetheless, the quality of this water is often better than the native groundwater, which implies that MAR can help dilute pollutants (Fernández Escalante 2015).

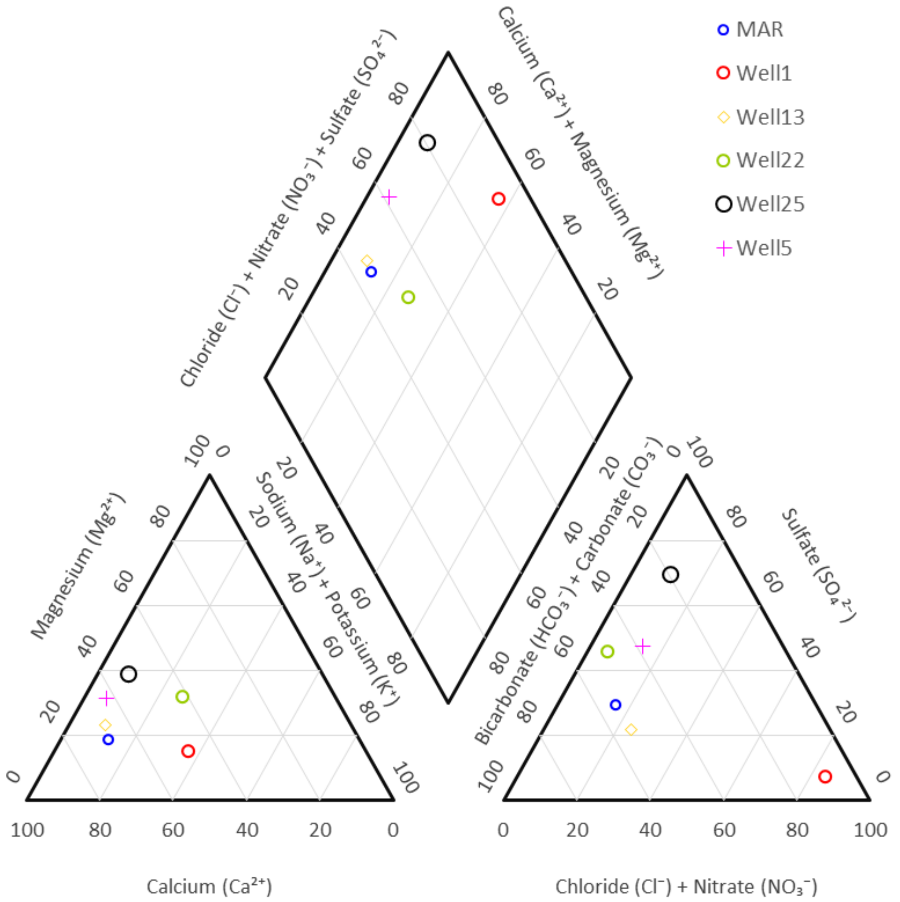


Figure 32. *Piper-Hill-Langelier hydrogram for MAR source water (river water) and groundwater at multiple wells employed for MAR. Own elaboration with data taken from Fernández Escalante (2015).*

6.2.7 The Los Arenales MAR sites (Segovia and Valladolid, Spain)

The Los Arenales MAR site consists of three large-scale systems that replenish an intensively exploited aquifer, namely, the Los Arenales aquifer. They are located on the Spanish side of the Douro River basin, Central Spain and are distributed in three main regions: Santiuste, El Carracillo, and Pedrajas-Alcazarén (**Figure 33**).

These MAR systems are a response to the considerable decline in groundwater levels (**Figure 34**) experienced in the southern region of the Douro River basin due to massive groundwater abstractions for irrigation. They also seek to ensure irrigation demands in the context of over-allocated water resources.

These systems rely on a combination of infiltration basins, infiltration canals, artificial wetlands, and wells (**Figure 35**) to recharge unconfined quaternary deposits that have, in some parts, direct connection with sand layers of deep tertiary semiconfined to confined aquifer systems.

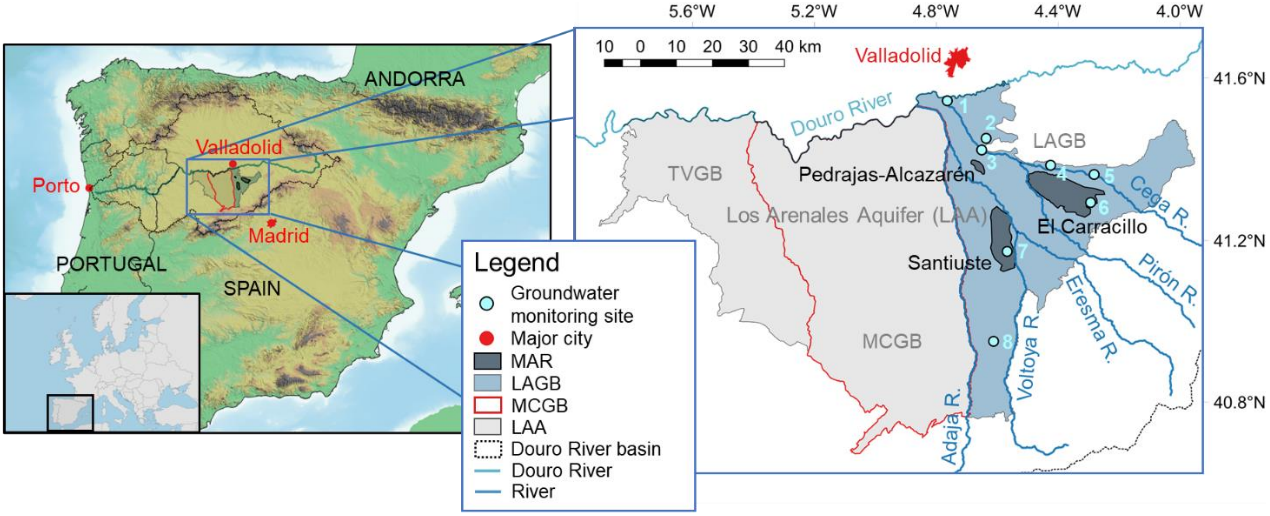


Figure 33. *Location of the Los Arenales Aquifer (LAA) and the Los Arenales MAR sites. LAGB and MCGB stand for Los Arenales groundwater body and Medina del Campo groundwater body. Taken from Henao Casas et al. (2022b).*

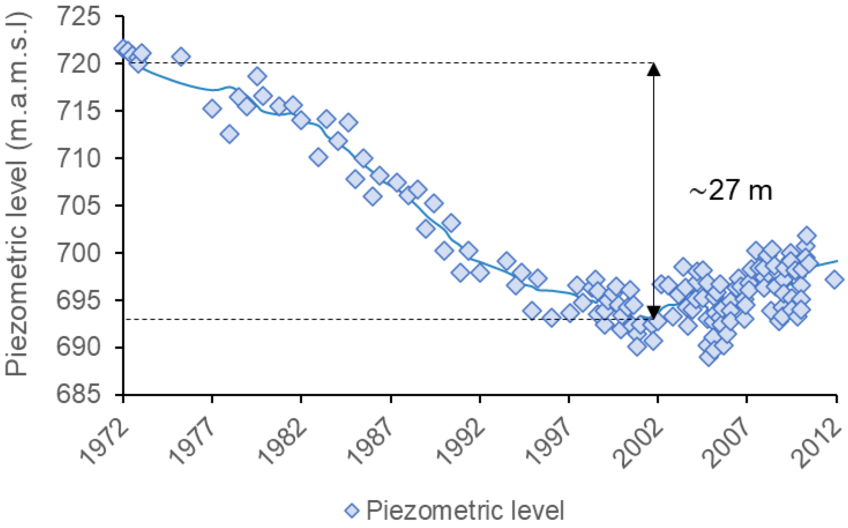


Figure 34. *Groundwater level decline measured at groundwater monitoring station PZ2045005, near the municipality of Mojados. Taken from Henao Casas et al. (2022b).*

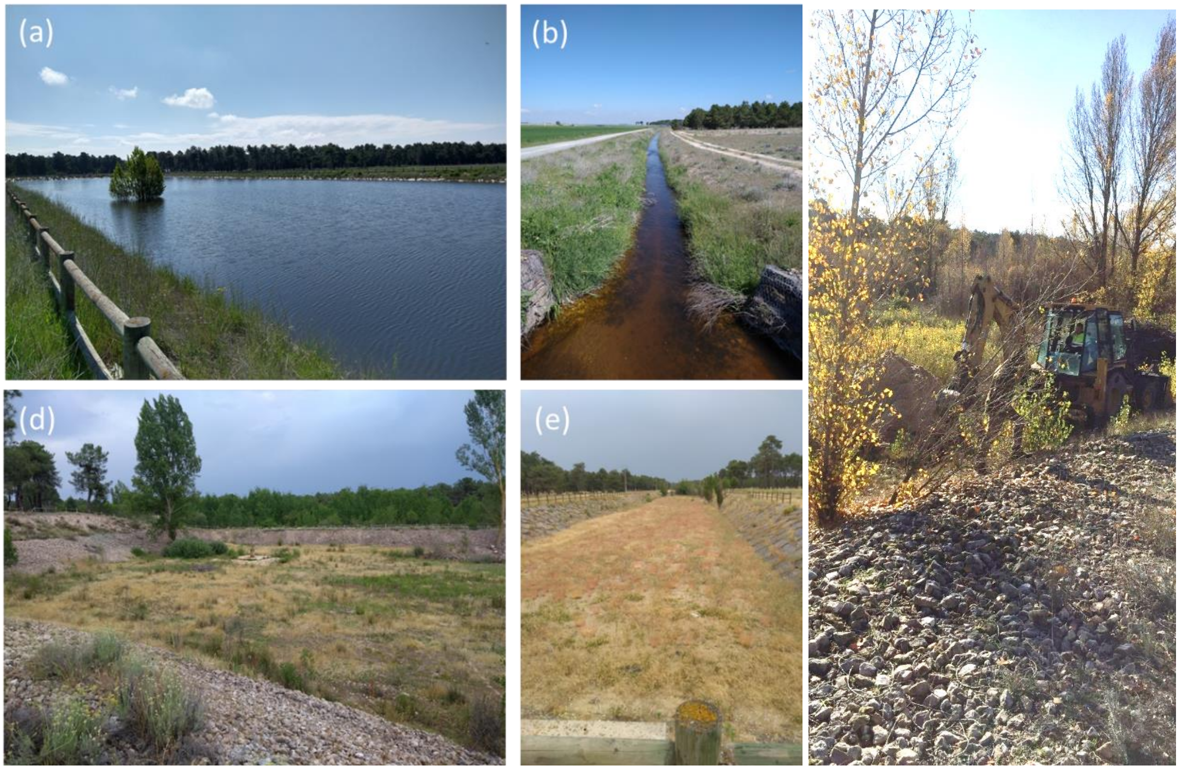


Figure 35. *Los Arenales MAR Sites: (a) large infiltration basin in Santiuste; (b) infiltration canal branching out of the large infiltration basin in Santiuste; (c,d) La Laguna del Señor in Gomezserracín, a large infiltration basin in El Carracillo; and (e) a large infiltration basin in the same village, El Carracillo MAR site.*

El Carracillo system relies on water surpluses from the Cega River, which features relatively high quality since the water intake is located at a relatively high altitude before water use could threaten water quality integrity. The water source in Santiuste is similar, but, in this case, the source river is the Voltoya River. Surpluses are granted only when river stages are above minimum ecological flows and during a period that varies according to the site and comprises some rainy winter months (e.g. December, January, February, and March).

The Pedrajas-Alcazarén site uses treated wastewater from the Pedrajas de San Esteban wastewater treatment plant. The main concerns related to this water source are emerging contaminants and Total Organic Carbon (TOC). Originally, the Pedrajas-Alcazarén was planned to use water surpluses from the Pirón River and urban runoff from the Pedrajas de San Esteban municipality. However, due to administrative conflicts concerning river water use and water quality issues, these sources are temporarily shut down. The Los Arenales MAR Sites have yielded an average recharge of about 4.8 Mm^3/year between 2002 and 2020 combined.

In Santiuste and El Carracillo sites, the predominant water facies are $Ca\text{-}HCO_3$, while in Pedrajas-Alcazarén SAT-MAR, the main water type is $Ca\text{-}SO_4$ (**Figure 36**). Chemical data have been obtained from MARSOL (2016b).

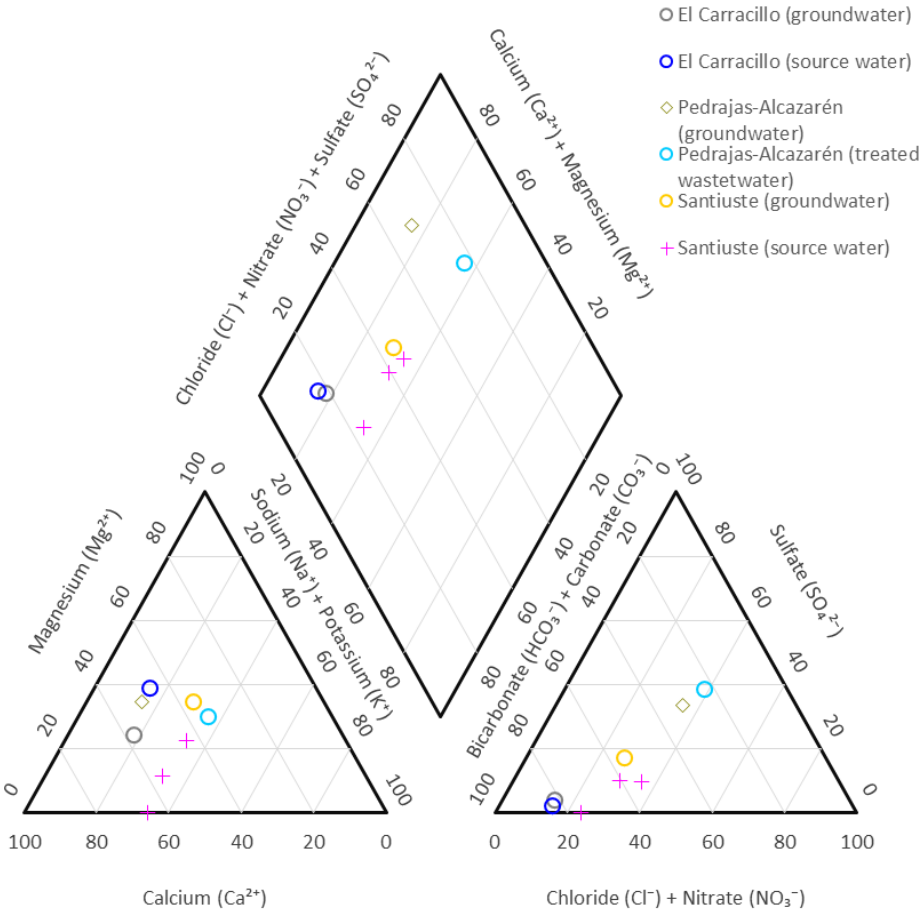


Figure 36. Piper-Hill-Langelier hydrogram for MAR water sources and groundwater at the Los Arenales MAR sites.

6.2.8 Mallorca experimental SAT-MAR site (Balearic Islands, Spain)

In this site, an experiment was undertaken, consisting of over-irrigating crops to recharge an underlying aquifer via irrigation returns. The agricultural area in which this experiment took place is distributed between the municipalities of Maria de la Salut, Sineu and Ariany. It is limited to the east by the road from Petra to Santa Margalida (Ma-3340) and to the south by the Ma-3301 road. This site consists of small or very small plots of land.

The irrigation system uses private wells that pump water at a corner of the plots and distribute it by gravity. The total area is 160 ha. The crops grown are mainly fodder crops, cereals, almonds, vegetables and, to a lesser extent, some fruits and citrus fruits.

Between 2013 and 2018, the experiment took place employing "stimulated recharge" by applying a dose of irrigation above the crop's necessities with reclaimed water proceeding from a Maria de la Salut wastewater treatment plant (**Figure 37**). The excess water reaching the aquifer and the interactions in the saturated and unsaturated zone were analysed through a well located at a lower hydraulic level.

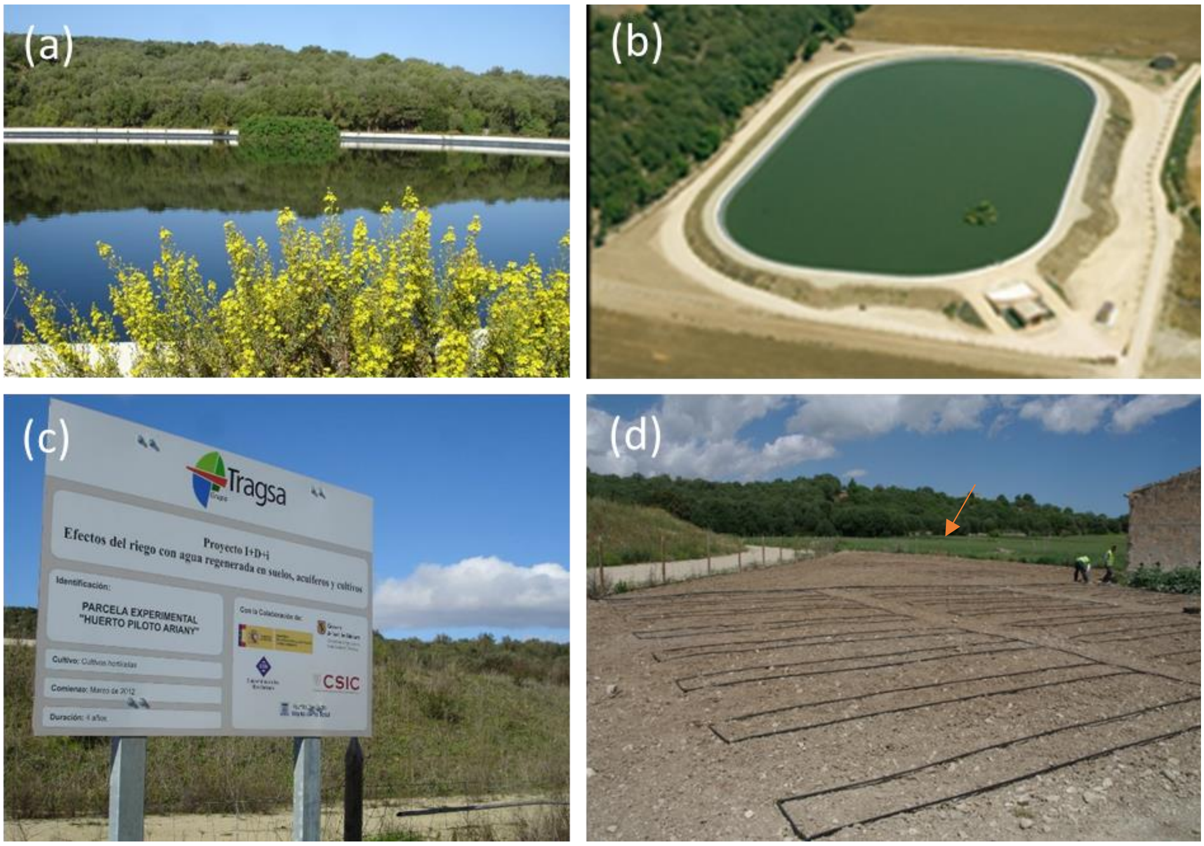


Figure 37. *Mallorca experimental SAT-MAR site: (a,b) Pond to store water from the Maria de Salut wastewater treatment plant; (c) on-site information about the EARSAC project; and (d) irrigation system at one of the plots studied. The orange arrow indicates the piezometer's position.*

Sequential analyses were conducted over five years, enabling the study of the interaction processes between reclaimed water and the receiving medium and water crops. The results are available in the book published at the final of the EARSAC project (https://dinamar.tragsa.es/pdf/libro-earsac.pdf, accessed on 28/02/2023). The results demonstrated that the system began to function in a permanent regime after five years of irrigation in terms of both groundwater quantity and quality.

The treated wastewater corresponds to Na-Cl hydrofacies while the groundwater varies considerably, showing Ca-Cl, Ca-SO_4, Na-Cl, and Na-HCO_3 water types (**Figure 38**).

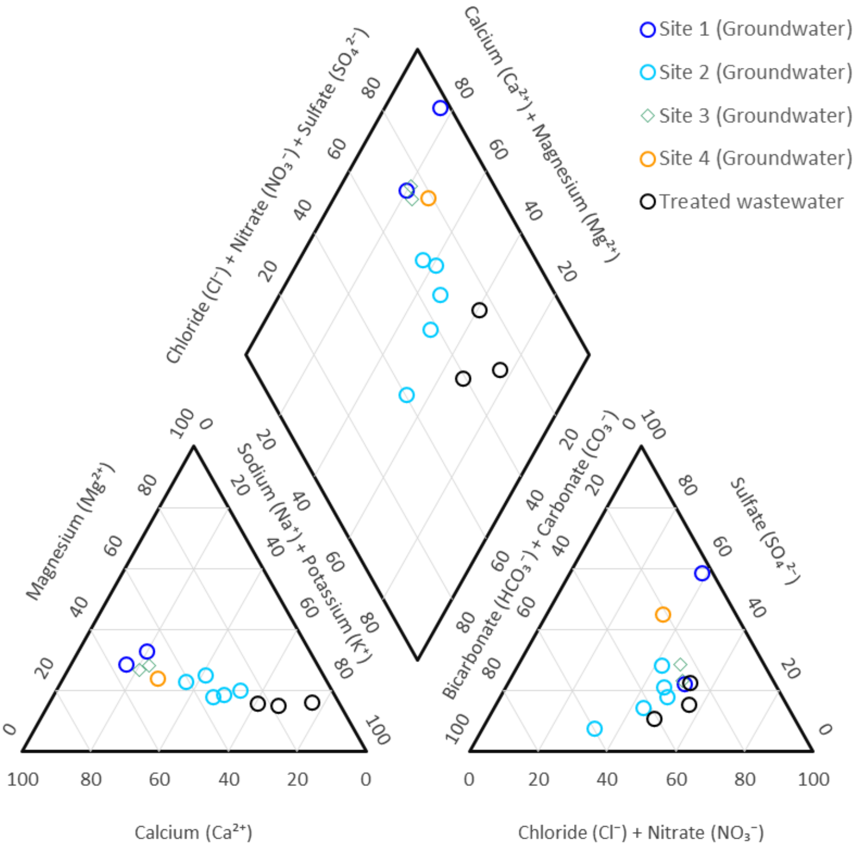


Figure 38. *Piper-Hill-Langelier hydrogram for MAR water source (treated wastewater) and several monitoring sites established during the EARSAC project.*

6.5.9 The Sant Vicenç dels Horts MAR site (Barcelona, Spain)

This MAR site is located in the Llobregat area and the vicinity of the municipality of Sant Vicenç dels Horts, Catalunya (**Figure 39**). Water from the Llobregat River is conducted to a decantation pond with an area of about 5,600 m^2. Subsequently, the water is taken to an infiltration pond (4,000 m^2), where water percolates into an unconfined aquifer a few metres thick (and up to 10 m). The main purpose of this MAR system is to increase groundwater storage at the local scale. Yearly recharge volumes are in the order of 1.2 Mm^3/year.

In 2011, the infiltration pond was upgraded with an organic layer of vegetal composts in order to enhance the removal of certain water constituents through processes such as adsorption and degradation.

In this site, MAR water source and groundwater have a very similar proportion of major ions and are predominantly of the in all cases of the Ca-HCO_3 hydrofacies (**Figure 40**). A major water quality concern of the recharge water is CECs.

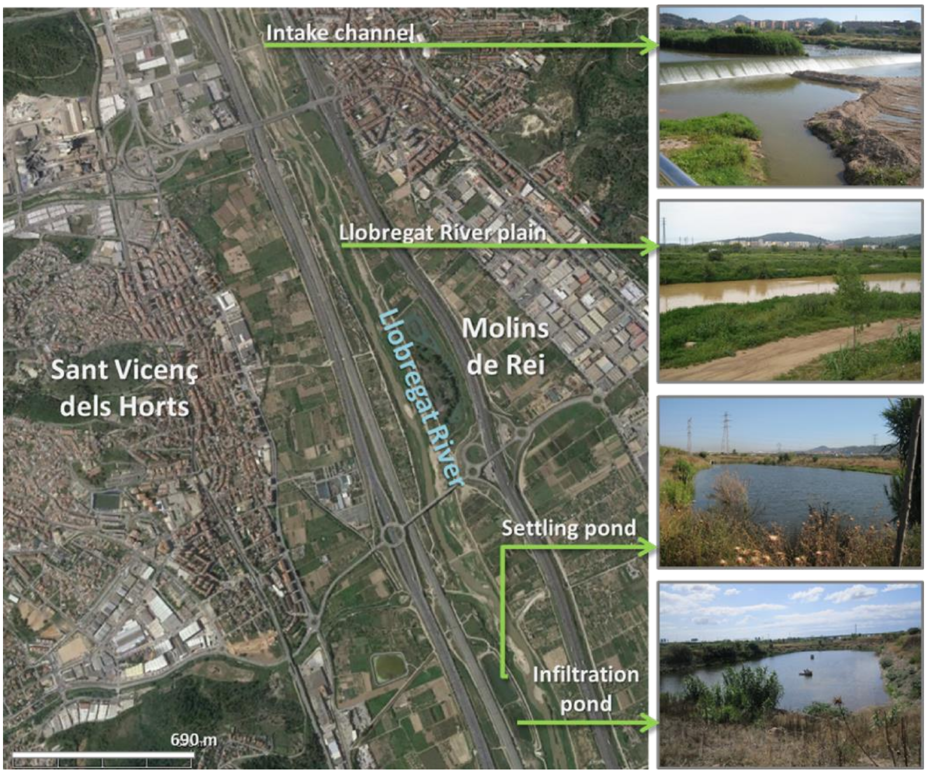


Figure 39. *The Sant Vicenç dels Horts MAR site. Location and images of the different parts of the system. Taken from the website of the DEMEAU project (https://demeau-fp7.eu/sites/files/SVH.png, accessed on 28/02/2023).*

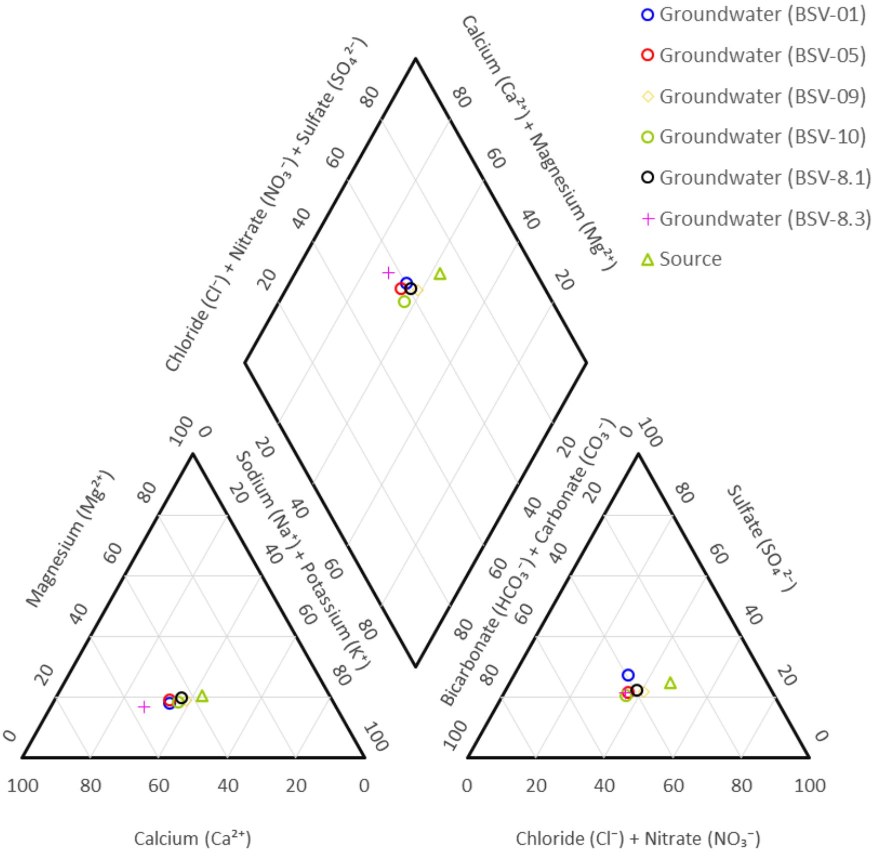


Figure 40. *Piper-Hill-Langelier hydrogram for MAR water source and groundwater at several monitoring sites in the Sant Vicenç dels Horts MAR site.*

6.5.10 The Tenerife pilot SAT-MAR site (Canary Islands, Spain)

A new experiment on Tenerife Island conducted by the Consejo Insular de Aguas de Tenerife (CIATF) is currently taking place, consisting of the surplus of the wastewater treatment plant Valle del Guerra (Northeast of the Island) to be injected into fractured basalts formations through a dug-well (**Figure 41**). The objective is to study the behaviour of the receiving medium and the interaction processes between reclaimed water and the aquifer. Also, this site aims to advance the knowledge of the groundwater movement through volcanic fractured aquifers, which behave as a heterogeneous and anisotropic aquifers.

The water is injected through the 20 m deep and 1.20 m of diameter dug-well, which in this particular case is known as a "Canarian well". The project will run for at least one year.

The water quality evolution will be tested in two exploitation wells located downwards according to the groundwater flow gradient, namely, Río Claro and La Noria wells. Both are used for the irrigation of banana trees' plots of land.

Figure 41. *EDRAR Noreste, Tenerife, Spain, where a new SAT-MAR experiment with reclaimed water in volcanic rocks is beginning. EDRAR Noreste (a), and future plot for the percolation well (b).*

Groundwater in this MAR site belongs to Na-Cl-HCO_3 hydrofacies (**Figure 42**).

The results of this MAR trial will be provided at the end of the project by 2024.

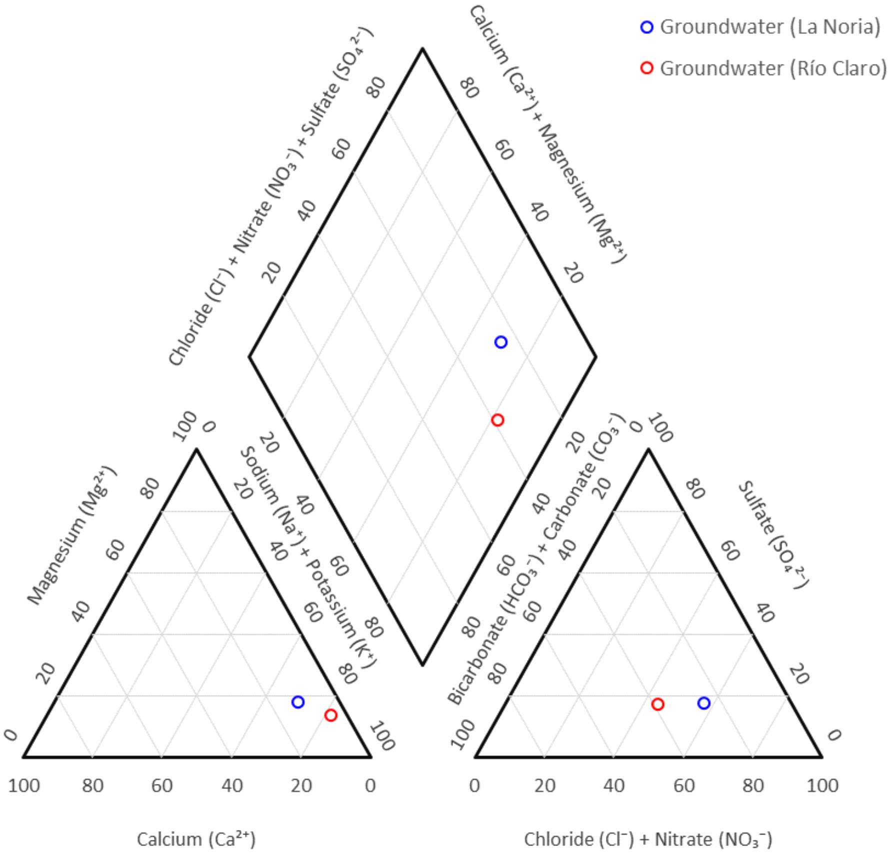


Figure 42. *Piper-Hill-Langelier hydrogram of the native groundwater at sampling wells Río Claro and La Noria.*

6.5.11 The Zorrilla urban water buffer (Valladolid, Spain)

This pilot MAR scheme is located at the José Zorrilla Stadium in Valladolid (**Figure 43**). It is expecting the final permission from water authorities to begin the activity. Initially have been conducted some experiments collecting rainwater from the parking area, which is infiltrated underground for later recovery (ASR MAR system) and reused as a source of irrigation for the football court. A gutter system collects and directs the water to a storage tank. Subsequently, water is conveyed to a biofilter with vegetation that improves water quality before injection underground. Finally, when required, water is pumped and used to irrigate the stadium. This scheme can meet up to 20% of the stadium irrigation needs (https://www.fieldfactors.com, Versteeg et al. 2021).

Rainwater in this site can be of Ca-HCO_3 type, while groundwater belongs to Mg-Ca-HCO_3 hydrofacies (**Figure 44**). The main water quality concern in this MAR site is Ca-HCO_3 hydrofacies.

Figure 43. *The urban water buffer Zorrilla. Taken from https://www.fieldfactors.com.*

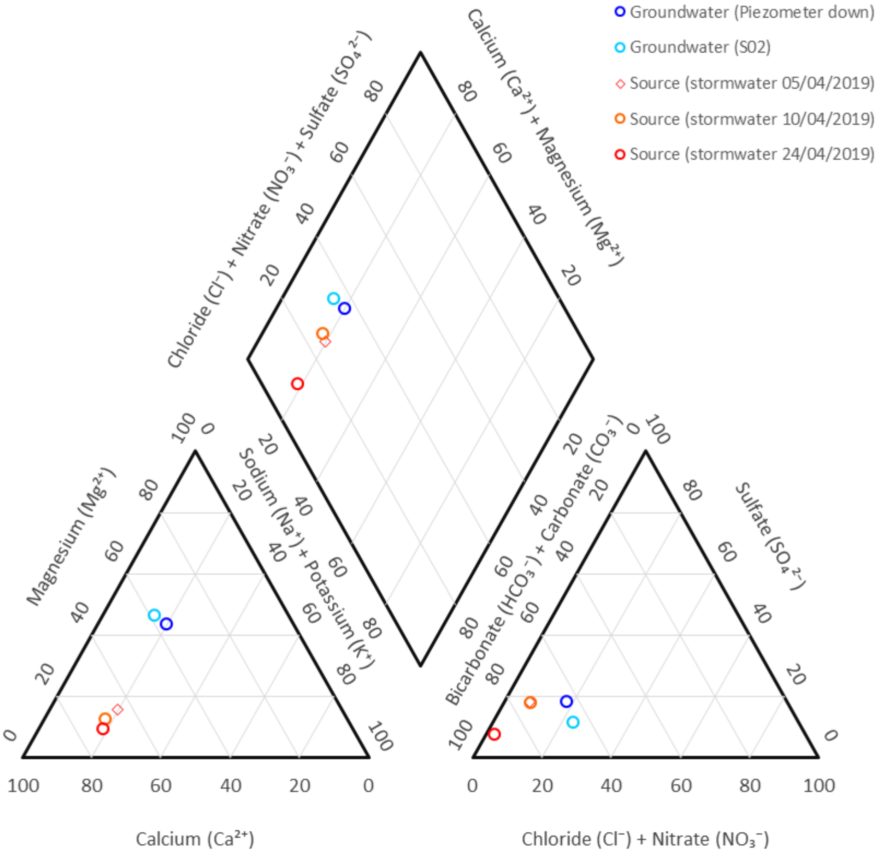


Figure 44. *Piper-Hill-Langelier hydrogram of the native groundwater and rainwater at the José Zorrila Stadium.*

6.6 Variability of water quality across MAR sites

The water quality of the Spanish MAR sites selected reflects a wide range of hydrochemical facies comprising the main water types, namely, $Ca\text{-}SO_4$, $Ca\text{-}HCO_3$, $Na\text{-}SO_4$, and $Na\text{-}Cl$ (**Figure 45**). The only hydrofacies not well represented is $Na\text{-}SO_4$, found in the Guadiana MAR site exclusively. Overall, water samples from a particular site tend to fall within the same hydrofacies, except for the Los Arenales MAR sites, which are relatively spread in the piper diagram due to the broad geographical area and the different water sources they entail (**Figure 45**).

Systems relying on wastewater (Pedrájas-Alcazarén, Tenerife Pilot SAT-MAR site, Mallorca Experimental SAT-MAR site, El Port de La Selva SAT-MAR site) as the main source for MAR focus predominantly on the control of CECs as effluents are often of decent quality or require some travel through the saturated and unsaturated zones to attain good quality. In nearly all sites involving this sort of water source, there is a large number of CECs analysed.

MAR sites relying on river water and snowmelt collected near orogenic barriers, such as El Carracillo, Santiuste, and Careos, face no water quality issues. This is likely due to the little chance water has to come into contact with anthropogenic or geogenic sources of contaminants. On the other hand, Sant Vicenç dels Horts and the Guadiana MAR sites exemplify the situation in which anthropogenic activity in upstream parts of the river has increased the concentration of many water constituents that could become a concern (attested by an electrical conductivity of 1,525 µS/cm and 746 µS/cm, respectively).

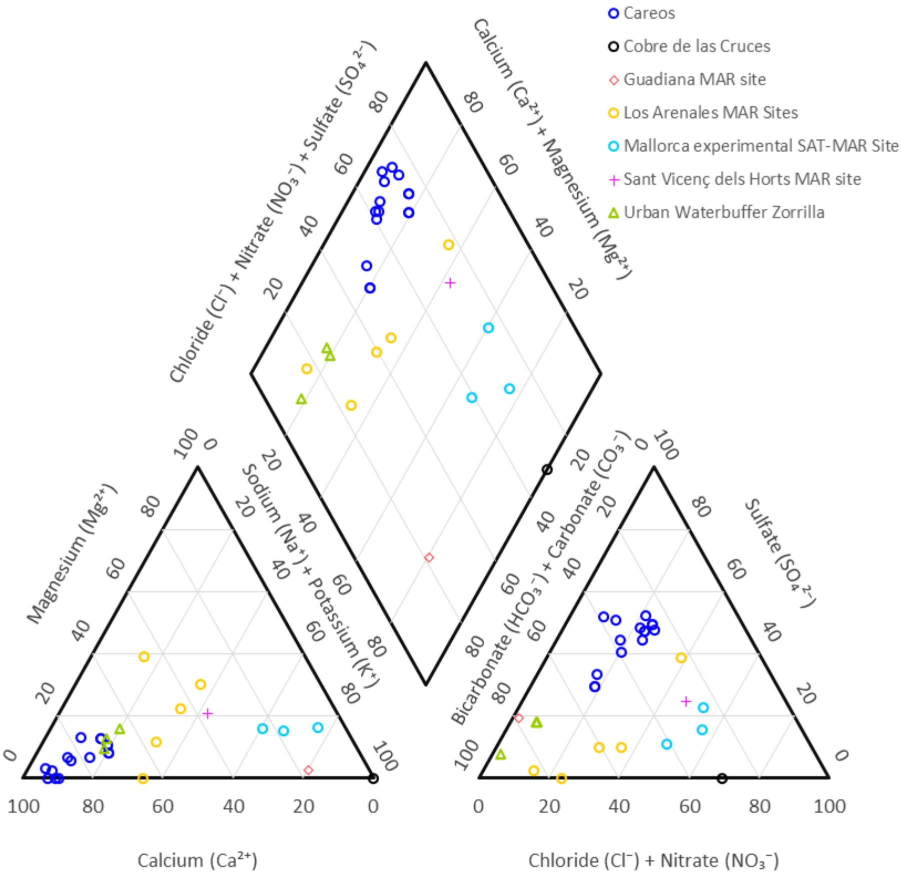


__Figure 45.__ Piper-Hill-Langelier hydrogram of MAR water sources for multiple MAR sites in Spain.

At this stage, it seems quite difficult to propose a single MAC regulation that can fit all sites without imposing too stringent limits on water quality for MAR to the point of rendering this technology practically not implementable.

The hydrofacies of groundwater at Spanish MAR sites are distributed across all domains of a piper diagram similar to the hydrofacies of MAR water sources, reflecting a considerable variability in the proportion of major ions (**Figure 46**). Nonetheless, magnesium cation is never prevalent in both MAR water sources and MAR site groundwater (**Figures 45** and **46**).

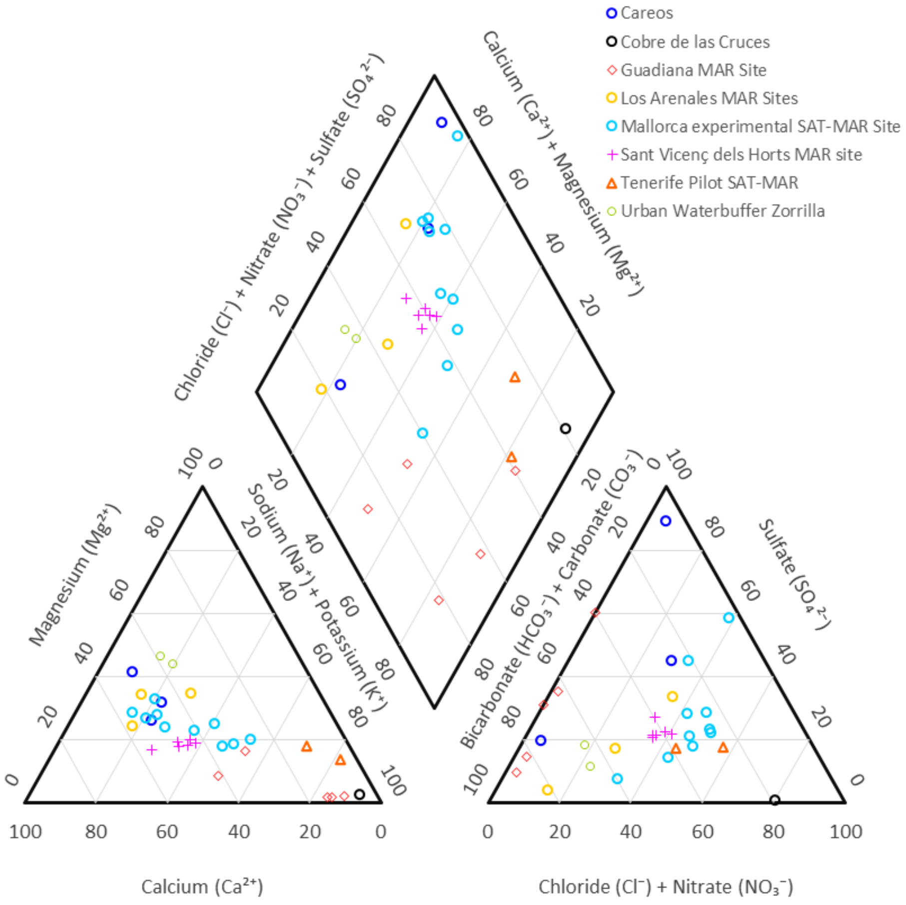


Figure 46. *Piper-Hill-Langelier hydrogram including groundwater quality at multiple MAR sites in Spain.*

6.7 Comparison of MAR water sources with MAC-based standards

The MAC standard for Italy has been breached 21 times. Chloride and ammonia are the parameters most commonly exceeded (six times), followed by Nickel (four times). The threshold of the latter parameter has been surpassed in 100% of the MAR water source samples **Table 11**. Italy's regulatory standard would prevent MAR implementation in six sites: Cobre de las Cruces Copper Mine, El Port de La Selva SAT-MAR site, the Urban Waterbuffer Zorrilla, and Tenerife pilot MAR site, Mallorca Experimental SAT-MAR site, and Sant Vicenç dels Horts MAR site. Note that many of these sites are legally operating and do not pose a risk of contamination to the native groundwater.

Table 11. *Analysis of exceedance of MACs in the standard for Italy. Total N represents the number of comparisons between a MAC and the value measured for a MAR water source. The exceeded columns represent the times a given MAC is exceeded in number (n) and percentage (%).*

Parameters	Total n	Exceeded (n)	Exceeded (%)
Conductivity (µS/cm)	27	0	0%
Chloride (Cl^-)	27	6	22%
Sulphate (SO_4^{2-})	28	0	0%
Fluoride	1	1	100%
Nitrate (NO_3^-)	31	1	3%
Nitrite (NO_2^-)	6	0	0%
Ammonia (NH_4^+)	11	6	55%
Boron (B)	4	1	25%
Arsenic (As) VI	4	2	50%
Lead (Pb)	1	0	0%
Nickel (Ni)	4	4	100%
Total	144	21	15%

The most commonly breached parameter in the Spanish standard for direct injection is nitrate, which was exceeded seven times. Nonetheless, total suspended solids are exceeded more frequently in terms of percentage (75%) (**Table 12**). This MAC standard would preclude operations in six MAR sites: the Guadiana MAR site, the Pedrajas-Alcazarén site of the Los Arenales MAR sites, the Urban Waterbuffer Zorrilla, the Tenerife pilot MAR Site, the Mallorca Experimental SAT-MAR Site, and the Sant Vicenç dels Horts MAR Site. Note that this standard is more restrictive as it deals with systems directly injecting water underground.

Table 12. *Analysis of exceedance of MACs in the standard for direct injection for Spain. Total N represents the number of comparisons between a MAC and the value measured for a MAR water source. The exceeded columns represent the times a given MAC is exceeded in number (n) and percentage (%).*

Parameters	Total n	Exceeded (n)	Exceeded (%)
Total nitrogen (N)	1	1	100%
Total Suspended Solids (TSS)	4	3	75%
Turbidity (NTU)	3	1	33%
Nitrate (NO_3^-)	31	7	23%
E.coli (UFC/100 mL)	1	1	100%
Total	40	13	33%

The other standard of the Spanish regulation, which addresses percolation and consequently is less restrictive, shows nitrate as the most exceeded parameter (two times) (**Table 13**). However, in terms of percentage, nitrate is rarely exceeded (6%). This standard would put in stake operations at three MAR sites.

The Dutch standard for MAR water is exceeded for most parameters, except lead and naphthalene. The most breached MAC were nitrate (eight times), chloride (eight times), and Nickel (four times). This standard might prevent MAR implementation at seven sites (**Table 14**).

Table 13. *Analysis of exceedance of MACs in the standard for percolation for Spain. Total N represents the number of comparisons between a MAC and the value measured for a MAR water source. The exceeded columns represent the times a given MAC is exceeded in number (n) and percentage (%).*

Parameters	Total N	Exceeded (N)	Exceeded (%)
Total nitrogen (N)	1	1	100%
Total Suspended Solids (TSS)	4	0	0%
Nitrate (NO_3^-)	31	2	6%
E.coli (UFC/100 mL)	1	1	100%
Total	37	4	11%

Table 14. *Analysis of exceedance of MACs in the standard for The Netherlands. Total N represents the number of comparisons between a MAC and the value measured for a MAR water source. The exceeded columns represent the times a given MAC is exceeded in number (n) and percentage (%).*

Parameters	Total n	Exceeded (n)	Exceeded (%)
Sodium (Na)	27	6	22%
Chloride (Cl-)	27	8	30%
Sulphate (SO_4^{2-})	28	5	18%
Fluoride	1	1	100%
Nitrate (NO_3^-)	31	8	26%
Ammonia (NH_4^+)	11	2	18%
Phosphates	5	3	60%
Cyanide (CN-)	1	1	100%
Arsenic (As)[6]	4	2	50%
Barium (Ba)	1	1	100%
Copper (Cu)	3	1	33%
Lead (Pb)	1	0	0%
Nickel (Ni)	4	4	100%
Zinc (Zn)	1	1	100%
Naphthalene	1	0	0%
Total	146	43	29%

The MAC that posed the most problems to the Spanish MAR sites was nitrate, probably due to the agricultural context in which many are involved directly or indirectly. Other frequently exceeded parameters were chloride, probably related to the proximity to the sea at many sites, and Nickel. The Spanish standard for direct injection was the most restrictive MAC standard in terms of the total percentage of parameters breached (i.e., 33%). Nonetheless, as stated above, this standard is aimed at particular projects and assumes no treatment in the vadose zone takes place. Consequently, it has more stringent thresholds.

The most restrictive MAC standard regarding the number of sites that wouldn't meet the requirements is the Dutch, which would preclude operations at seven locations. This standard also had the second-highest rate of parameter rejections (i.e., 29%).

6.8 Preliminary conclusions

There is a high diversity of MAR water sources in terms of chemical constituents, hydrofacies, and significant water quality issues. These waters comprise all sites in a piper diagram and deal with potential pollution issues ranging from nitrates to heavy metals and CECs. The sites also include unconventional sources of water, including treated groundwater and drinking water.

Statistical analysis and evaluation of long-term trends from hydrodynamic monitoring provides site upgrade and allows identifying water quality hotspots.

Watersheds with a relatively low anthropic intervention other than MAR (e.g., Acequias de Careos) or MAR sites in which the water intake was at a high topographical point in a watershed had the least water quality issues. On the other hand, sites relying on water from highly intervened sources had the highest risk of water pollution.

A MAC approach to control water quality during MAR seems limited and inadequate. On the one hand, it has been demonstrated that waters from MAR are highly variable and hardly well addressed by a single threshold list. On the other hand, MACs could restrict operations at sites that are currently legally operating without contaminating aquifers. For instance, the Guadiana MAR site couldn't be implemented as it is under Italian and Dutch standards because the water source breaches MACs. Nonetheless, in this site, the water percolated has a higher quality than the native groundwater (which does not meet the MAC standards either) and is helping to, at least locally, improve quality.

In case of including MACs in regulations, those should be "aquifer-wide". The self purification capacity for each receiving medium is different and must be considered as long as its capacity is not exceeded, what depends, not only on the initial water quality, but also on the pre-treatment and post-treatment processes, the characteristics of the receiving medium (e.g. granular aquifers poses a higher self-purification than hard rocks; the final use (irrigation in less demanding than industrial use or urban supply). In summary, a detailed study should be conducted for each specific case when granting a MAR permission or allowance.

7. Review of Low-cost Techniques to Improve Water Quality in MAR Systems: The Potential of the Biochar

Biochar is a carbon-rich and porous material which results from the thermochemical decomposition (i.e. pyrolysis) of biomass in the absence of oxygen (Xiang et al. 2020). The interest in this material has increased after the pioneering work of Glaser et al. (2001) and Cueto García (2016), who showed that soils rich in black carbon amendment ("Terra preta") in the Amazon were responsible for high crop yield and could be a potential method to mitigate climate change.

One of the most significant potentials of biochar is as a carbon sequestration option to mitigate climate change. When used as a soil amendment, it fixes carbon which would otherwise return to the atmosphere after the decomposition of biomass (Woolf et al. 2010). Furthermore, liquid and gaseous substances obtained during its production can provide energy and offset fossil fuel emissions, as only half of the original photo-synthetical carbon is released into the atmosphere (Woolf et al. 2010). According to Woolf et al. (2010), biochar used in stringent sustainable ways could reduce anthropogenic GHGs emissions by up to 12%.

Biochar has a wide variety of uses apart from a CC mitigation option. It can be used to amend soils and increase crop productivity by reducing soil acidity, enhancing cation exchange capacity (CEC) and nutrient retention, providing room for air, water and microorganism growth, and contributing with nutrients for direct plant uptake or soil microorganism (Glaser et al. 2001; Lehmann 2007; Cueto García 2016; Cha et al. 2016). Biochar is also used as a catalyst to remove tar from the gasification process and to produce biodiesel (Cha et al. 2016; Xiang et al. 2020).

Moreover, this material is also applied in soil remediation by reducing the mobility of metals, which end up entrapped in biochar's pores and surface (Cueto García 2016). Its elevated surface area, high porosity, functional groups and medium CEC (Streubel 2010) also make it appropriate to absorb air and water pollutants (Cha et al. 2016). Biochar has been used to remove toxic metals, nutrients, and organic pollutants in water (Xiang et al. 2020) similarly to activated carbon but at a considerably lower cost and environmental impacts (Mohanty et al. 2018).

Using biochar in water decontamination hints at the possibility of applying this material to MAR scheme. Recent studies suggest that biochar could help remove antibiotic-resistant genes from water (Cui et al. 2016). This set of genes, frequently found in effluent from WWTP, can potentially be transferred to microorganisms and develop into antibiotic-resistant bacteria (Valhondo et al. 2020). Biochar could also be employed in pre- and post-treatment stages, passively enhancing water quality at a low cost. Furthermore, it could help remove micropollutants, one of the most significant concerns in MAR systems relying on wastewater. One of the primary mechanisms mediating the removal of contaminants through biochar is the space it provides to microorganisms, which enhances biodegradation. Moreover, the fact that biochar is a relatively low-cost option could help to overcome in an affordable way possible hindrances to MAR implementation, such as the concern of aquifer pollution (Valhondo et al. 2020).

This section explores the possibility of employing biochar in MAR systems, providing an overview of the removal of pollutants, how the material and its properties change over time, and how it affects infiltration rates, among other factors. The final part of this review studies links between biochar and MAR from the literature.

Biochar comprises highly resistant aromatic carbon substances with a ring structure, minerals, and more readily degradable aliphatic and oxidised carbon forms (Lehmann 2007). A wide range of biochars is often characterised based on their composition and physicochemical properties, such as CEC, surface area, pore-volume, surface chemistry, surface functional groups, pH, etc. (Streubel 2010; Xiang et al. 2020). The wide variety of properties and compositions depend on two main factors: the feedstock material employed and the production process (Zhao et al. 2013; Cha et al. 2016).

Due to the fact that this specific topic emerged collateral to this deliverable's content, the extended development of the biochar technical solution is included in this report as **ANNEX 1**.

8. Conclusions and Recommendations

Managed Aquifer Recharge regulations and guidelines are under permanent improvement, but they need more modern considerations and adaptation to the current climate change context, under varied threats.

The application of the precautionary principle has been extreme in European regulations when it comes to Managed Aquifer Recharge. However, a novel approach is needed that on the one hand serves the protection of groundwater bodies but at the same time allows applying climate change adaptation principles.

The potential for water reuse in the European context, and specifically within Spain, should prioritise reuse actions aimed at achieving the good status of water bodies and to improve the regulatory and financial framework for reuse (Revision and Adaptation of RD 1620/2007 to Regulation 2020/741). Some actions might be to develop a section dedicated to reusing on the MITECO website; to perform a communication campaign on consuming recycled water (MITERD 2021); and to give MAR technique the consideration that it deserves in the most modern regulations and plans, as it is (and has been demonstrated along the whole MARSoluT deliverables) a good measure for climate change adaptation and mitigation of adverse impacts.

Linked to the specific conclusions of the deliverable, some key messages deserve to be included obtained from the project´s activity and related to this report´s approach.

Pressure is increasing on water resources and "something must be done". Managed Aquifer Recharge (MAR) is part of the solution. It is also a "balancing measure" between high availability and limited availability of water resources, as well as a system to balance groundwater disposal and demand.

MAR has become, according the whole results of MARSoluT, a system to increase water security, economic wellbeing, and it is even a climate change adaptation measure; but MAR is very much more than a simple technology. Water proceeding from MAR can still be considered "new water" from regeneration. Other developments may be energy transition, economical improvements, and water-energy-food nexus.

The "more dams" persistent claim from authorities should be questioned presenting examples of groundwater storage volumes and cost of investment. The time to implement subsurface storage of water – particularly when this storage space exists following years of overexploitation of groundwater – is greater than ever.

Solutions to preserve water quality must be in permanent improvement to cope with pharmaceutical, industrial spills, etc. Preventive measures are still important. There is an increasing need to look at the confidence in the quality of the water to recharge. To note, the WFD/GWD requirements of no deterioration and the ECJ interpretation claim about no water deterioration, even at a local scale.

The establishment of Maximum Allowable Concentrations (MACs) in the regulation should include what is the final risk. MACs cannot be regulated for national or European levels, but rather aquifer-wide. Within this context, this statement needs to be discussed in view of the GWD prevent and limit objectives, and the WFD.

Most important is the final quality of the water after MAR, rather than the original quality. Interaction processes modeling should be incorporated into usual tools for regulators. It is noticeable that the saturated zone should not be used for quality betterment purposes, in particular if this leads to the deterioration of the groundwater. The option of using the effect of the unsaturated zone to better recharge water quality must be studied carefully.

The trend for MAR from water reuse perspective (specifically reclaimed water as another source of the several options for different water sources) should guarantee that SAT-MAR or Intentional Recharge with reclaimed water will not damage any aquifer (precautionary principle must be applied, but in a more rational and permissive manner). The balance between jeopardizing groundwater quality and the precautionary principle application may be delicate. MARSoluT sticks to the "not to deteriorate the final quality" rule. A proper "deterioration" definition is pendant in the regulations.

Interoperability in MAR monitoring and operation is a promising field to increase system efficiency and foster communication and data exchange.

Also, water availability should be unlinked from electricity price (carbonization, desalination, etc.).

Water quality from about ten real MAR sites in Spain has been characterized and compared. The selected sites employ different water sources, their functioning is quite diverse, and final uses are varied too. After comparing each other and confronting them with the Maximum Allowable Concentrations (MACs) regulated in some European countries and beyond, we have concluded that limiting standards in the regulation is not the best way to ensure water security, due to the fact that the selected systems are working well despite some MACs are exceeded in certain occasions. We persist MACs limitations, in case of establishing them in the regulations, should be at "aquifer-wide" level, all the more so for a national territory with diverse lithology, dissimilar self-purification capacity, varied water sources, and different final uses.

Water quality control in MAR systems operations requires a clear normative body to avoid harm to humans and ecosystems. Conceptual models for formulating norms, such as the MIR conceptual model, can considerably help implement MAR appropriately worldwide.

Long-term experiences, e.g. the Shafdan site in Israel, are important to prove the effectiveness of MAR. The new EU regulations could be applied on Shafdan and other successful not disputed international experiences, to check whether the water bodies would have been affected applying a different regulation.

At European level, there is probably no need for new regulations, in case the WFD is wisely modified, and the 2020/741 sets minimum requirements for water quality according to final uses, initially for agricultural irrigation. This statement agrees with the CIS GW Working Group´s final conclusions.

Groundwater models can be used to support decision-making for MAR, by quantifying and reducing uncertainty through the assimilation of existing data.

Formulating MAR systems as low-regret measures to climate change adaptation provide tools to cope simultaneously with, at least, two fronts: extreme water-related events (natural climate variability), and global warming. Therefore, the value of MAR as an adaptation measure to climate change is more and more important, stressing also its circularity principles, less energy consumption, etc.

Using endemic on-site plants, biochar, and other nature-based solutions could considerably increase the performance of MAR system at a low financial cost and with no harm to the environment. The importance of activated carbon for water quality improvement is a key solution thanks to interactive processes including the carbon source as a cathalizer.

The natural retention measures (dykes and structures transversal to river courses) help storing groundwater reservoirs for the future.

The challenge of "Do Minimum Impact Principle" (DMPH) for reclaimed water is a current line of research to be enhanced by means of future project proposals.

The tools for freshwater sustainability include artificial intelligence techniques, ontology, and special attention on the third dimension of the groundwater bodies.

At the communication level, how to engage policy makers is still a pendant issue. The route to the market is also important. It is imperative to "pass the message", and policy brief documents may play an important role in this regards. The message must be conveyed in understandable language.

The term "co-managed aquifer recharge" (Co-MAR) is an innovative procedure to include stakeholders in decision making regarding IWRM. Co-MAR is related to multi-level governance, a bottom up approach and a scale-up system. It is also useful for optimizing designs, looking for ways to finance the MAR system, and applied research.

A particular challenge for local water engineers, practitioners, and scientists is to find out practical solutions in order to ensure that freshwater source can keep playing its role well in the future.

Nowadays MAR is an option, you can do it or not. Currently climate change (CC) indicators are pointing out draught and extreme events in permanent raise, therefore, we need capacitated technicians to give response to new challenges and to reduce impacts once politics will finally react against CC threat.

The absence of hydrogeologists and specialists in water resources at the public level has been a constant problem for years in developing countries when activities are not subcontracted to consultancies companies or autonomous bodies. The lack of academic programs and specialized research centres in water engineering leads local authorities to replace roles of hydrogeologists with other professionals, lacking in-depth knowledge required to implement the sought mitigation measures. Probably a remarkable issue is that hydrogeologists need to speak the language of the policy maker and the general public, i.e. enhancing their communication skills.

MARSoluT advocates for continuing investing in (1) applied research to improve insights into development of fresh water bells in saline environments, (2) define measures to increase efficiency of MAR-systems and social acceptance, and (3) consider the beneficial impact of the unsaturated zone.

MARSoluT report deliverables will improve the understanding and acceptance of MAR. In many countries and at a national level, there is currently no support for MAR; however at regional level, there is increasing understanding that MAR can be important. We hope that the MARSoluT report deliverables will improve the understanding and acceptance of MAR, and allow MAR schemes to be considered along with other water resource options.

Capacity development is key for future. We need more support to wise young generations on IWRM and MAR, for them to face the new coming environmental context.

According to the exposed items, we may conclude, **"MAR is a *must*"**. MAR is safe, sound and sustainable. Consequently, there is a safe opportunity which can be used with other water management tools to ensure an intergrated water management framework. It is important to define the direction to go in the coming decade. The knowledge to ensure safety is available. Most of these statements are underlined in the MARSoluT´s policy brief document.

Some **specific recommendations** have been proposed to be considered when drafting a more modern regulatory framework:

- Developing a common terminology with legal implications. A homogeneous definition of Artificial Recharge or Managed Aquifer Recharge is needed, at least for areas which have a common regulation (e.g. the EU).
- Including a permitting process. Water allocation permits and water extraction rights ownerships must be considered in all regulations and established well in advance, including the simple right of use.
- Legal development. There is an insufficient theoretical background on legal aspects of MAR.
- Independent control and surveillance. A "structured reporting process" should be developed.
- Time continuity. The Administration and the Water Basin Authorities should study continuity mechanisms to allow assessing the long-term effects of MAR.
- Inclusion of budgetary aspects. The financial aspects of MAR projects are frequently excluded in both, the regulations and the granting of authorisations. In this way, the un-monetised benefits of MAR would be included in the equation, and a net positive effect of MAR systems would be guaranteed.
- Including the technical background for authorisations. Allowances to grant a MAR implementtation must take into account the specific water quality standard for an area. This aspect could be particularly relevant when dealing with the potential impact of the unsaturated zone, so important in the final groundwater quality due to interaction processes.
- Moving forward with the WFD. The implementation of MAR and SAT-MAR in the EU may be facilitated by taking the following measures: 1) Establishing a framework of permit or authorisations (EC, 2006); 2) Establishing control and surveillance mechanisms to ensure the implementation of the permit conditions; and 3) Undertaking the necessary oversight of MAR systems to renew any permission or concession (EC, 2007).
- Water standards for MAR must be designed at the aquifer level (aquifer-wide), and taking into account the interactions between the source water and the aquifer. It might be feasible to extend water quality standards across aquifers with similar characteristics. The nation-wide standards seem to be the most straightforward approach, but the aquifer-wide standards would be the safest. Therefore, authorizations should be granted at local level by real specialist in the site where any MAR or water reuse activity is proposed.
- High number of pollutants to be regulated. The more stringent the controls on the quality of the source of water, the fewer constraints would need to be taken into consideration.

- MAR sources and receiving medium considerations. A risk analysis approach usually counts on this capability, while water quality standards consider, to a limited extent, the aquifer´s self-purification capacity.
- Water quality standards should be differentiated according to the MAR technology involved to minimise the impact of the previous points exposed, as it has been done for instance in Spain, Mexico, and in the GWD.
- Updating some water quality standards. Some pollutants with water quality standards should be reviewed and updated periodically, according to the instrumental measuring capabilities (for "aquifer-wide" standards).
- Considering the monitoring cost. Guidelines must consider the cost of analyses.
- The Monitored and Intentional Recharge (MIR) concept includes nine blocks for planning a detailed "hydrodynamic monitoring". It is a huge compendium of elements to be taken into consideration at different scales. MIR also includes the aspects already outlined in previous guidelines documents, such as considering monitoring frequencies for each parameter; including common parameters; considering the final use, participating stakeholders, etc.

9. References

9.1 Literature

Alidina M, Li D, Drewes JE (2014) Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Research 56, 172-180. https://doi.org/10.1016/j.watres.2014.02.046

Amphos 21 (2016) Short report on the travel time between the infiltration ponds and the drinking water wells in el Port de la selva. status of september 22nd, 2016. Informative report.

Appelo CAJ, Postma D (2013) Geochemistry, groundwater and pollution, 2. ed., 10. corr. repr., CRC Press, Boca Raton.

Aragón CA, Ortega E, Ferrer Y, Salas JJ (2013) Current situation of sanitation and wastewater treatment in small Spanish agglomerations. Desalination and Water Treatment 51, 2480-2487. https://doi.org/10.1080/19443994.2012.747651

Baquero JC, De los Reyes MJ, Custodio E, et al. (2016) Groundwater Management in Mining: The Drainage and Reinjection System in Cobre Las Cruces, Spain. MESE 2, 631-646. https://doi.org/10.15341/mese(2333-2581)/10.02.2016/001

Barberá JA, Jódar J, Custodio E, et al. (2018) Groundwater dynamics in a hydrologically-modified alpine watershed from an ancient managed recharge system (Sierra Nevada National Park, Southern Spain - Insights from hydrogeochemical and isotopic information. Science of The Total Environment 640-641, 874-893. https://doi.org/10.1016/j.scitotenv.2018.05.305

Barbieri M, Carrera J, Ayora C, et al. (2012) Formation of diclofenac and sulfamethoxazole reversible transformation products in aquifer material under denitrifying conditions: Batch experiments. Science of The Total Environment 426, 256-263. https://doi.org/10.1016/j.scitotenv.2012.02.058

Brangarí AC, Fernàndez-Garcia D, Sanchez-Vila X, Manzoni S (2018) Ecological and soil hydraulic implications of microbial responses to stress – A modeling analysis. Advances in Water Resources 116, 178-194. https://doi.org/10.1016/j.advwatres.2017.11.005

Cha JS, Park SH, Jung S-C, et al. (2016) Production and utilization of biochar: A review. Journal of Industrial and Engineering Chemistry 40, 1-15. https://doi.org/10.1016/j.jiec.2016.06.002

CNR, SCIRO (2020) Guía Metodológica - Marco Operativo para Proyectos de Recarga Artificial de Acuíferos (Methodological Guidance - Operational Framework for Artificial Aquifer Recharge Projects). Consejor Nacional de Riego - CSIRO Chile.

Conagua (2009) Norma Oficial Mexicana NOM-014-Cona-gua-2003, Requisitos para la recarga artificial de acuíferos con agua residual tratada, s 17.

Council of the European Communities (1975) Council Directive of 16th June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States (75/440/EEC). Official Journal of the European Communities 6.

Council of the European Communities (1979) Council Directive of 17th December 1979 on the protecttion of groundwater against pollution caused by certain dangerous substances (80/68/EEC). Official Journal of the European Communities 6.

Council of the European Communities (1991) Council Directive of 21 May 1991 concerning urban waste water treatment (91/271 /EEC). Official Journal of the European Communities 30, 13.

Cruz-García R, Gámiz-Fortis SR, Castro-Díez Y, Esteban-Parra MJ (2016) Climate Change Projections for Winter Streamflow in Douro River. In Clima, Sociedad, Riesgos y Ordenación del Territorio, Servicio de Publicaciones de la UA, Alicante, Spain, pp. 437-447. ISBN 978-84-16724-19-2.

Cueto García MJ (2016) Potencial de producción de biochar en España a partir de residuos de la industria papelera, de lodos de E.D.A.R., de residuos sólidos urbanos y de residuos ganaderos: Estudio de la fijación de carbono. PhD Thesis, Universidad Politécnica de Madrid

Cui E, Wu Y, Zuo Y, Chen H (2016) Effect of different biochars on antibiotic resistance genes and bacterial community during chicken manure composting. Bioresource Technology 203, 11-17. https://doi.org/10.1016/j.biortech.2015.12.030

Department of Groundwater Resources (DGR, 2022) Standard Guidelines for Artificial Groundwater Recharge in Thailand. Ministry of Natural Resources and Environment, Thailand.

Dillon P, Stuyfzand P, Grischek T, et al. (2019) Sixty years of global progress in managed aquifer recharge. Hydrogeol J 27, 1-30.

Dillon P, Alley W, Zheng Y, Vanderzalm J (eds., 2022) Managed Aquifer Recharge: Overview and Governance. IAH Special Publication. https://recharge.iah.org/ ISBN 978-1-3999-2814-4

Ensink JHJ, van der Hoek W (2009) Implementation of the WHO guidelines for the safe use of wastewater in Pakistan: balancing risks and benefits. Journal of Water and Health 7, 464-468. https://doi.org/10.2166/wh.2009.061

European Commission (2007) Guidance on preventing or limiting direct and indirect inputs in the context of the Groundwater Directive 2006/118/EC. WFD CIS Guidance Document No. 17, Publications Office of the European Union, Luxembourg.

European Commission (2012) Report from the Commission to the European Parliament and the Council on The Implementation of the Water Framework Directive (2000/60/EC) - River Basin Management Plans. COM(2012) 670 final, Brussels, 14.11.2012

European Commission (2022) Guidelines to support the application of Regulation 2020/741 on minimum requirements for water reuse (2022/C 298/01). OJEU C 298/1, 5.08.2022.

European Parliament and Council of the European Union (2000) Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy. OJEU L 327/1, 22.12.2000.

European Parliament and Council of the European Union (2013) Directive 2013/39/EU of the European Parliament and of the Council of 12th August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. OJEU L 226/1, 24.08.2013.

European Parliament (2020) Regulation (EU) 2020/741 of the European Parliament and of the Council of May 25th 2020 on minimum requirements for water reuse. OJEU L 177/32, 5.06.2020.

Fajnorová S, Sprenger C, Hermes N, et al. (2021) Assessment of Full-Scale Indirect Potable Water Reuse in El Port de la Selva, Spain. Water 13, 325. https://doi.org/10.3390/w13030325

Fernández Escalante AE, García Rodríguez M, Villarroya Gil, F (2005) The 'careos' from Alpujarra (Granada, Spain), an historical example of previous to XII century artificial recharge system applicable to the XXI century – Characterization and inventory. 5th International Symposium on Managed Aquifer Recharge ISMAR 5, proceedings book, 665-670, Berlin. https://recharge.iah.org/ismar/ismar5

Fernández Escalante E (2015) Practical Management to Minimize the Effects of Clogging in Managed Aquifer Recharge Wells at Two Sites in the Guadiana Basin, Spain. J Hydrol Eng 20. https://doi.org/10.1061/(ASCE)HE.1943-5584.0001047

Fernández-Escalante E, García Rodríguez M (2004) La recarga artificial de acuíferos. Marco legal que regula sus aplicaciones. Presentación.

Fernández Escalante E, Henao Casas JD, Vidal Medeiros AM, San Sebastián Sauto J (2020) Regulations and guidelines on water quality requirements for Managed Aquifer Recharge. International comparison. AS-ITJGW. https://doi.org/10.7343/as-2020-462

Fernández Escalante E, Henao Casas JD, Calero Gil R (2021) Sugerencias para las futuras directrices europeas de recarga intencionada de acuíferos con aguas regeneradas y de otras fuentes (Suggestions for future European guidelines for intentional recharge of aquifers with reclaimed and other water sources). Revista IDI+, 15-18. https://doi.org/10.5281/ZENODO.7540695

Fernández Escalante E, Paredes Núñez JM (2022) MAR to improve water security and rural development using drainage water sources, Arabayona demo-site, Salamanca, Spain. In: P-ISMAR11-11th International Symposium on Managed Aquifer Recharge. ISMAR 11, Long Beach, California, 16 p. https://dinamar.tragsa.es/file.axd?file=/PDFS/P-ISMAR-11.pdf

Fernández Escalante E, Henao Casas JD, San Sebastián Sauto J, Calero Gil R (2022) Monitored and Intentional Recharge (MIR) - A Model for Managed Aquifer Recharge (MAR) Guideline and Regulation Formulation. Water 14, 3405. https://doi.org/10.3390/w14213405

Flemming H-C (1995) Sorption sites in biofilms. Water Science and Technology 32(8), 27-33. https://doi.org/10.1016/0273-1223(96)00004-2

Franco A, Fu W, Trapp S (2009) Influence of soil ph on the sorption of ionizable chemicals: modeling advances. Environ Toxicol Chem 28, 458. https://doi.org/10.1897/08-178.1

García J, Mujeriego R, Obis JM, Bou J (2001) Wastewater treatment for small communities in Catalonia (Mediterranean region). Water Policy 3, 341-350. https://doi.org/10.1016/S1366-7017(01)00080-0

Glaser B, Haumaier L, Guggenberger G, Zech W (2001) The "Terra Preta" phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37-41. https://doi.org/10.1007/s001140000193

Goren O, Burg A, Gavrieli I, Negev I, Guttman J, Kraitzer T, Kloppmann W, Lazar B (2014) Biogeochemical processes in infiltration basins and their impact on the recharging effluent, the soil aquifer treatment (SAT) system of the Shafdan plant, Israel. Applied Geochemistry 48, 58-69.

Grau-Martínez A, Torrentó C, Carrey R, et al. (2017) Feasibility of two low-cost organic substrates for inducing denitrification in artificial recharge ponds: Batch and flow-through experiments. Journal of Contaminant Hydrology 198, 48-58. https://doi.org/10.1016/j.jconhyd.2017.01.001

Greskowiak J, Hamann E, Burke V, Massmann G (2017) The uncertainty of biodegradation rate constants of emerging organic compounds in soil and groundwater – A compilation of literature values for 82 substances. Water Research 126, 122-133. https://doi.org/10.1016/j.watres.2017.09.017

Guerreiro SB, Birkinshaw S, Kilsby C, Fowler HJ, Lewis E (2017) Dry Getting Drier – The Future of Transnational River Basins in Iberia. J. Hydrol. Reg. Stud. 12, 238-252.

Henao Casas JD, Fernández Escalante E, Calero Gil R (2022a) La estandarización e interoperabilidad como tecnologías TICs facilitadoras de la recarga gestionada de acuíferos (Standardisation and interoperability as enabling ICT technologies for managed aquifer recharge). Revista IDI+, 58-63. https://doi.org/10.5281/zenodo.7498433

Henao Casas JD, Fernández Escalante E, Calero Gil R, Ayuga F (2022b) Managed Aquifer Recharge as a Low-Regret Measure for Climate Change Adaptation: Insights from Los Arenales, Spain. Water 14, 3703. https://doi.org/10.3390/w14223703

Henzler AF, Greskowiak J, Massmann G (2014) Modeling the fate of organic micropollutants during river bank filtration (Berlin, Germany). Journal of Contaminant Hydrology 156, 78-92. https://doi.org/10.1016/j.jconhyd.2013.10.005

Huertas R, Marcos C, Ibarguren N, Ordás S (2013) Guía práctica para la depuración de aguas residuales en pequeñas poblaciones (Practical guide to wastewater treatment in small settlements). Confederación Hidrográfica del Duero, Valladolid.

Imig A, Szabó Z, Halytsia O, Vrachioli M, Kleinert V, Rein A (2022) A review on risk assessment in managed aquifer recharge. Integr Environ Assess Manag 00, 1-17. https://doi.org/10.1002/ieam.4584

Jódar J, Zakaluk T, González-Ramón A, et al. (2022) Artificial recharge by means of careo channels versus natural aquifer recharge in a semi-arid, high-mountain watershed (Sierra Nevada, Spain). Science of The Total Environment 825, 153937. https://doi.org/10.1016/j.scitotenv.2022.153937

Jodar-Abellan A, López-Ortiz MI, Melgarejo-Moreno J (2019) Wastewater Treatment and Water Reuse in Spain. Current Situation and Perspectives. Water 11, 1551. https://doi.org/10.3390/w11081551

Kleineidam S, Schüth C, Grathwohl P (2002) Solubility-Normalized Combined Adsorption-Partitioning Sorption Isotherms for Organic Pollutants. Environ Sci Technol 36, 4689-4697. https://doi.org/10.1021/es010293b

Lehmann J (2007) Bio-energy in the black. Frontiers in Ecology and the Environment 5, 381-387. https://doi.org/10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

Maliva RG (2020) Anthropogenic Aquifer Recharge. WSP Methods in Water Resources Evaluation Series No. 5, 861 p., Springer Hydrogeology, Springer International Publishing, Cham. https://doi.org/10.1007/978-3-030-11084-0

MARSOL (2015) Legislative Framework Review and Analysis. Capone F, Bonfanti ME. MARSOL, Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought, project deliverable D17.1.

MARSOL (2016a) Guideline for water quality requirements. Kübeck C, Nottebohm M. MARSOL, Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought, project deliverable D14.4.

MARSOL (2016b) Appropriate MAR methodology and tested knowhow for the general rural development. Fernández Escalante E, Calero Gil R, Villanueva Lago M, San Sebastián Sauto J, Martínez Tejero O, Valiente Blázquez JA. MARSOL, Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought, project deliverable D5.3.

MARSoluT (2023a) Guideline for Regional Implementation of MAR Systems. Monteiro JP, Standen K, Sapiano M, Fernández Escalante E, Schüth C. MARSoluT, Managed Aquifer Recharge Solutions Training Network, project deliverable D2.2.

MARSoluT (2023b) Flow model and monitoring system for the Malta South MAR site. Demichele F, Sapiano M, Schembri M, Mamo J. MARSoluT, Managed Aquifer Recharge Solutions Training Network, project deliverable D4.1.

Ministero dell’Ambiente e della Tutela del Territorio e del Mare (2016) Decreto 2 maggio 2016, n. 100. Gazzetta Ufficiale della Repubblica Italiana, n 136 13 giugno 2016, serie generale.

MITERD (2021) Plan Nacional de Depuración, Saneamiento, Eficiencia, Ahorro y Reutilización - Plan DSEAR (National plan for purification, sanitation, efficiency, savings and reuse - DSEAR Plan). Ministerio de la Transición Ecológica y el Reto Demográfico

Mohanty SK, Valenca R, Berger AW, et al. (2018) Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. Science of The Total Environment 625, 1644-1658. https://doi.org/10.1016/j.scitotenv.2018.01.037

Müller B, Scheytt T, Grützmacher G (2013) Transport of primidone, carbamazepine, and sulfamethoxazole in thermally treated sediments - laboratory column experiments. J Soils Sediments 13, 953-965. https://doi.org/10.1007/s11368-013-0671-9

Nogueras R, Donoso L, Iglesias J, Martínez I (2019) Review of groundwater recharge experiences in Madrid tertiary detrital aquifer. In: Managed Aquifer Recharge: Local solutions to the global water crisis - Proceedings of the symposium ISMAR 10. Madrid, Spain, pp. 358-366.

NRMMC, EPHC, NHMRC (2009) Australian Guidelines for Water Recycling, Managing Health and Environmental Risks, Volume 2C - Managed Aquifer Recharge. In: Nat. Resour. Manag. Minist. Counc. Environ. Prot. Herit. Counc. Natl. Heal. Med. Res. Counc. https://recharge.iah.org/files/2016/11/Australian-MAR-Guidelines-2009.pdf. Accessed 20 Jan 2023

OECD (2019) Spain country report. Organisation for Economic Co-operation and Development, Madrid, Spain.

Owen D (2021) Law, land use, and groundwater recharge. Stan L Rev 73, 1163.

Persson L, Carney Almroth BM, Collins CD, et al. (2022) Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. Environ Sci Technol 56 (3), 1510-1521. https://doi.org/10.1021/acs.est.1c04158

Pistocchi A, Aloe A, Dorati C, et al. (2017) The Potential of Water Reuse for Agricultural Irrigation in the EU - A Hydro-Economic Analysis. EUR 28980 EN, European Commission, Joint Research Centre. https://doi.org/10.2760/263713

Primo CM (2013) Actuaciones de la Confederación Hidrográfica del Duero para el tratamiento de vertidos en pequeñas poblaciones. Proyecto de Tratamientos singulares de carácter experimental de vertidos en pequeñas poblaciones de la cuenca del Duero.

Rauch-Williams T, Hoppe-Jones C, Drewes JE (2010) The role of organic matter in the removal of emerging trace organic chemicals during managed aquifer recharge. Water Research 44, 449-460. https://doi.org/10.1016/j.watres.2009.08.027

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

Rossetto R, Bonari E. (2014) Il futuro della ricarica delle falde in condizioni controllate in Italia: il progetto europeo FPVII MARSOL e la EIP on Water MAR to MARKET. Acque Sotterranee, Italian Journal of Groundwater 3/137, 9-12.

Sánchez E, Gutiérrez E (2019) ASTR facility design in a deep aquifer destined to supply the Community of Madrid. In: Managed Aquifer Recharge: Local solutions to the global water crisis, Proceedings of the symposium ISMAR 10. Madrid, Spain, pp. 402-417.

Sastre-Beceiro M (2009) Aspectos jurídicos de la recarga artificial de acuíferos: regulación actual y retos. Boletín Geológico y Minero 120, 10.

Schaffer M, Kröger KF, Nödler K, et al. (2015) Influence of a compost layer on the attenuation of 28 selected organic micropollutants under realistic soil aquifer treatment conditions: Insights from a large scale column experiment. Water Research 74, 110-121. https://doi.org/10.1016/j.watres.2015.02.010

Schwarzenbach RP, Gschwend PM, Imboden DM (2017) Environmental organic chemistry. Third edition, Wiley, Hoboken, N.J.

Shubo T, Fernandes L, Montenegro SG (2020) An Overview of Managed Aquifer Recharge in Brazil. Water 12, 1072. https://doi.org/10.3390/w12041072

Silver M, Wefer-Roehl A, Kuebeck C, Schüth C (2016) Transformations of Nitrogen from Secondary Treated Wastewater when Infiltrated in Managed Aquifer Recharge Schemes. EGU General Assembly 2016, Vienna, Geophysical Research Abstracts, Vol. 18, EGU2016-4862.

Silver M, Selke S, Balsaa P, Wefer-Roehl A, Kübeck C, Schüth C (2018) Fate of five pharmaceuticals under different infiltration conditions for managed aquifer Recharge. Science of the Total Environment 642, 914-924. https://doi.org/10.1016/j.scitotenv.2018.06.120

Späth R, Flemming H-C, Wuertz S (1998) Sorption properties of biofilms. Water Science and Technology 37, 207-210. https://doi.org/10.2166/wst.1998.0623

Sprenger C, Hartog N, Hernández M, et al. (2017) Inventory of managed aquifer recharge sites in Europe: historical development, current situation and perspectives. Hydrogeol J 25, 1909-1922.

Stefan C, Ansems N (2018) Web-based global inventory of managed aquifer recharge applications. Sustain Water Resour Manag 4, 153-162. https://doi.org/10.1007/s40899-017-0212-6

Streubel J (2010) Biochar: Physical and Chemical Characteristics. YouTube, accessed 4 Apr 2020. https://www.youtube.com/watch?v=PN02I_GnO6s

Torresi E, Polesel F, Bester K, et al. (2017) Diffusion and sorption of organic micropollutants in biofilms with varying thicknesses. Water Research 123, 388-400. https://doi.org/10.1016/j.watres.2017.06.027

Tran NH, Urase T, Ngo HH, et al. (2013) Insight into metabolic and cometabolic activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging trace organic contaminants. Bioresource Technology 146, 721-731. https://doi.org/10.1016/j.biortech.2013.07.083

Valhondo C, Carrera J, Ayora C, et al. (2015) Characterizing redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer. Science of the Total Environment 512-513, 240-250. https://doi.org/10.1016/j.scitotenv.2015.01.030

Valhondo C, Carrera J, Martínez-Landa L, et al. (2020) Reactive Barriers for Renaturalization of Reclaimed Water during Soil Aquifer Treatment. Water 12, 1012. https://doi.org/10.3390/w12041012

Valhondo C, Martinez-Landa L, Carrera J, et al. (2018) Evaluation of EOC removal processes during artificial recharge through a reactive barrier. Science of The Total Environment 612, 985-994. https://doi.org/10.1016/j.scitotenv.2017.08.054

Versteeg P, Peña K, Gallegos J, Fernández-Escalante E (2021) Urban Waterbuffer Zorrilla, Valladolid - Proyecto piloto de recarga gestionada de acuífero y recuperación de aguas pluviales para riego (Urban Waterbuffer Zorrilla, Valladolid - Pilot project for managed aquifer recharge and rainwater recovery for irrigation). Field Factors.

Watanabe N, Bergamaschi BA, Loftin KA, et al. (2010) Use and Environmental Occurrence of Antibiotics in Freestall Dairy Farms with Manured Forage Fields. Environ Sci Technol 44, 6591-6600. https://doi.org/10.1021/es100834s

Weber WJ, McGinley PM, Katz LE (1992) A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. Environ Sci Technol 26, 1955-1962. https://doi.org/10.1021/es00034a012

WHO (2003) State of the art report health risks in aquifer recharge using reclaimed water. World Health Organization.

Woolf D, Amonette JE, Street-Perrott FA, et al. (2010) Sustainable biochar to mitigate global climate change. Nat Commun 1, 56. https://doi.org/10.1038/ncomms1053

Xiang W, Zhang X, Chen J, et al. (2020) Biochar technology in wastewater treatment: A critical review. Chemosphere 252, 126539. https://doi.org/10.1016/j.chemosphere.2020.126539

Ying G-G, Kookana RS (2005) Sorption and Degradation of Estrogen-Like Endocrine Disrupting Chemicals in Soil. Environ Toxicol Chem 24, 2640. https://doi.org/10.1897/05-074R.1

Yuan J, Van Dyke MI, Huck PM (2016) Water reuse through managed aquifer recharge (MAR): assessment of regulations/guidelines and case studies. Water Quality Research Journal 51, 357-376. https://doi.org/10.2166/wqrjc.2016.02

Zhao L, Cao X, Mašek O, Zimmerman A (2013) Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. Journal of Hazardous Materials 256-257, 1-9. https://doi.org/10.1016/j.jhazmat.2013.04.015

Zheng Y, Artimo A, Puurunen O, Saraperä S (2021) Chapter 3 Assessment of environmental and social sustainability of Managed Aquifer Recharge schemes. In: Managing Aquifer Eecharge: A Showcase for Resilience and Sustainability, UNESCO, Paris, pp. 47-72.

Zheng Y, Vanderzalm J, Hartog N, Fernández Escalante E, Stefan C (2023) The 21st Century Water Quality Challenges for Managed Aquifer Recharge: Towards a Risk-Based Approach. Hydrogeol J 31, 31-34. https://doi.org/10.1007/s10040-022-02543-z

9.2 Web accesses

- IAH. Commission on Managing Aquifer Recharge. International Association of Hydrogeologists. https://recharge.iah.org. Accessed 20 Jan 2023
- MARSOLUT project web site. www.marsolut-itn.eu. Accessed 20 Jan 2023
- IGRAC (International Groundwater Resources Assessment Centre) (2022) MAR portal. https://ggis.un-igrac.org/view/marportal. Accessed 20 Jan 2023
- Spanish Groundwater Action Plan. https://www.miteco.gob.es/es/agua/participacion-publica/Plan_Accion_Aguas_Subterraneas_2023_2030.aspx
- Real Decreto 1620/2007, de 7 de diciembre, por el que se establece el régimen jurídico de la reutilización de las aguas depuradas. https://boe.es/buscar/doc.php?id=BOE-A-2007-21092
- Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on minimum requirements for water reuse. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32020R0741
- National Plan for Purification, Sanitation Efficiency, Saving and Reusing (DSEAR). https://www.miteco.gob.es/es/agua/temas/planificacion-hidrologica/planificacion-hidrologica/planes-programas-relacionados/
- Dinamar.tragsa.es. Accessed 20 Jan 2023
- https://dessin-project.eu/ Accessed 20 Jan 2023
- https://www.fieldfactors.com/ Accessed 28 Feb 2023
- https://dinamar.tragsa.es/file.axd?file=/PDFS/P-ISMAR-11.pdf Accessed 28/02/2023.
- https://dinamar.tragsa.es/pdf/libro-earsac.pdf. Accessed on 28/02/2023
- https://demeau-fp7.eu/sites/files/SVH.png Accessed on 28/02/2023

Annex 1

Assessing the Potential of Biochar for MAR

1. Previous studies

Some studies have approached the intended application relatively closely, but none of them assesses the application of biochar in MAR sites. The following articles have been reviewed from the most recent to the oldest publications.

Valhondo et al. (2020) - Reactive Barriers for Renaturalization of Reclaimed Water During Soil Aquifer Treatment

This study assessed the use of a reactive layer in MAR infiltration systems. The aim was to explore low-cost options to remove emergent pollutants, which pose a significant concern for recycling water through SAT systems. To accomplish this objective, the authors revisited the experience of two SAT sites using reactive barriers.

Both sites were located in Spain. The first one, Sant Vicenç dels Horts (4 years of operation), consisted of a basin with a 65 cm thick reactive barrier made up of compost, clay and metals (e.g., iron oxide). In this basin, water from the Llobregat River was infiltrated. The second site consisted of a series of 6 small SAT basins called Palamos, in which two 1-m-thick reactive barriers were evaluated, one consisting of compost and another of woodchip. The water infiltrated consisted of effluent from a WWTP.

Using organic materials as a reactive layer to treat the infiltrating water had multiple purposes. First, to provide additional sorption sites for pollutants and pathogens. Second, to change the redox conditions to anoxic, promoting the removal of more recalcitrant contaminants. Third, to support plant growth, which provides more organic matter (offering additional sorption sites) and reduces clogging.

The reactive layers effectively removed the organic pollutants considered in the study, including pharmaceuticals and personal care products. However, reactive barriers did not enhance a reduction in pathogens. Infiltration rates in the basin remained almost constant throughout the experiments.

In this study, they considered compost and woodchips instead of biochar. However, these materials have common properties; therefore, this study provides insight into the use of biochar. The shared properties that hint at a successful application of biochar in MAR are 1) an increase in DOC in water, which would cause reducing conditions in the porous medium; 2) increasing the available space for bacterial growth; and 3) providing additional sorption sites. This study also shows that a top layer of organic matter might be more suitable than mixing the amendments with the soil. A limitation of the study is that they did not assess the removal of other possible contaminants, such as nitrate, which was measured.

Valhondo et al. (2019) - Six artificial recharge pilot replicates to gain insight into water quality enhancement processes

This article focuses on the six SAT sites in Palamos, already described in the study above. It presents the preliminary results of the sites after one year of operation.

They found that reactive barriers helped considerably reduce the concentration of emerging contaminants, with removals ranging between 40% and 100%. Unlike the most recent work, they concluded that the systems could reduce pathogens (as indicated by E. Coli and Enterococci) by 3 to 5 log units. The infiltration rates in the basin remained constant, despite the presence of the reactive layer. Vegetation that grew within contributed via root macropore to maintain favourable hydraulic conditions.

This article further proves that carbon-rich reactive layers might help enhance water quality in infiltration basins. It also proves that plants can help to reduce maintenance by sustaining infiltration rates thanks to root macropores.

Valhondo et al. (2018) - Evaluation of EOC removal processes during artificial recharge through a reactive barrier

This study focused on the Sant Vicenç dels Horts site described in the first article of this review. Valhondo et al. (2018) evaluated the degradation rates and retention coefficients of ten organic emerging contaminants using a multi-layer reactive transport model in this research paper. The model was calibrated using Sant Vicenç dels Horts SAT site data.

The results showed that the degradation coefficients and retardation coefficient of the reactive barrier were the highest, proving the suitability of reactive layers based on organic materials to enhance the performance of SAT systems.

Yan et al. (2017) - Effect of biochar on anaerobic degradation of pentabromodiphenyl ether (BDE-99) by archaea during natural groundwater recharge with treated municipal wastewater

This study's objective was to evaluate biochar's effect on archaeal communities under anaerobic conditions and their impact on the removal of Pentabromodiphenyl ether (BDE-99), a compound employed as a flame retardant in a variety of products (e.g., textiles, electronics, and electrical equipment). BDE-99 is a persistent pollutant, toxic, and bioaccumulate and has not been removed by conventional wastewater treatment.

The authors used laboratory-scale soil columns. These columns simulated WWTP effluent's groundwater recharge through the Chaobai River's river bed. The authors contrasted the effect of a column with biochar, which represented the southern portion of the Chaobai River, and a control column, with a stratigraphic distribution typical of the central part of the Chaobai River. Biochar was not added but was already contained in the soil used since the southern part of the Chaobai River burning of stalk takes place. Both columns were run under continuous infiltration. The effluent water was taken from the YinWen JiChao WWTP.

They found that biochar effectively reduced the concentration of BDE-99. The primary mechanism over the long term was the debromination mediated by colonies of microbes, namely archaea and bacteria. Archaea biodiversity increased with biochar, enhancing the overall removal. This research points to the fact that the microbial colonies, which grow partly because of biochar, might be an important additional mechanism in removing pollutants.

MARSOL (2016a) - D6.4 MAR to Improve Groundwater Quantity and Quality by Infiltration of River Water. The Llobregat Demonstration Site, Catalonia, Spain

In this report, the authors evaluated two critical aspects of the SAT site Sant Vicenç dels Horts: First, denitrification due to a reactive layer and microorganism. Second, the microbiological activity of the site.

They performed three sets of experiments at different scales for the first objective. In the first one, they used a model calibrated with a soil column resembling the Vicenç dels Horts site. Carbon input from the reactive layer was emulated through the injection of ethanol. In the second experiment, the authors conducted batch experiments using reactive layers. In the third experiment, the authors corroborated the information gathered in the other two experiments with field investigation at the Vicenç dels Horts MAR site. The microbiological activity was evaluated by sampling sediments and water in the infiltration basins.

The research showed that the reactive layer promoted denitrification. It also proved that infiltration decreased partly over time due to clogging and, notably, bioclogging. The authors also determined that biodiversity was maximum during infiltration periods and that organisms are mostly present in the sediments.

MARSOL (2016b) - D6.2 Llobregat Recharge Site. Water Quality

This document reviews a series of advances in the Sant Vicenç dels Horts site regarding water quality, with a focus on bioclogging and the impact of hydrochemical parameters on biological processes. This research also studied the carbon cycle concerning the organic-rich reactive barrier and the oxygen dynamics in the vadose zone related to wetting and drying cycles.

During the wetting cycle, the infiltration rate was diminished exponentially and partly recovered during the drying period, especially if surface scrapping was performed. The authors also found a clear oxygen profile during infiltration and some oxygen-depleted zones due to bacterial activity. Such activity remained practically constant regardless of the phase (i.e., wetting or drying).

This study provides insight into infiltration rates in SAT systems with a reactive layer. Furthermore, it shows how bioclogging can affect SAT projects and how this adverse phenomenon is linked to oxygen dynamics in the vadose zone.

Valhondo et al. (2015) - Characterising redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer

This study took place in the Sant Vicenç dels Horts SAT site (described in the revision of Valhondo et al. 2020) and showed results on how reactive barriers affect the dynamics of four pharmaceuticals. The authors found that three pharmaceuticals were removed beyond the amount usually provided by SAT alone. The barrier helped to reduce concentrations of atenolol below detection limits and gemfibrozil and cetirizine by 20% and 40%, respectively. Before installing the reactive barrier, pharmaceuticals were found in the aquifer at concentrations exceeding 60% of the initial values. On the other hand, carbamazepine concentration did not change.

Schaffer et al. (2015) - Influence of a compost layer on the attenuation of 28 selected organic micropollutants under realistic soil aquifer treatment conditions: Insights from a large scale column experiment

In this study, the authors employed two parallel columns emulating SAT systems to study the effect of compost on the removal of emerging pollutants. The authors focused on 28 emerging pollutants. The water used in the experiments was derived from a WWTP after secondary treatment. The water was spiked with ten compounds which were not detectable in the original wastewater. Compost was mixed with the sand and also poured on the surface of one of the columns as a layer. One column was fixed with clean sand as a reference for comparison.

The authors found that the column with the compost layer on top had reducing conditions due to DOC originating from the compost. These conditions increased the removal of organic acids and beta-blocker compounds, while they did not have a measurable effect on conservative compounds. The organic cations were removed entirely in both columns.

This article provides a detailed discussion on the role of compost layers in the removal of various pollutants, including an examination of the plausible hydrochemical processes entailed, providing a point of reference for biochar mechanisms mediating the removal of contaminants.

Wei et al. (2015) - Dissolved organic matter removal during coal slag additive soil aquifer treatment for secondary effluent recharging: Contribution of aerobic biodegradation

Wei et al. (2015) investigated the effect of carbon slag in the removal of dissolved organic matter (DOM) in SAT systems.

The research was carried out with soil column experiments. The soil columns were packed with soil from the dry river bed of the Songhua River (China), consisting mostly of sand and silt. The soil was packed into columns and combined with different proportions of carbon slag. Multiple layer configurations involving these materials were also explored. The infiltrating water was secondary effluent from a WWTP. DOC, UV-254 and EEM were measured throughout the experiments. The columns were operated with a wet cycle of 16 hours and a dry cycle of 8 hours.

The authors found that the carbon slag enhanced the anaerobic degradation and sorption of DOM to the same level of the aerobic degradation (31.7% vs 32.2%). In this way, the total removal of DOM in SAT using carbon slag could be more than 60%. They also found that the addition of carbon slag could improve the removal of aromatic carbons and the hydrophobic components of DOM.

This article point in the same direction as the studies by Valhondo et al. (2015, 2018, 2019, 2020), which found an enhancement of the anaerobic conditions and biodegradation when a carbon-rich amendment is introduced in SAT systems.

ENSAT (2012) - Enhancement of Soil Aquifer Treatment to Improve the Quality of Recharge Water in the Llobregat River Delta Aquifer

This report contains the final results of the ENSAT project, in which the reactive barrier of the Sant Vicenç dels Horts SAT site was installed and assessed. The project aimed to demonstrate the suitability of SAT in water recycling and the usefulness of reactive barriers to enhance decontamination.

This document deals with three different stages of setting up reactive barriers: i) selecting the most suitable materials for the reactive barrier, ii) choosing and installing monitoring devices, and iii) a preliminary evaluation of the effects of carbon-rich layers.

As the prior studies, this project showed that reactive barriers increase the removal of some contaminants, notably gemfibrozil and carbamazepine, two of the eleven micropollutants evaluated in the project. The project also delivered a software tool, hydROL, which can be employed in analysing hydrochemical changes during water infiltration.

2. Biochar production process

Xiang et al. (2020) distinguish three stages to produce biochar: pre-treatment, thermal carbonisation, and post-treatment. The pre-treatment is applied to the feedstock, and the existing techniques can be categorised as physical, biological and chemical.

2.1 Pre-treatment

Pre-treatment includes physical processes such as drying, crushing, sieving and washing the biomass. These activities are often specific to the feedstock. For instance, biomass from sewage sludge is subjected to drying, crushing, sieving and sealed storage before biochar production (Agrafioti et al. 2013; Xiang et al. 2020). In chemical treatment, compounds are used to promote the precursors of functional groups (Xiang et al. 2020). The biological pre-treatment of feedstock is a relatively new concept and aims to produce engineered biochar (Xiang et al. 2020). An example of such processes is anaerobic digestion, which has been employed in different feedstocks (e.g. sugar beet tailings) to improve the specific surface area and adsorption properties of the biochar (Yao et al. 2011; Xiang et al. 2020).

2.2 Thermal carbonisation

Subsequently, the feedstock is subject to thermal carbonisation through one of several methods. The thermal carbonisation results in three different phases: liquid, which is referred to as bio-fuel; gaseous, known as syngas; and solid, i.e., biochar (Cueto García 2016; Cha et al. 2016).

The most common carbonisation method is pyrolysis. In this process, biomass decomposes at high temperatures (300-900°C) without oxygen. The proportion and characteristics of the resulting phases are controlled by the pyrolysis heating rate (how fast the temperature is increased), the reaction temperature and the residence time (the time that biomass is subject to the reaction temperature) (**Figure 1**) (Cha et al. 2016). Depending on such factors, pyrolysis can be classified as slow-, fast-, and flash-pyrolysis.

Pyrolysis is commonly carried out through electrical heating. Xiang et al. (2020) consider an additional production technique in which feedstock is pyrolysed through microwaves. Such a method is referred to as microwave-assisted pyrolysis. The quantities and characteristics of the obtained phases are controlled by other factors, such as microwave power and irradiation time (Zhang et al. 2017). Pyrolysis is a dry process to produce biochar because the biomass has low initial moisture content. Hydrothermal carbonisation (HTC) is another biochar production method that allows obtaining biochar without the need for considerable energy for drying by placing feedstock and water inside a reactor in which pressure and temperature are increased in such a way that water remains liquid (Cha et al. 2016).

Another way to produce biochar is gasification. This process consists of three steps: drying, combustion, and gasification (or reduction) (Yao et al. 2011; Cha et al. 2016). Gasification generally aims to produce gas phases; therefore, the amount of biochar obtained is usually around 5-10% (Cha et al. 2016).

Other technologies used to produce biochar are flash carbonisation (Nunoura et al. 2006; Cha et al. 2016) and torrefaction (Chen et al. 2016; Cha et al. 2016). **Table 1** provides typical values of production variables and characteristics of the obtained biochar.

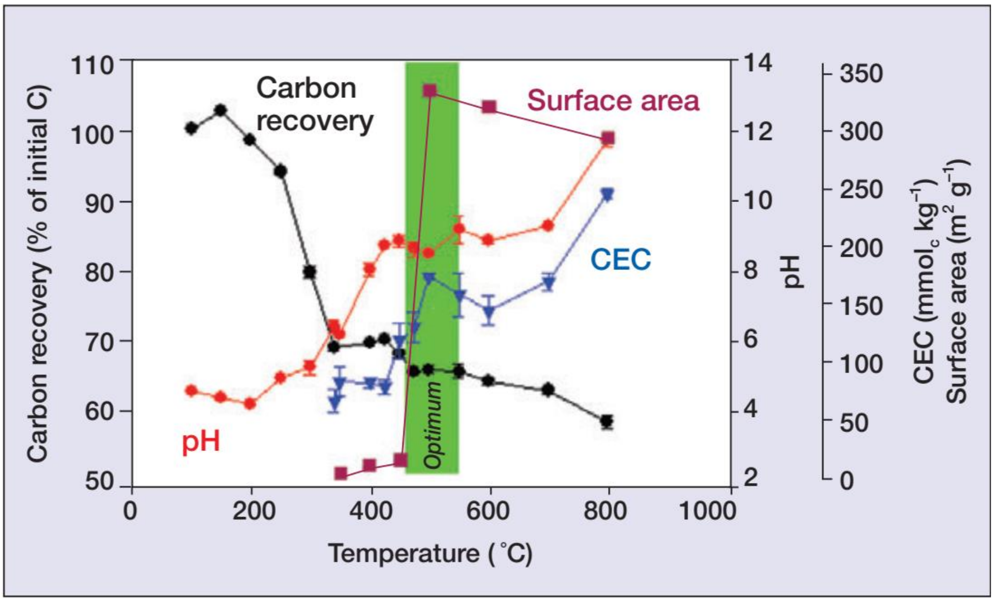


Figure 1. *Properties of biochar as a function of pyrolysis temperature. The feedstock for the experiments reflected in the chart is dried wood from Robinia Pseudoacacia L. The optimum temperature range in the graph is for obtaining properties for soil amendment. From Lehmann (2007).*

Table 1. *Typical ranges of temperature, residence times and products of various biochar production methods. From Meyer et al. (2011).*

Process	**Temperatures (°c)**	**Residence time**	**Solid product yield on a dry wood feedstock basis (in mass %)**	**Carbon content of the solid product (in mass %)**	**Carbon yield (mass carbon, product/mass carbon, feedstock)**
Torrefaction	~ 290	10 -60 min	61 - 84%	51 - 55%	0.67 - 0.85
Slow pyrolysis	~ 400	Minutes to days	≈ 30%	95%	≈ 0.58
Fast pyrolysis	~ 500	1 s	12 -26 %	74%	0.2 - 0.26
Gasification	~ 800	10 to 20 s	≈ 10%		
HTC	~ 180-250	1 - 12 h	<66%	<70%	≈ 0.88
Flash carbonisation	~ 300-600	< 30 min	37%	85%	≈ 0.65

2.3 Post-treatment

The thermal carbonisation might be followed by post-treatments (Xiang et al. 2020) that aim to improve the resulting material's properties for a specific application or to mend some disadvantages. Studies compiled by Tan et al. (2016) have shown that raw biochar has a limited capacity to reduce contamination in wastewater, mainly when the concentrations of pollutants are high. Furthermore, very fine biochar can be challenging to separate from the water solution (Tan et al. 2016). Post-treatment techniques can contribute to solving these shortcomings.

There is a considerable number of post-treatment techniques. Comprehensive compilations can be found in Tan et al. (2016), Wang et al. (2017) and Xiang et al. (2020). A few of them are discussed here: magnetisation, corrosive chemical treatment, and activation. Also, a short exploration of biochar-based nanocomposites is provided. A visual summary of various engineering biochar modification procedures and their effects on the properties of the resulting material are presented in **Figure 2**. Some of these procedures constitute post-treatment techniques, such as acid and alkali treatments that enhance the material's surface to remove a wide range of pollutants (e.g., heavy metals).

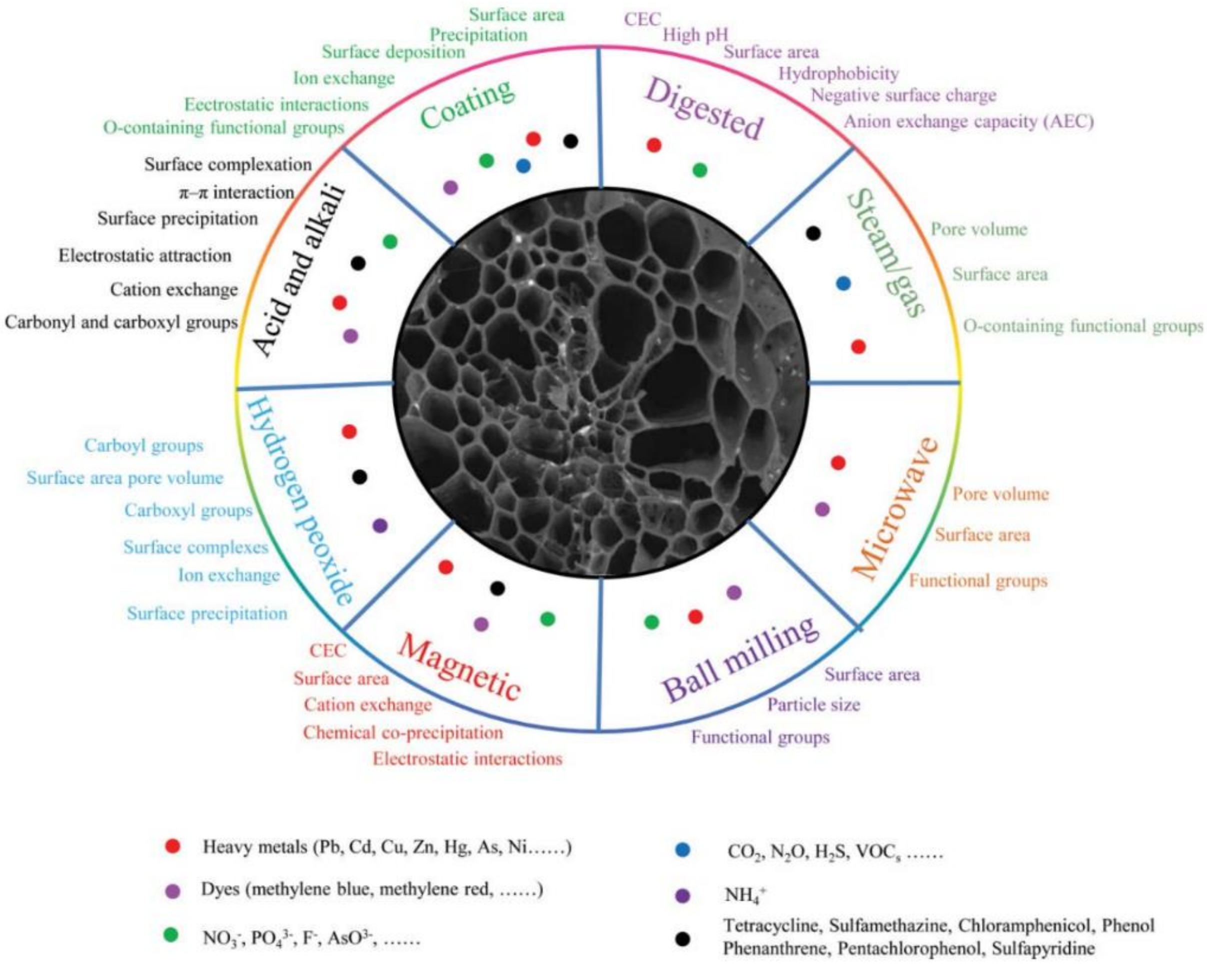


Figure 2. *Effect of various modifications on the properties of the biochar. From Wang et al. (2017).*

Corrosive chemical post-treatment entails using acids, alkalis and oxidation agents to modify the surface properties of the biochar (Xiang et al. 2020). This type of post-treatment enhances features such as the specific surface area, the porous volume, the functional groups, and the sorption capacity (Xiang et al. 2020).

Magnetisation converts biochar into a magnetic material by adding magnetic iron oxides. This form of biochar has enhanced capabilities (e.g. higher Cr^{+6} removal rate) and can be quickly recovered from the water once contaminant sorption has occurred (Xiang et al. 2020).

Biochar activation increases specific surface area, and pore fraction and generates functional groups (Cha et al. 2016). These modifications improve contaminants' sorption, including heavy metals (Mohan et al. 2007; Lima et al. 2010). Activation can be accomplished by physical or chemical means. In the former process, biochar is subject to gases and high temperatures to modify the structure (Cha et al. 2016). The chemical activation involves several steps, including mixing the biochar with an activating agent, heating in an inert atmosphere, and subsequent actions to remove the chemical agents (Azargohar & Dalai 2006). Chemical activation tends to have more shortcomings than physical activation, such as higher cost and the complexity of recovering the involved chemical agents. However, it is more efficient to enhance certain aspects (Cha et al. 2016).

Biochar can be employed to create nanocomposites, which involves employing biochar as a matrix to attach nanoparticles of another compound. The added nanoparticles can be, for instance, metal oxides, and the resulting material has advantages for specific applications (Tan et al. 2016). For example, adding carbon nanotubes to biochar helps to increase the sorption of methylene blue dye through stronger electrostatic attraction (Tan et al. 2016).

2.4 Atmospheric modifications and ageing

The properties of biochar can also be modified by the environment (Lehmann 2007). Moreover, some of the valuable properties of this material require time to develop. The CEC of freshly produced biochar is low and increases over time, mainly as oxygenated functional groups, such as hydroxyl and carboxylic acids, are added to the material through oxidation (Cheng et al. 2006; Lehmann 2007; Nartey & Zhao 2014). In this regard, Cheng et al. (2006) found that abiotic processes are responsible for creating a negative surface charge that increases the CEC of Robinia Pseudoacacia L biochar. In this study, CEC developed after four months of incubation at temperatures above 30°C without bacterial activity. However, some processes contributing to CEC formation might downgrade the material (Cheng et al. 2006). The increase of carboxyl and hydroxyl functional groups as a consequence of oxidation can result in lower metal adsorption (Frišták et al. 2015).

The sorption of biochar decreases with time as the reactive spots of the material are occupied (Kizito et al. 2017). This effect is, in some cases, counteracted by the microbe-mediated sorption, which increases as microbial colonies grow. Kizito et al. (2017) conducted experiments to assess the removal of organic matter, nitrogen and phosphorus in columns simulating constructed wetlands. They attributed the good performance of the columns with biochar to adsorption and microbial colonisation. Furthermore, they suggest that the increase in microbial biodegradation compensated for the decrease over time of biochar adsorption. This pattern has also been corroborated by Yan et al. (2017), who hypothesised for their column experiment results that the initial removal capacity of biochar was due initially to adsorption and subsequently to the metabolic effect of archaea and bacteria.

2.5 Feedstock

The other factor that profoundly influences the properties of biochar is the precursory biomass or feedstock. Feedstocks affect not only composition but also the amount of biochar obtained, structure, and properties. For instance, after the pyrolysis, biochar tends to preserve the pore structure of the feedstock (Mohanty et al. 2018). Therefore, surface area and porosity distribution are directly linked to the precursor material (Mohanty et al. 2018).

The feedstocks employed are highly varied and are often waste and residue from different industries (Cueto García 2016; Xiang et al. 2020). Examples of these precursory materials are sewage sludge, paper waste, agricultural residue (e.g. straw, rice husk, bagasse), forestall residue (e.g. wood chip, bark, sawdust), agri-food waste, livestock waste (e.g. manure, slurry), animal litter, and municipal solid waste (Ahmad et al. 2014; Cueto García 2016). **Table 2** and **Table 3** provide some examples of the chemical and property variability of biochar as a function of the feedstock material.

Table 2. *Biochar yield and properties as a function of feedstock material. Yield is based on the precursor weight. Modified from Lima et al. (2010).*

Feedstock	Biochar Yield (%)	Bulk Density (G Ml^{-1})	Moisture Content (%)	Ash Content (%)	pH	Burn-Off Loss (%)
Broiler litter	42.3	0.2	4	32	7.7	21.7
Alfalfa stems	36.3	0.65	4.6	57.6	8.5	26.7
Switchgrass	13.5	0.46	12.1	58	8.7	39.7
Corn cob	18.9	0.37	11.1	16.3	7.8	25.3
Corn stover	17	0.18	8.8	26	7.2	35.8
Guayule bagasse	20.6	0.21	9.9	23.5	8.3	40.4
Guayule shrub	33.2	0.22	8.1	46.8	8.1	47.6
Soybean straw	22.1	0.19	9.4	22.2	7.7	42.6

Table 3. *Yield composition of biochar as a function of the feedstock and pyrolysis production temperature. From Granatstein et al. (2009).*

Source	Production Temperature (°C)	C (g/kg)	N (g/kg)	S (g/kg)
Switchgrass	350	589	19	0.9
	500	641	17.9	1.4
Digested fibre	350	650	22.6	2.9
	500	709	23.4	3.2
Softwood bark	350	656	3	0.4
	500	737	3.5	0.3
Wood pellets	350	723	1.1	0.7
	500	785	1.5	0.9
Peanut hull	500	711	17.9	0.2
Bark-UGA	500	758	4.1	0.1
Activated charcoal	-	867	5.8	7.6

3. Characteristics of biochar

Biochar can be characterised according to its properties and chemical composition. The properties can be further subdivided into physical and chemical (Yu et al. 2019).

3.1 Physical properties

According to Yu et al. (2019), the main physical properties of biochar are density, porosity, surface area, pore size, and hydrophobicity. Biochar is a light material with a bulk density below 0.6 g/cm^3 (Yu et al. 2019). Feedstock material strongly influences surface area, which ranges between 100 m^2/g and 800 m^2/g (Weber & Quicker 2018; Yu et al. 2019). However, some varieties exhibit surface areas below this range, such as the biochar derived from sewage feedstock (Weber & Quicker 2018).

Porosity is frequently categorised into three groups, namely macropores (1 mm - 0.05 µm), mesopores (0.05-0.002 µm) and micropores (0.002-0.0001 µm) (Weber & Quicker 2018; Yu et al. 2019). Around 80% of pores in biochar are macropores, while micropores are often below 10% (Weber & Quicker 2018). Porosity is an important property since it controls some of the functions of biochar. It is responsible for water holding, the amount of water that can be retained in the material one or two days after being saturated (Rai et al. 2017). Porosity also affects hydrophobicity, which is the ability of a molecule to repel water and is often measured as a function of surface contact angle (Law 2014). Both properties, namely, hydrophobicity and water-holding capacity, increase along with porosity (Yu et al. 2019).

The physical properties are controlled by feedstock material and, to a very good extent, by the pyrolysis temperature. As the production temperature increases, porosity, surface area, micropore proportion, and water-holding capacity increase while bulk density slightly decreases (Weber & Quicker 2018). Hydrophobicity shows a more complex pattern, having its highest value between 300 and 500 °C (Weber & Quicker 2018; Xiao et al. 2018).

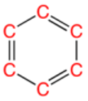
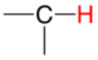
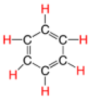
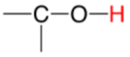
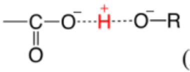
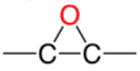
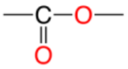
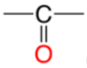
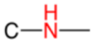
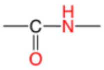
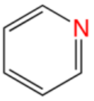
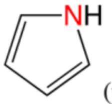
3.2 Chemical properties and composition

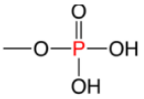
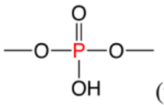
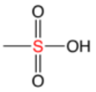
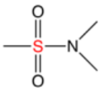
Important chemical properties of biochar are pH, atomic ratios (O/C and H/C), and surface functionality (Yu et al. 2019). The pH of biochar ranges between 5.9 to 12.3 and is, on average, 8.9 (Ahmad et al. 2014). It increases with increasing pyrolysis temperature (Weber & Quicker 2018).

Chemically, the most abundant elements in biochar are C, H, O and N. Other elements can be found in this material in minor quantities, such as P, S, Si, Cu, Fe, Mn, Ni, Mg, Ca, K, Na and Zn (Xiao et al. 2018; Yu et al. 2019). These elements are distributed in organic and inorganic solids, and their concentration tends to increase with increasing pyrolysis temperature (Yu et al. 2019).

Carbon is present in biochar as organic compounds, such as aromatic, aliphatic, and functionalised carbon, and inorganic compounds, primarily as carbonates and bicarbonates (Xiao et al. 2018; Yu et al. 2019). As the temperature of pyrolysis increases, the aromatic components augment at the expense of the aliphatic carbon. Overall, the aliphatic phase is liable, soluble and experiences chemical partition. On the other hand, the aromatic phase tends to be stable, remain undissolved and increase adsorption (Xiao et al. 2018). Oxygen occurs both in organic and inorganic compounds. Nitrogen often derives from plant precursors, especially leaves and herbaceous species, and can be found in organic and inorganic phases (e.g. ammonium) (Yu et al. 2019). Elements such as Ca and Mg play an essential role in removing heavy metals since they enable cationic exchange (Ippolito et al. 2012). The most common elements in biochar and some of their functions are summarised in **Table 4**.

Table 4. *Principal elements in biochar and their function. From Xiao et al. (2018).*

ELEMENT	**SPECIES**	**FUNCTIONS**
C	Organic: $C-C$ (single bond), $C=C$ (double bond),  (aromatic carbon), $C-X$ (functionalized carbon) Inorganic: HCO_3^-, CO_3^{2-}	a) Key element within biochar. b) Develops functional groups by linking to other elements. c) Inorganic carbon contributes to the alkalinity and buffering properties of biochar. d) Carbon sequestration
Si	Inorganic: Silicon acid, polymeric Si, crystal Si.	a) Nutrient element. b) Precipitates with heavy metals. c) Major component of the biochar inorganic phases. d) Protect the organic phase
H	 $-\underset{\vert}{C}-H$ (aliphatic H),  (aromatic H),  $-\underset{\vert}{C}-O-H$ (hydrogen in functional groups),  $-\underset{\overset{\Vert}{O}}{C}-\overset{-}{O}\cdots\overset{+}{H}\cdots\overset{-}{O}-R$ (hydrogen in hydrogen bond)	a) For association/dissociation. b) Forms the hydrogen bond. c) H/C atomic ratio is the aromaticity index of biochar
O	Organic: $C-O-C$ (ether), $-C-O-H$ (hydroxyl),  (epoxy),  $-\underset{\overset{\Vert}{O}}{C}-O-$ (carboxyl, ester),  $-\underset{\overset{\Vert}{O}}{C}-$ (acyl, carbonyl) Inorganic: M_xO_y, HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^- etc.	a) Forms functional groups. b) Complexation with metal ions. c) O/C atomic ratio is an index of the degree of ageing of biochar.
N	Organic: $C=N-R$ (imine-N),  $C-\overset{H}{N}-$ (amine-N),  $-\underset{\overset{\Vert}{O}}{C}-\overset{H}{N}-$ (acylamide-N),  (pyridine-N),  (pyrrole-N), protein-N Inorganic: NH_4^+, NO_3^-, NO_2^-	a) Nutrient element. b) Improve the thermal stability. c) Active sites for reaction and modification. d) Nitrogen fixation

P	Organic:  (mono- phosphate ester),  (phosphate di-ester) Inorganic: PO_4^{3-}, $P_2O_7^{4-}$	a) Nutrient element. b) Precipitates with heavy metals
S	Organic:  (sulfonate),  (sulfonamide) Inorganic: sulfate	a) Increase the solubility of carbon materials. b) Solid acid catalyst. c) Nutrient element
Fe	Fe_2O_3, Fe_3O_4, FeO, α-Fe, Fe_3C, FeO(OH), Zero valent iron, other metal complex	a) Provides magnetism. b) Increases the sorption ability of anions. c) Promote graphitising during pyrolysis. d) Catalysis/activator for organic pollutant degradation
Mg	MgO, $MgCO_3$, other metal complex	a) Increases anions sorption. b) CO_2 capture. c) Nutrient element
Mn	MnO_x, $Mn(OH)_x$, other metal complex	a) Increases heavy metal sorption;
Ni	$Ni(OH)_2$, NiO, Ni_2O_3, other metal complex	a) H_2 evolution. b) Catalyses the formation of syngas during pyrolysis

The nature of the inorganic phases in biochar has been reviewed by Xiao et al. (2018), who point to the fact that inorganic fractions are highly dependent on the pyrolysis temperature (**Figure 3**). These inorganic fractions are responsible for some of the sorption properties of biochar. For instance, they can co-precipitate with some heavy metals in water. An example is the reaction of carbonate (CO_3^{-2}) with Pb^{+2} and Cd^{+2} to produce precipitates like $Pb(CO_3)_2(OH)_2$ and $CdCO_3$ (Xiao et al. 2018).

The atomic ratios O/C and H/C are often applied to detect the degree of maturity of biochar. As the temperature of carbonisation gets higher, dihydroxylation, dehydrogenation and an increase in the aromaticity decrease the ratios (Li et al. 2013; Xiao et al. 2018). Aromaticity is the stability associated with aromatic compounds (Carey 2000). As this property increases, there are more aromatic compounds, which are organic rings in which electrons are delocalised. Aromatic compounds have higher stability than compounds featuring the same composition and having unpaired or compromised (e.g., to covalent bonds) electrons (Carey 2000). As pyrolysis temperature increases, the aromaticity of the biomass increases (Li et al. 2013, and **Figure 4**), and the resulting biochar has a more recalcitrant nature and is less vulnerable to decomposition (Zhu et al. 2017).

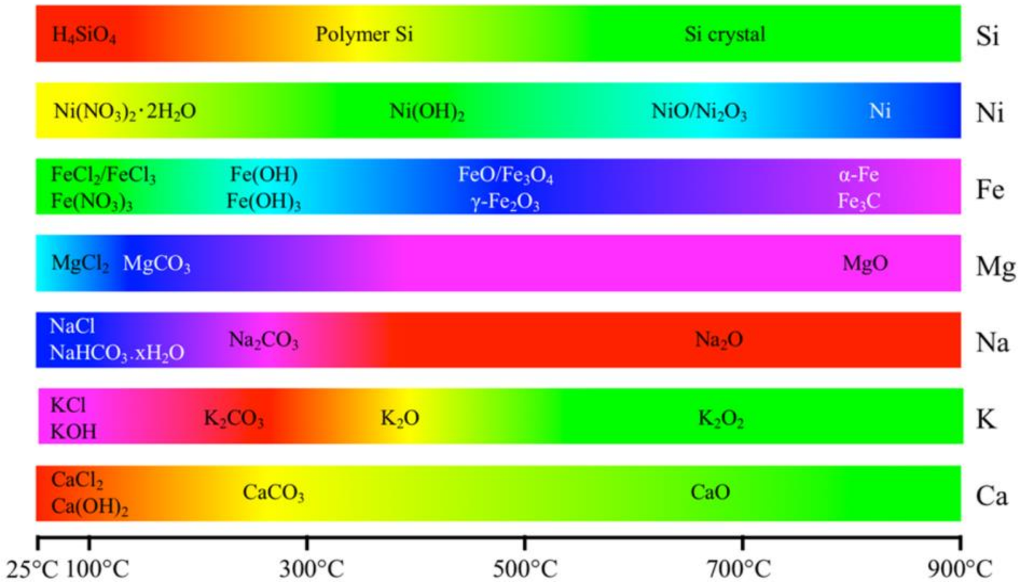


Figure 3. *Inorganic phases as a function of pyrolysis temperature. From Xiao et al. (2018).*

Surface functionality is responsible for the chemical and electrostatic interaction of the organic biochar compounds with other molecules. This property is due to the surface functional groups, the free radicals, structure-related functionality, and the surface charge (Xiao et al. 2018).

The presence of several functional groups characterises biochar. A functional group is a set of atoms within a molecule responsible for its characteristic behaviour during reactions (Carey 2000). Some functional groups are depicted in **Table 4** (above). According to Yu et al. (2019), the main functional groups in biochar are phenolic-OH, carboxyl, carbonyl, and ester, and to a minor extent, epoxy, acyl, ether, amido, sulfonic, and acyl groups. Generally, the biochar functional groups interact with dissolved species through adsorption, electrostatic attraction, ion exchange and hydrogen bonding (Payne et al. 2013).

Functional groups provide sorption sites for metal cations and ionisable organic compounds and can be modified to enhance sorption properties through oxidation, amination, and sulfonation, among others (Xiao et al. 2018). The most common functional groups can dissociate or associate with hydrogen atoms. This interaction with hydrogen leads to a series of biochar properties, such as sorption induced by hydrogen bonds, pH buffering capacity, cation exchange capacity, hydrophobicity or hydrophilicity, and surface charge alterations, among others (Xiao et al. 2018).

Functional group composition and density are highly dependent on the production procedure since and can transform during feedstock carbonisation. For instance, free hydroxyls transform into carboxyl. Furthermore, the higher the pyrolysis temperature, the higher the aromaticity, the lower the hydrogen concentration, and the lower the oxygen-bearing groups (Li et al. 2013; Xiao et al. 2018).

Free radicals are molecules characterised by an unpair electron, which makes them highly reactive (Cheeseman & Slater 1993). Depending on the application considered, they can have both beneficial and adverse effects. Experiments have shown that free radicals are important reactive sites impacting plants' growth negatively (Liao et al. 2014). On the other hand, free-radicals can also react to generate hydrogen peroxide and persulfate, which has been found to contribute to the degradation of organic pollutants such as 2-chlorobiphenyl, diethyl phthalate, and polychlorinated biphenyls (Xiao et al. 2018). Free radicals in biochar are generated during the carbonisation of the precursor materials and tend to increase with carbonisation temperature (Liao et al. 2014; Xiao et al. 2018).

Surface charge makes the biochar surface electrically attractive or repulsive to molecules with charge. This property is developed on the surface of organic carbon compounds and is highly affectable by pH. Surface charge is negative under common pH conditions (4-12) and positive when the pH of the solution is lower than 4 (Xiao et al. 2018). In general, the surface of biochar becomes less polar with increasing pyrolysis temperature. **Figure 4** summarises how the properties of biochar change as a function of the pyrolysis temperature.

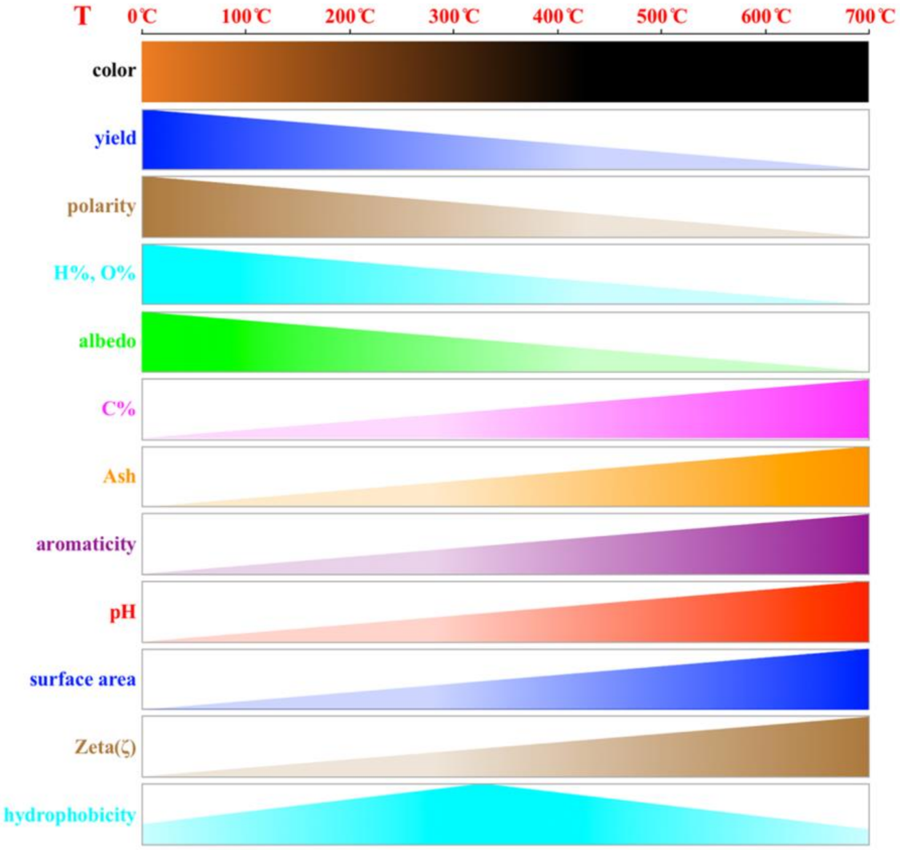


Figure 4. *Modification of relevant biochar properties as a function of the pyrolysis temperature. From Xiao et al. (2018).*

4. Application of biochar to water purification and soil remediation

Biochar is commonly employed to remove pollutants from water (e.g., urban wastewater, stormwater, agricultural runoff, and effluent from industrial facilities) and soils (i.e., soil remediation) (Ahmad et al. 2014; Xiang et al. 2020). The contaminants usually can be grouped into heavy metals, inorganic pollutants (e.g., ammonium and phosphorus), and organic pollutants.

Overall, biochar most easily removes organic contaminants due to its high surface area and microporosity (Ahmad et al. 2014). However, the affinity to remove either organic or inorganic pollutants is related to the production process, among other factors. Biochars carbonised at high temperatures have a higher surface area and microporosity and therefore are more likely to retain organic contaminants. On the other hand, low-temperature biochar has a higher amount of oxygen functional groups and cation release and can absorb inorganic contaminants better (Ahmad et al. 2014).

Biochar and activated carbon are both carbonaceous materials but differ in cost and post-production processes/activation (Mohanty et al. 2018). Activated carbon is more expensive due to higher energy requirements and lower yields. However, its properties are more consistent, and it has a higher removal performance (Mohanty et al. 2018). Nonetheless, in some cases, biochar adsorption can be better than activated carbon (Huggins et al. 2016). A clear advantage of biochar is its reduced environmental impact reflected in less production energy consumption and its CC mitigation potential (Mohanty et al. 2018).

4.1 Heavy metal removal from contaminated water

Biochar has been successfully applied to remove heavy metals such as As^{+3}, As^{+5}, Cd^{+2}, Ni, Cr^{+3}, Ni^{+2}, Cu^{+2}, and Pb^{+2} from water (Ahmad et al. 2014; Inyang & Dickenson 2015; Xiang et al. 2020). The feedstocks used for this application are varied and include sugarcane straw, dehydrated banana peels, alfalfa stems, corn cobs, and chicken manure (Ahmad et al. 2014; Xiang et al. 2020). Removal percentages vary across the implied heavy metal and depend on several conditions, including the ionic radius, the pH, post-treatment, and the competition among species in solution (Lima et al. 2010; Ahmad et al. 2014). For instance, a study of sorption equilibrium involving Cu, Zn and Cd leads Ko et al. (2004) to conclude that biochar adsorbs better the metals with a small ionic radius.

The variation of heavy metal sorption as a function of pH is well illustrated by the study of Mohan et al. (2007). The authors evaluated three different biochars (i.e., from oak bark, oak wood, and pine bark) and their corresponding heavy metal (i.e., Cd^{+2}, As^{+3}, Pb^{+2}) removal from water. They found that the maximum reduction of As^{+3} occurred over a pH range of 3-4 and 4-5 for Pb^{+2}. Moreover, in the study of Ippolito et al. (2012), steam-activated pecan shell biochar showed that copper sorption was maximum at a pH of 6.

The post-treatment of the biochar also influences metal removal. For instance, Lima et al. (2010) tested the removal of four heavy metals (namely Cu^{+2}, Ni^{+2}, Zn^{+2}, and Cd^{+2}) through fast-pyrolysis biochar from six feedstock (i.e. broiler litter, alfalfa stems, switchgrass, corn cob, corn stover, guayule bagasse, guayule shrub, and soybean straw) in activated and not-activated form. Removals ranged between 10% and 96%, with higher values for activated biochar. Furthermore, this study also shows that several species in solution can compete for the sorption sites, as also pointed out by Suffet (1980) for activated carbon. In the study of Lima et al. (2010), copper had a higher affinity for biochar, as revealed by the high removals percentages and higher sorption compared to other metals simultaneously present in the solution.

A summary of findings from different studies is provided in **Table 5**.

Table 5. *Summary of heavy metal sorption from different studies. From Xiang et al. (2020).*

Biochar feedstock	**Pre-treatment**	**Thermal process**	**Post-treatment**	**Pyrolysis temperature (°C)**	**Biochar dose (g/L)**	**Adsorption pH**	**Heavy metals**	**Initial concentration (mg/L)**	**Adsorption capacity (mg/g)**	**Removal mechanism**	**Ref. ***
Bamboo wood	Oven-dried	Pyrolysis	HNO_3+nZVI treated	600	2	-	Ag+	200	584	Innesphere complexation and electrostatic attraction by outer-layer Fe oxides under oxic conditions	Wang et al. 2017 b
Bamboo wood	Oven-dried	Pyrolysis	H_2O_2+nZVI treated	600	2	-	Ag+	200	1217	Innesphere complexation and electrostatic attraction by outer-layer Fe oxides under oxic conditions	Wang et al. 2017 b
Pomelo peal	Dried + H_3PO_4 impregnated	Pyrolysis	Pristine	250	2	6	Ag+	50	137.4	Chemical adsorption with oxygenic functional groups	Zhao et al. 2018
Pine wood	Oven-dried and milled	Pyrolysis	Ni/Fe-LDH modified	600	2.5	7.5	As^{3+}	20	4.38	Electrostatic attraction and surface complexation with hydroxyl groups	Wang et al. 2016 b
Pine wood	Ni/Fe-LDH modified	Pyrolysis	Pristine	600	2.5	7.5	As^{3+}	20	1.56	Electrostatic attraction and surface complexation with hydroxyl groups	Wang et al. 2016 b
Paper mill sludge	Oven and washed	Pyrolysis	Pristine	720	1	2.7-10.4	As^{5+}	26.7	34.1	Chemisorption or chemical reaction process between available adsorption sites and adsorbate	Cho et al. 2017
Sewage sludge	Stirred heated	Pyrolysis	Pristine	300	4	-	As^{5+}	0.05	-	Chemical sorption	Agrafioti et al. 2013
Sewage sludge	Stirred heated	Pyrolysis	Pristine	300	4	-	Cr^{3+}	0.2	-	Chemical sorption	Agrafioti et al. 2013
Rice husk	Washed	Pyrolysis	Polyethene nimine modified	450-500	1	-	Cr^{6+}	100	435.7	The introduction of the amino group facilitates the chemical reduction of Cr6* and increases the sorption capacity	Rajapaksha et al. 2016
Green waste	Dried	Pyrolysis	HCL modified	600	2	3-8	Cd^{2+}	5.6	6.72	Chemisorption	Zhang et al. 2018
Peanut shell	Washed, dried and milled	Pyrolysis	Hydrated manganese oxide treated	400	0.2	6.5	Cd^{2+}	10	10	Nonspecific outer-sphere surface complexation provided by	Wan et al. 2018

										oxygen-containing groups	
Marine macro-algal	$FeCl_3$ immersed	Pyrolysis	Pristine	500	16.7	-	Cu^{2+}	-	69.37	Specific outer-sphere surface complexation offered by the impregnated HMO	Son et al. 2018
Banana peels	Oven-dried	Pyrolysis	Pristine	600	2.5	-	Cu^{2+}	200	75.99	Oxygen-containing functional groups as potential adsorption sites	Ahmad et al. 2018
Cauliflower leaves	Oven-dried	Pyrolysis	Pristine	600	2.5	-	Cu^{2+}	150	53.96	Electrostatic attraction, partial physisorption, ion exchange and precipitation	Ahmad et al. 2018
Pomelo peel	Dried + H_3PO_4 impregnated	Pyrolysis	Pristine	250	2	6	Pb^{2+}	50	88.7	Precipitated by phosphorus functional groups	Zhao et al. 2018
Peanut shell	Washed, dried and milled	Pyrolysis	Hydrated manganese oxide treated	400	0.2	6.5	Pb^{2+}	20	36	Nonspecific outer-sphere surface complexation provided by oxygen-containing groups	Wan et al. 2018
Banana peels	Oven-dried	Pyrolysis	Pristine	600	2.5	-	Pb^{2+}	600	247.1	Electrostatic attraction, partial physisorption, ion exchange and precipitation	Ahmad et al. 2018
Cauliflower leaves	Oven-dried	Pyrolysis	Pristine	600	2.5	-	Pb^{2+}	200	177.8	Electrostatic attraction, partial physisorption, ion exchange and precipitation	Ahmad et al. 2018
Maple wood	Dried	Pyrolysis	H2O2 modified	500	5	7	Pb^{2+}	50	43.3	Complexation by oxygen functional groups	Wang et al. 2018
Pecan nutshell	Dried milled	MAP	Pristine	-	2	3	Pb^{2+}	500	80.3	Ion-exchange by calcium ions on the material surface	Jimenez et al. 2017
Banana peels	Dehydrated and grinded	HTC	Pristine	230	0.25	7	Pb^{2+}	200	359	Ion exchange and surface complexation	Zhou et al. 2017a
Banana peels	H_3PO_4 soaked	HTC	Pristine	230	0.25	7	Pb^{2+}	200	193	Ion exchange and surface complexation	Zhou et al. 2017a
Peanut hull	Dried	HTC	Pristine	300	2	-	Pb^{2+}	50	0.88	Complexation with carboxyl surface functional groups	Xue et al. 2012
Peanut hull	Dried	HTC	H_2O_2 modified	300	2	-	Pb^{2+}	50	22.82	Complexation with carboxyl surface functional groups	Xue et al. 2012

* For the references s. Xiang et al. (2020).

4.2 Heavy metal(loids) removal from soils

Heavy metals in soils can undergo different processes (**Figure 5**). They can be immobilised through adsorption onto a soil amendment, such as biochar. They can also be mobilised or reduced. The reduction can further change the mobility of the elements (Park et al. 2011b). For instance, Cr^{+4} is weakly adsorbed to soil particles, is often available for plants, and is easy to mobilise, leaching to groundwater. Its reduced state, Cr^{+3}, is strongly bonded to soil particles and, therefore, can be retained and neutralised (Choppala et al. 2012). Other mechanisms for remediation through amendments are rhizosphere modification, which implies the roots of the plants in the soil, and volatilisation, in which As, Hg and Se, are reduced and/or subject to methylation and released into the atmosphere.

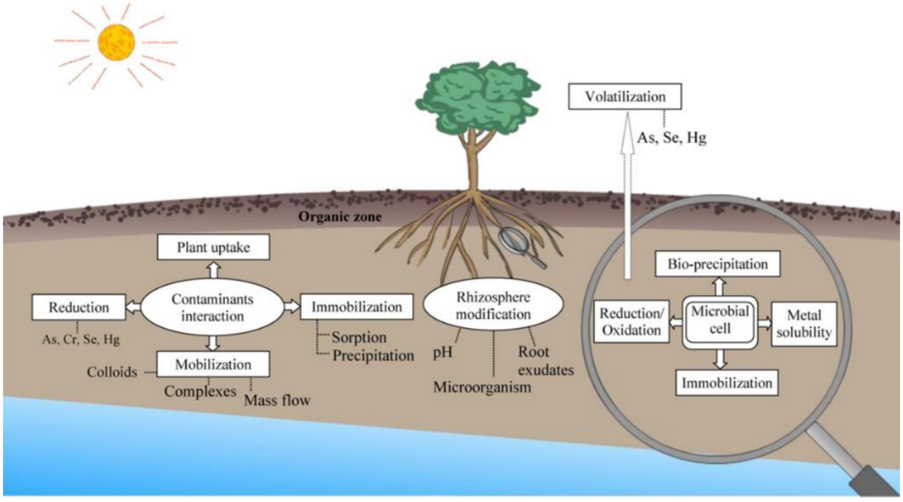


***Figure 5**. Mechanism of soil remediation through the addition of soil amendments. From Park et al. (2011b).*

The effects of biochar, when applied to the removal of heavy metals from soils, might be diverging. Some heavy metals are effectively removed and sorbed into the biochar, while others are mobilised. For instance, in a study by Beesley et al. (2010), hardwood-derived biochar was added to contaminated soil, and the removal of As, Cu, Zn, and Cd was assessed. In the case of Cu and As, the concentrations in the pore water increased as much as 30 times. Such concentrations were related to high pH and dissolved organic carbon (DOC) concentrations. On the other hand, Zn and Cd were effectively removed from the pore water and sorbed. Cd decreased by tenfold.

Other authors also found higher Cu, Sb and As mobility when adding biochar to remediate soils. The increase in pH associated with biochar seems to facilitate the mobility of these metals, while other mechanisms act on specific elements (Ahmad et al. 2014). For instance, higher mobility of copper has been linked to a biochar-mediated increase of DOC and the formation of soluble copper complexes (Beesley et al. 2010; Park et al. 2011a; Ahmad et al. 2014). Furthermore, biochar can reduce arsenic from As^{+4} to As^{+3}, being the latter a more mobile state (Park et al. 2011b; Ahmad et al. 2014). Sb is likely desorbed from soils due to repulsion between this anion and the negative charges in biochar (Ahmad et al. 2014).

The evidence suggests that lead is stabilised by the electrostatic interaction between functional groups of biochar and this metal and the formation of precipitates in soils due to the increase in pH (e.g. $Pb_5(PO_4)_3$) (Park et al. 2011a; Uchimiya et al. 2012), among other mechanisms.

The toxic form of chromium can be effectively retained in soils thanks to biochar. The functional groups in this material can contribute to reducing Cr^{+4} (i.e. the toxic form of chromium) to Cr^{+3}, which is non-toxic and readily fixed to the soil particles (Choppala et al. 2012). This reduction can also be mediated by bacteria which use carbon from biochar as a source of energy (Ahmad et al. 2014).

The soil characteristics also seem to affect the effectiveness of biochar in removing heavy metals. Uchimiya et al. (2011) showed that Cu^{+2} and Pb^{+2} could be effectively and simultaneously stabilised when biochar with elevated oxygen functional groups is applied to soils with low CEC, total carbon content and low pH.

The most common chemical interactions between biochar, metals and inorganic compounds are summarised by Ahmad et al. (2014) (**Figure 6**) and by Lu et al. (2012) for Pb^{+2} (**Figure 7**). Ahmad et al. (2014) consider four main interactions: ion exchange, anionic metal attraction, cationic metal attracttion and precipitation. The ion exchange is well exemplified with Pb^{+2} (**Figure 7**, *I-cation release*). According to Lu et al. (2012), it happens through the complexation of the inner-sphere by exchange with cations (e.g. Ca^{+2}, Mg^{+2}) contained in the biochar and co-precipitation. Complexation refers to the association of two molecules to create a nonbonded entity. The molecules associate through relatively weak forces, including London forces, hydrogen bonds and hydrophobic interactions (Viswanathan et al. 2017). The molecule is partly dehydrated in the inner-sphere complexation and directly interacts with the surface (Payne et al. 2013). Co-precipitation is "…the carrying down by a precipitate of substances normally soluble under the conditions employed" (Patnaik 2004).

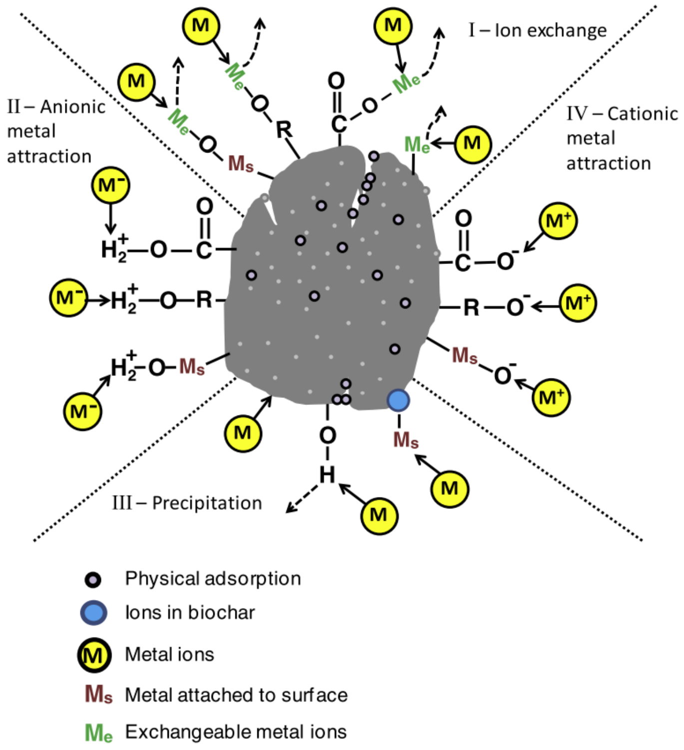


Figure 6. *Interactions of biochar with inorganic compounds (Ahmad et al. 2014).*

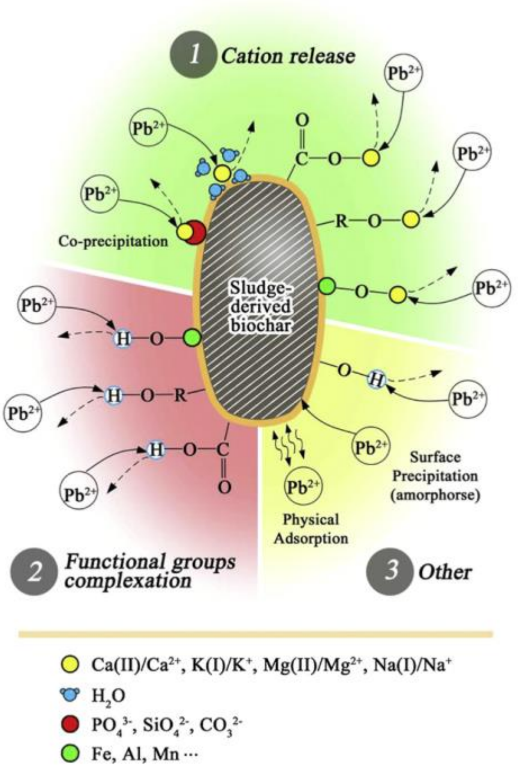


Figure 7. *Primary mechanisms proposed by Lu et al. (2012) for the adsorption of Pb to sludge-derived biochar. From Lu et al. (2012).*

Another type of interaction is ionic attraction (II and IV, in **Figure 6**). This interaction is well exemplified by Pb^{+2} adsorption, which occurs due to functional group interaction (**Figure 7**, *functional groups complexation*). It happens through outer-sphere complexation with functional hydroxyl and carboxyl groups and inner-sphere complexation with hydroxyl groups from oxides contained in the biochar (Lu et al. 2012). In the outer-sphere complexation, the inorganic compound interacts with the surface without losing the hydration sphere, as illustrated with uranium by Payne et al. (2013) (**Figure 8**).

Moreover, inorganic ions can be subject to other interactions with biochar, such as surface precipitation (**Figure 6**, *III-precipitation*, and **Figure 7**, *other types*) and physical adsorption (Lu et al. 2012; Ahmad et al. 2014).

According to Xiao et al. (2018), the main interactions between biochar and inorganic compounds are complexation, electrostatic effects and co-precipitation. They also state that the highest adsorption of metals is observed in biochars produced at low to moderate pyrolysis temperatures. On the other hand, the anionic inorganic pollutants are preferentially sorbed into biochar produced at high pyrolysis temperatures. However, these pollutants are generally less sorbed by biochar due to repulsive forces (Xiao et al. 2018). Hydrogen-bonding to oxygen functional groups, favoured by increasing hydrophobicity and aromaticity, is the mechanism that facilitates the adsorption of anionic inorganic compounds (Xiao et al. 2018).

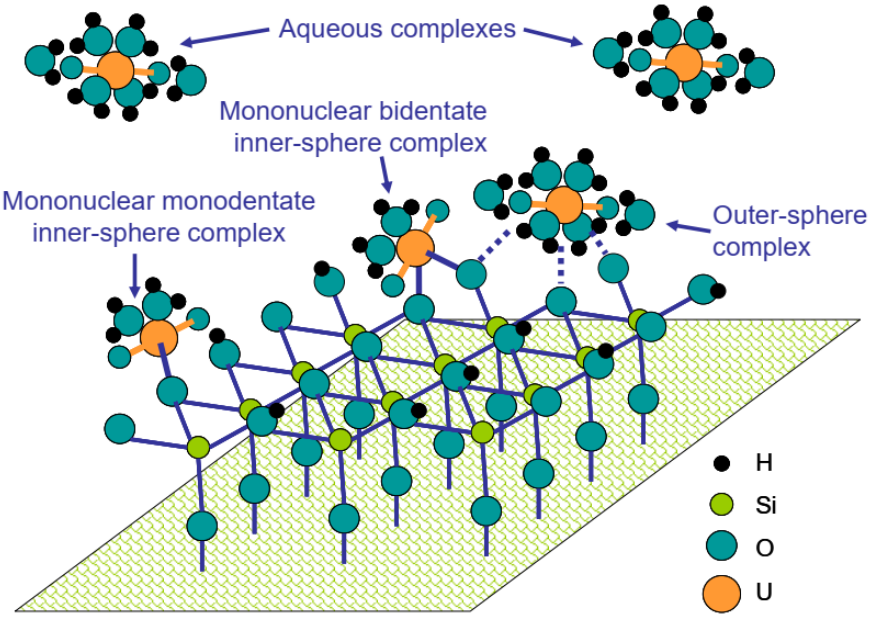


Figure 8. *Outer- and inner-sphere complexation illustrated for U and a surface. From Payne et al. (2013).*

4.3 Removal of nitrogen and phosphorus from water

Biochar reduces nitrogen and phosphorus concentration in water. The reduction is particularly effecttive with the reactive forms of these elements, which are ammonium, nitrate, and phosphate (Xiang et al. 2020) and is better when the biochar surface chemistry is modified through pre- and post-treatment processes, increasing the sorption capacity (Xiang et al. 2020).

For instance, phosphate and ammonium have been effectively removed from urine using biochar post-treated with magnesium oxides (Xu et al. 2018). The primary removal mechanism was struvite precipitation for both pollutants and surface sorption for phosphate (Xu et al. 2018). Struvite is a mineral ($MgNH_4(PO_4)_3)6H_2O$) that can be found in wastewater treatment schemes, especially pipes and equipment of anaerobic digestion (Bouropoulos & Koutsoukos 2000).

Ammonium removal seems to be better with low temperature biochars, which have a higher density of functional groups that allow chemical and electrostatic interaction. The study by Yang et al. (2018) found that sawdust biochar pyrolysed at 300°C had a better ammonium removal efficiency than higher-temperature biochar. The role of functional groups as the biochar moiety retaining ammonium was confirmed by Petit et al. (2010). The experiments of these authors showed that activated carbon reduced ammonium concentration in the air due to the interaction with the sulfonic functional groups. A summary of studies concerning nitrogen and phosphorous removal and their findings is provided in **Table 6**.

Table 6. *Compilation of studies focusing on phosphorus and ammonium removal. From (Xiang et al. 2020).*

Biochar feedstock	**Treatment/ modification**	**Pyrolysis temperature (°C)**	**Biochar dose (g/L)**	**Nutrient**	**Initial concen-tration (mg/L)**	**Adsorption capacity (mg/g)**	**Removal mechanism**	**Ref. ***
Pine sawdust	Pristine	300	3	NH_4^+	100	5.38	Chemical bonding and electrostatic interaction of NH_4^+ with the surface functional group	Yang et al. 2017
Wheat straw	Pristine	550	3	NH_4^+	100	2.08	Chemical bonding and electrostatic interaction of NH_4^+ with the surface functional group	Yang et al. 2017
Wood waste	MgO Modified	600	2	NH_4^+	8203	47.5	Struvite precipitation	Xu et al. 2018
Sugarcane harvest residue	MgO particle-impregnated	550	1.25	NH_4^+	200	22	Struvite crystallization, electrostatic attraction, and π-π interaction	Li et al. 2017
Wheat straw	Mg-Fe layered double hydroxides (LDH)	600	2	NO_3^-	45	24.8	Surface adsorption and the interlayer anion exchange	Xue et al. 2016
Peanut shells	$MgCl_2$ solution immersed	600	2	NO_3^-	20	94	Surface adsorption	Zhang et al. 2012a
Hickory wood chips	Aluminium salt treated	600	2.5	P	6.4	8.346	Electrostatic attraction	Zhang et al. 2019a
Wheat straw	Acid wash and water wash	500-560	12.5	P	25	1.06	Adsorption and surface precipitation	Dugdug et al. 2018
Hardwood	Acid wash and water wash	500-550	12.5	P	25	1.2	Adsorption and surface precipitation	Dugdug et al. 2018
Willow wood	Acid wash and water wash	500-550	12.5	P	25	1.93	Adsorption and surface precipitation	Dugdug et al. 2018
Wood waste	MgO Modified	600	2	PO_4^{3-}	318.5	116.4	Struvite precipitation, surface adsorption	Xu et al. 2018
Bamboo	Mg-Al layered double hydroxides (LDH)	600	2	PO_4^{3-}	50	13.11	Interlayer anion exchange and surface adsorption	Wan et al. 2017
Anaerobically digested sugar beet tailings	Pristine	600	2	PO_4^{3-}	61.5	25	Surface adsorption by colloidal and nano-sized MgO particles	Yao et al. 2011b
Cottonwood	$AlCl_3$ solution immersed	600	2	PO_4^{3-}	1600	135	Adsorption by unique nanostructure	Zhang & Gao 2013
Sugar beet tailings	$MgCl_2$ solution immersed	600	2	PO_4^{3-}	1600	835	Surface adsorption	Zhung et al. 2012a
Tomato leaves	Mg enriched	600	2	PO_4^{3-}	588.1	100	Precipitation, surface deposition	Yao et al. 2013a

* For the references s. Xiang et al. (2020).

4.4 Removal of organic compounds from water

According to Xiao et al. (2018), the research on the potential of biochar as an absorbent of organic contaminants has focused primarily on water. Fewer studies have been conducted to assess their use to remediate contaminated soils. The pollutants most frequently evaluated are herbicides, pesticides, polycyclic aromatic hydrocarbons, dyes, and antibiotics (Ahmad et al. 2014).

Overall, biochar retention of organic pollutants is enabled chiefly by sorption, which increases along with the pyrolysis temperature (Ahmad et al. 2014; Xiao et al. 2018). It explains why organic compounds such as de-isopropyl atrazine and trichloroethylene, the degradation products of atrazine (an herbicide), are effectively retained by high-temperature biochar (Ahmad et al. 2014).

However, the effects of biochar are strongly linked to the type of organic pollutant considered. Herbicides such as norflurazon and fluoridone are more easily removed at higher polarities, a characteristic of biochar produced at low pyrolysis temperatures (Sun et al. 2011).

Organic pollutants are generally removed through partition and adsorption (Ahmad et al. 2014; Xiao et al. 2018). Adsorption tends to be the dominant interaction of high-temperature biochar, while partition tends to be more common when the involved biochar is produced at low-temperature (**Figure 9**, *left circle*).

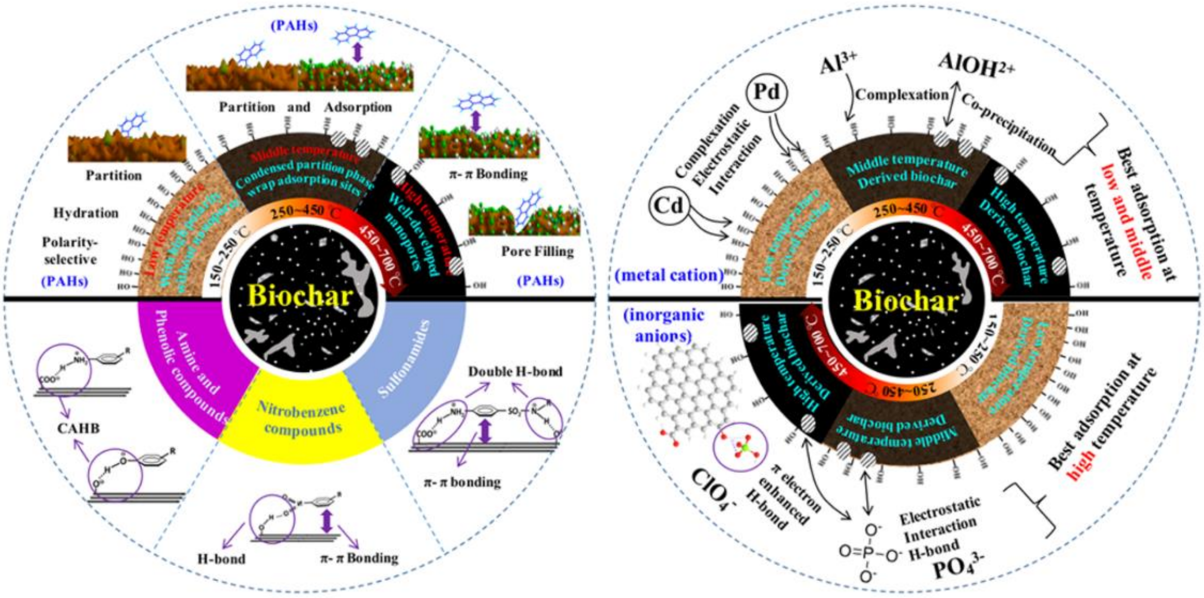


Figure 9. The predominant biochar mechanisms for pollutant removal. The circle on the left is for organic compounds, while the right circle is for inorganic ones. From Xiao et al. (2018).

Partitioning (**Figure 10**) (absorption), which is considered a hydrophobic interaction (Murphy et al. 1994), refers to the transference of an organic compound from water into an organic phase (Chiou et al. 1979; Murphy et al. 1994; Chen et al. 2008). The partitioned compound is solvated into the organic phase, which is sorbed or "dissolved" (Murphy et al. 1994). Partition occurs predominantly in the noncarbonised fraction of biochar at high solute concentration or volatile content (Inyang & Dickenson 2015). This mechanism of sorption has been proved to be slow (Inyang & Dickenson 2015).

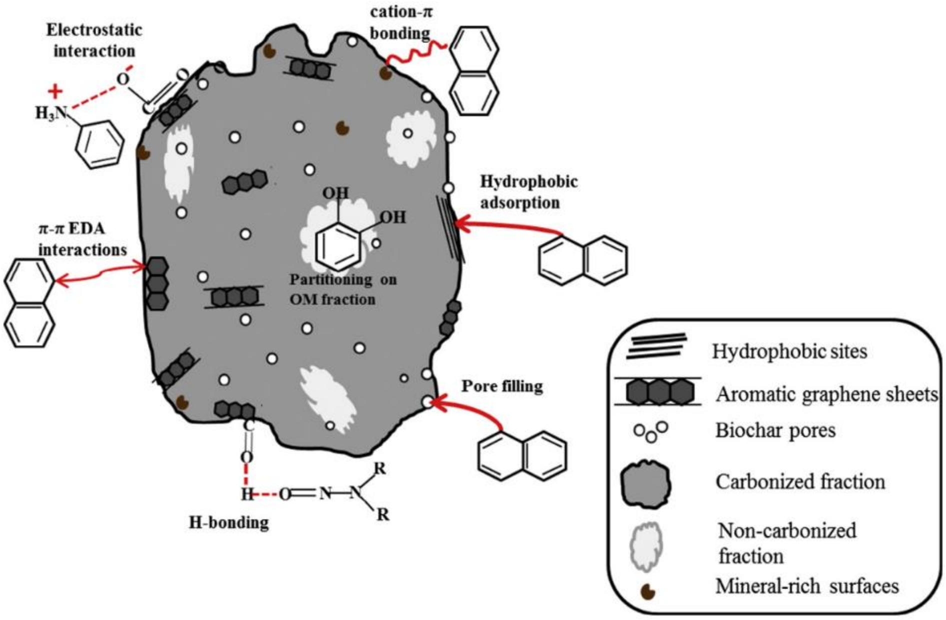


Figure 10. *Mechanism of organic compound adsorption into biochar. From Inyang & Dickenson (2015).*

In the case of the herbicides norflurazon and fluoridone, retention happens thanks to hydrogen bonding with the oxygen-bearing moieties of biochar (Sun et al. 2011), while trichloroethylene attaches to hydrophobic sites (Ahmad et al. 2014). Hydrogen bonding (**Figure 10**) is one of the adsorption mechanisms of polar organic pollutants. It takes place through the interaction between some of the functional groups of biochar and organic compounds that bear electronegative elements (Inyang & Dickenson 2015). Hydrophobic adsorption is a surface reaction in which the pollutant's molecules attach to the sorbent's surface (Murphy et al. 1994) (**Figure 10**).

Besides the mechanisms of sorption explained, additional interactions account for the removal of organic compounds by biochar. For instance, some cationic dies (e.g. methyl violet and rhodamine) can precipitate into biochar or be attracted to the negative surface of the material (especially when it is produced at relatively low temperatures, e.g., 400°C) (Xu et al. 2011). Such dyes can also be removed through the electrostatic interaction between them and the biochar's carboxylate and phenolic hydroxyl groups (Xu et al. 2011). These interactions are electrostatic (**Figure 10**).

Electrostatic interactions are the primary mechanism for removing ionic and ionisable organic compounds (Inyang & Dickenson 2015). Cationic compounds are attracted to the negative surface of biochar, while anionic molecules interact electrostatically with anionic mineral-rich phases of the biochar. Furthermore, the biochar's carboxyl and phenolic functional groups can deprotonate and react with cationic compounds (Inyang & Dickenson 2015).

Qiu et al. (2009) conducted experiments on dye removal with straw-based biochar. They found that the predominant mechanism for removing these pollutants were electrostatic attraction/repulsion and π-π interactions.

The π interactions are often of electron-donor-acceptor (EDA) character (**Figure 10**). Under different production conditions, the biochar can have a high or low density of electrons in the π orbitals of the aromatic rings. Under such electron-rich or poor conditions, the aromatic rings can bind electron-withdrawing or donor compounds respectively (Inyang & Dickenson 2015). Antibiotics such as sulfamethoxazole, used for humans and animals, are removed from the solution by the π-π interactions with the biochar (Xiang et al. 2020) (**Figure 9**, *left circle*).

Finally, pore-filling (**Figure 9**, *left circle*, and **Figure 10**) refers to the sorption of substances into biochar, mainly as a function of surface interaction in micro and mesopores. This removal mechanism is especially effective when the solute is low or the volatile matter content is minimal (Inyang & Dickenson 2015).

Two critical factors controlling the removal of organic pollutants from water are the pH and ionic strength of the solution (Ahmad et al. 2014). For instance, the pH of the solution can affect the surface charge of biochar. Solutions with a pH below the pH of biochar's point zero charge will render the net external surface of the material positive and vice versa (Inyang & Dickenson 2015). This behaviour was observed by Xu et al. (2011), who found an increase in the retention of methyl violet dye when pH increased. The likely cause of this observation was the dissociation of OH-phenolic groups of biochar, rendering a net negative charge that increased electrostatic attraction (Xu et al. 2011). Regarding ionic strength, its net effect will depend on the pH of the solution and the point zero charge of the biochar (Ahmad et al. 2014).

The sorption can also be enhanced through post-treatment processes. For instance, biochar can be washed or dewatered to increase its hydrophobicity. This modification results in higher adsorption of some organic contaminants. Another example of post-treatment, which enhances the removal of organic pollutants, was provided by Zhang et al. (2013). They removed the ash from pig manure biochar or deashed it, improving the removal of carbaryl and atrazine. The reason for the improvement is that ash can block the adsorption sites of organic moieties (Zhang et al. 2013). A summary of organic contaminant removals is provided in **Table 7**.

Table 7. *Summary of studies proving the removal of organic contaminants through biochar. From Inyang & Dickenson (2015).*

Organic contaminants	**Pyrolysis treatment temperature in °C (time in hours)**	**Biochar type**	**Removal performance**	**Proposed sorption mechanism**	**References ***
Pesticides and herbicides					
Atrazine	200 (4)	Dairy manure	0.02 mg/g	Partitioning	Cao et al. 2009
Catechol	400 (3)	Oak	20 mg/g	Pore-filling and diffusion	Kasozi et al. 2010
Carbaryl	700 (2)	Pig manure	1 mg/g	Hydrophobic and π-π EDA interactions	Zhang et al. 2013
Diazinon	450(2)	$H_3PO_4^-$ treated rice straw	99% sorbed	H-bonding with polar groups	Taha et al. 2014
2,4-Dichlophenoxyacetic acid	600(4)	wood chips	0.72 mg/g	Surface adsorption	Kearns et al. 2014
Fluoridone	3''(1)	Grass	10 mg/g	Partitioning on amorphous C	Sun et al. 2011a
1-Naphthol	200(6)	Orange peel	23 mg/g	Partitioning and surface adsorption	Chen 2009
Naphthalene	520	Wood chips	80%	Partitioning of aliphatic C	Reddy et al. 2014
Oxamyl	450 (2)	Rice straw	99% sorbed	H-bonding with polar groups	Taha et al. 2014
Pharmaceutical and personal care products					
Carbamazepine	300 (0.25)	Loblolly pine chips	80% sorbed	Hydrophobic adsorption	Jung et al. 2013
Diclofenac	300 (0.25)	Loblolly pine chips	70% sorbed	Hydrophobic adsorption	Jung et al. 2013
Ethinylestradiol	400 (2-7)	HCJl-treated poultry litter	0.001 mg/g	Pore-filling	Sun et al. 2011b
Ibuprofen	300 (0.25)	Loblolly pine chips	30% sorbed	Hydrophobic adsorption and π-π EDA interactions	Jung et al. 2013
Sulfamethazine	600	Hardwood litter	Over 27%	π-π EDA interaction	Teixido et al. 2011
Sulfamethoxazole	400	Giant reed	4 mg/g	Pore-filling and hydrophobic interaction	Zheng et al. 2023
Sulphapyridine	600 (2)	CNT modified-hickory chip	15 mg/g	π-π EDA interaction	Inyang et al. 2014b
Tetracycline	30 (24)	KOH-treated rice husk	58.8 mg/g	π-π EDA interaction	Liu et al. 2012
Plasticizers					
2,4 4'-Trichlorobiphenyl	550 (1.5)	Pine needles	0,4 mg/g	π-π EDA interaction, H-bonding	Wang et al. 2013
Bisphenol A	400 (2-7)	Poultry litter	10 mg/g	π-π EDA interaction and pore filling mechanism	Sun et al. 2011b
Butyl benzyl phthalate	400 (1)	Wood	10 mg/g	H-bonding	Sun et al. 2012
Dibutyl phthalate	400 (2)	HCl-treated swine manure	20-80% sorbed	H-bonding	Jin et al. 2014
Diethyl phthalate	700 (1)	Grass	10 mg/g	π-π EDA interaction	Sun et al. 2012
Dyes					

Methylene blue	600 (6)	CNT modified-hickory chip	2.4 mg/g	Electrostatic interaction, diffusion, and π-π EDA Interactions	Inyang et al. 2014a
Methyl violet	350 (4)	Peanut straw	104.4 mg/g	Electrostatic interaction	Xu et al. 2011
Volatile organic compounds					
Nitrobenzene	700 (6)	Pine needles	208 mg/g	Pore-filling	Chen et al. 2008
P-nitrotoluene	400 (6)	Orange peel	29.7 mg/g	Partitioning	Chen et al. 2011a
Phenol	NA	Hydrogel/HCl-treated chicken waste	20 mg/g	H-bonding	Karakoyun et al. 2011
Trichloroethylene	700 (3)	Soybean stover	31.7 mg/g	Hydrophobic adsorption	Ahmad et al. 2010
Microbial and organic matter					
DNA	600 (0.4)	HCl-treated willow wood	5.1 mg/g	Pore-filling	Wang et al. 2014
E. Coli	300 (NA)	Stream-activated wood	2.5% immobilised	Surface attachment	Mohanty and Boehm. 2014
Humic acid	400 (3)	Grass	60 mg/g	Hydrophobic interactions	Kasozi et al. 2010
Food additives					
P-coumaric acid	NA	Hardwood litter	10 mg/g	H-bonding	Ni et al. 2011
t-Cinnamic acid	NA	Hardwood litter	10 mg/g	H-bonding	Ni et al. 2011
Polycyclic aromatic compounds					
Phenanthrene	600 (1)	Rice straw	20-80% sorbed	π-π EDA interactions	Jin et al. 2014
Perfluoroalkyl acids					
Perfluoro octane sulfonate	400 (2)	Maise	164 mg/g	Hydrophobic adsorption	Chen et al. 2011b
N-nitrosomodimethyl-amine	500	Bamboo	3 mg/g	H-bonding and hydrophobic interaction	Chen et al. 2015

* For the references s. Inyang & Dickenson (2015).

4.6 Removal of organic compounds from soils

According to Ahmad et al. (2014), the effect of biochar on remediating organic contaminants in soils has been less explored than the remediation of the same compounds in water. Some of the few studies point to biochar's usefulness in this regard. Herbicide simazine was sorbed to biochar, preventing further leaching into groundwater and reducing availability for soil bacteria (Jones et al. 2011). Cao & Harris (2010) proved that manure-based biochar carbonised at 450°C was sufficient to remove atrazine from the soil at an efficiency as high as 77%. Yu et al. (2009) obtained similar results for chlorpyrifos and carbofuran (i.e. pesticides). After amending soil with different percentages of biochar, they found that the pesticides are tightly retained in the soil, preventing leaching and decreasing bioavailability. Furthermore, this study proved that biochar produced at higher temperatures (850°C) had better sorption capacity than the same feedstock carbonised at a lower temperature (450°C). Zhang et al. (2010) found that biochar derived from Pinus Radiata enhanced the soil capacity to sorb phenanthrene and that biochars produced at a higher temperature (i.e. 700°C) had a better sorption performance.

4.7 Impact of biochar on soil infiltration rate and hydraulic conductivity

Biochar does not consistently affect soil infiltration rates. Some authors have found that biochar increases the infiltration capacity, while others do the opposite. According to (Mohanty et al. 2018), in general, these discrepancies are probably a result of the difference between the soil's and the biochar's particle sizes, the changes in tortuosity and the hydrophobicity of the medium. However, there are likely more factors involved.

For instance, biochar has been found to decrease the saturated hydraulic conductivity (K_{sat}) of soils whose grain size tends to be coarse, such as sandy soils and loamy, sandy soils (Ibrahim et al. 2013; Abel et al. 2013; Lim et al. 2016; Liu et al. 2016). The decrease in K_{sat} is likely the result of increased tortuosity (Barnes et al. 2014; Lim et al. 2016) and a more compact arrangement (Liu et al. 2016). Furthermore, coarse biochar decreased K_{sat} significantly more than small-grained varieties (Lim et al. 2016).

On the other hand, the application of biochar to fine-grained soils, such as clay loam (Lim et al. 2016), clay-rich soils (Barnes et al. 2014), and silty loam (Herath et al. 2013), augments K_{sat} by up to 328% (Barnes et al. 2014).

However, differing outcomes have also been observed. Sandy soil in the vicinity of charcoal production sites showed an increase in K_{sat} (Oguntunde et al. 2008). Adding biochar to sandy soil in a rainfall simulation experiment resulted in higher infiltration rates. In the same set of experiments, changing soil to a calcareous loam showed no change in the infiltration rate due to biochar amendment (Abrol et al. 2016).

Omondi et al. (2016) examined changes in soil hydraulic properties due to adding biochar to soils through a meta-analysis. They found that, on average, biochar increased the hydraulic conductivity of soils by 25%. Furthermore, they found that wood (35.7%) and manure (6.6%) were the feedstock which enhanced K_{sat} the most. Contrary to the findings of other works, Omondi et al. (2016) concluded that a greater increase in K_{sat} was found in coarse-textured soils (36.5%) followed by medium (27.3%) and fine grained-soils (17.8%).

A way to use biochar in MAR systems is by spreading it in a surface layer over the topsoil. This configuration has been explored chiefly with a carbon-rich reactive layer aiming to enhance SAT MAR sites (ENSAT 2012; Valhondo et al. 2020). In the Sant Vicenç dels Horts site, infiltration rates were not visibly affected by a reactive layer (Valhondo et al. 2020).

4.8 Other factors influencing water purification through biochar

Water is usually infiltrated in water-spreading MAR systems (e.g., infiltration basins, SAT) following wet and dry cycles. The wet cycles correspond to the water infiltration phase, while the dry period to a pause in filtration to re-oxygenate the vadose zone. According to Kizito et al. (2017), the removal of organic pollutants and phosphorus and nitrogen chemical species during the wet phase is predominantly mediated by adsorption. During dry periods, the soil's microbes enhance the pollutants' oxidation, increasing their mobility and allowing for removal in the following wetting phase.

Mohanty et al. (2018) found through a literature review that sorption is affected by residence time. The longer the residence time, the higher the removal of pollutants through sorption. This parameter can be controlled by factors such as the continuity and amount of water provided to an infiltration system, the depth of the reactive layer, the grain-size distribution, the porosity structure, and the surface area (Mohanty et al. 2018).

5. Identified gaps and opportunities

The articles reviewed focus mostly on SAT systems. The effect of a reactive layer seems to remain for relatively long periods, as attested by the number of publications stemming from the Sant Vicenç dels Horts SAT site. Furthermore, all the articles reviewed point to the fact that the inclusion of a carbon-rich additive into the soil (either mixed in the matrix or as a layer) can benefit the removal of some contaminants, especially emerging pollutants. The articles do not assess the potential benefits of biochar to remove other relevant pollutants (e.g., nitrogen and phosphorus), which can be found in wastewater and waters from other sources.

The review of articles carried out to construct a conceptual basis showed that most studies of biochar contaminant removal are based on laboratory experiments. Such experiments have the limitation of oversimplifying the systems, sometimes missing the complexity and factors affecting systems under normal operating conditions. For instance, many laboratory experiments use water with a limited number of species in solution and controlled pH. Furthermore, the ageing of biochar has been poorly studied in the lab and, when assessed, is done by indirect chemical methods (Mohanty et al. 2018). Such a way to conduct research leaves some questions open. What effect can atmospheric field conditions have on removing pollutants by biochar? How does the competition of different species in solution affect the interaction between biochar and some contaminants? What is the effect when the source water quality is not constant? How do the infiltration rates variate not just as a consequence of water infiltration but also when further field factors play a role?

6. References

Abel S, Peters A, Trinks S, et al. (2013) Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. Geoderma 202-203, 183-191. https://doi.org/10.1016/j.geoderma.2013.03.003

Abrol V, Ben-Hur M, Verheijen FGA, et al. (2016) Biochar effects on soil water infiltration and erosion under seal formation conditions: rainfall simulation experiment. J Soils Sediments 16, 2709-2719. https://doi.org/10.1007/s11368-016-1448-8

Agrafioti E, Bouras G, Kalderis D, Diamadopoulos E (2013) Biochar production by sewage sludge pyrolysis. Journal of Analytical and Applied Pyrolysis 101, 72-78. https://doi.org/10.1016/j.jaap.2013.02.010

Ahmad M, Rajapaksha AU, Lim JE, et al. (2014) Biochar as a sorbent for contaminant management in soil and water: A review. Chemosphere 99, 19-33. https://doi.org/10.1016/j.chemosphere.2013.10.071

Azargohar R, Dalai AK (2006) Biochar as a Precursor of Activated Carbon. In: Twenty-Seventh Symposium on Biotechnology for Fuels and Chemicals. ABAB Symposium. Humana Press.

Barnes RT, Gallagher ME, Masiello CA, et al. (2014) Biochar-Induced Changes in Soil Hydraulic Conductivity and Dissolved Nutrient Fluxes Constrained by Laboratory Experiments. PLoS ONE 9, e108340. https://doi.org/10.1371/journal.pone.0108340

Beesley L, Moreno-Jiménez E, Gomez-Eyles JL (2010) Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. Environmental Pollution 158, 2282-2287. https://doi.org/10.1016/j.envpol.2010.02.003

Bouropoulos NC, Koutsoukos PG (2000) Spontaneous precipitation of struvite from aqueous solutions. Journal of Crystal Growth 213, 381-388. https://doi.org/10.1016/S0022-0248(00)00351-1

Cao X, Harris W (2010) Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresource Technology 101, 5222-5228. https://doi.org/10.1016/j.biortech.2010.02.052

Carey FA (2000) Organic chemistry, 4th ed., McGraw-Hill, Boston.

Cha JS, Park SH, Jung S-C, et al. (2016) Production and utilization of biochar: A review. Journal of Industrial and Engineering Chemistry 40, 1-15. https://doi.org/10.1016/j.jiec.2016.06.002

Cheeseman KH, Slater TF (1993) An introduction to free radical biochemistry. British Medical Bulletin 49, 481-493. https://doi.org/10.1093/oxfordjournals.bmb.a072625

Chen B, Zhou D, Zhu L (2008) Transitional Adsorption and Partition of Nonpolar and Polar Aromatic Contaminants by Biochars of Pine Needles with Different Pyrolytic Temperatures. Environ Sci Technol 42, 5137-5143. https://doi.org/10.1021/es8002684

Chen W-H, Zhuang Y-Q, Liu S-H, et al. (2016) Product characteristics from the torrefaction of oil palm fiber pellets in inert and oxidative atmospheres. Bioresource Technology 199, 367-374. https://doi.org/10.1016/j.biortech.2015.08.066

Cheng C-H, Lehmann J, Thies JE, et al. (2006) Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37, 1477-1488. https://doi.org/10.1016/j.orggeochem.2006.06.022

Chiou CT, Peters LJ, Freed VH (1979) A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds. Science 206, 831-832.

Choppala GK, Bolan NS, Megharaj M, et al. (2012) The Influence of Biochar and Black Carbon on Reduction and Bioavailability of Chromate in Soils. J Environ Qual 41, 1175-1184. https://doi.org/10.2134/jeq2011.0145

Cueto García MJ (2016) Potencial de producción de biochar en España a partir de residuos de la industria papelera, de lodos de E.D.A.R., de residuos sólidos urbanos y de residuos ganaderos: Estudio de la fijación de carbono. PhD Thesis, Universidad Politécnica de Madrid

ENSAT (2012) Technical final report (December 2012). European Commission, Barcelona, Spain.

Frišták V, Friesl-Hanl W, Wawra A, et al. (2015) Effect of biochar artificial ageing on Cd and Cu sorption characteristics. Journal of Geochemical Exploration 159, 178-184. https://doi.org/10.1016/j.gexplo.2015.09.006

Granatstein D, Kruger EC, Collins H, et al. (2009) Use of biochar from the pyrolysis of organic water mateiral as a soil amendment. Final project report, Center for Sustaining Agriculture and Natural Resouces, Washington State University, Wenatchee, WA, USA.

Herath HMSK, Camps-Arbestain M, Hedley M (2013) Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol. Geoderma 209-210, 188-197. https://doi.org/10.1016/j.geoderma.2013.06.016

Huggins TM, Haeger A, Biffinger JC, Ren ZJ (2016) Granular biochar compared with activated carbon for wastewater treatment and resource recovery. Water Research 94, 225-232. https://doi.org/10.1016/j.watres.2016.02.059

Ibrahim HM, Al-Wabel MI, Usman ARA, Al-Omran A (2013) Effect of Conocarpus Biochar Application on the Hydraulic Properties of a Sandy Loam Soil: Soil Science 178, 165-173. https://doi.org/10.1097/SS.0b013e3182979eac

Inyang M, Dickenson E (2015) The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: A review. Chemosphere 134, 232-240. https://doi.org/10.1016/j.chemosphere.2015.03.072

Ippolito JA, Strawn DG, Scheckel KG, et al. (2012) Macroscopic and Molecular Investigations of Copper Sorption by a Steam-Activated Biochar. J Environ Qual 41, 1150-1156. https://doi.org/10.2134/jeq2011.0113

Jones DL, Edwards-Jones G, Murphy DV (2011) Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biology and Biochemistry 43, 804-813. https://doi.org/10.1016/j.soilbio.2010.12.015

Kizito S, Lv T, Wu S, et al. (2017) Treatment of anaerobic digested effluent in biochar-packed vertical flow constructed wetland columns: Role of media and tidal operation. Science of The Total Environment 592, 197-205. https://doi.org/10.1016/j.scitotenv.2017.03.125

Ko DC, Cheung CW, Choy KK, Porter JF, McKay G (2004) Sorption equilibria of metal ions on bone char. Chemosphere 54(3), 273-281.

Law KY (2014) Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity: Getting the Basics Right. J Phys Chem Lett 5, 686-688. https://doi.org/10.1021/jz402762h

Lehmann J (2007) Bio-energy in the black. Frontiers in Ecology and the Environment 5, 381-387. https://doi.org/10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

Li X, Shen Q, Zhang D, et al. (2013) Functional Groups Determine Biochar Properties (pH and EC) as Studied by Two-Dimensional 13C NMR Correlation Spectroscopy. PLoS ONE 8, 1-7. https://doi.org/10.1371/journal.pone.0065949

Liao S, Pan B, Li H, et al. (2014) Detecting Free Radicals in Biochars and Determining Their Ability to Inhibit the Germination and Growth of Corn, Wheat and Rice Seedlings. Environ Sci Technol 48, 8581-8587. https://doi.org/10.1021/es404250a

Lim TJ, Spokas KA, Feyereisen G, Novak JM (2016) Predicting the impact of biochar additions on soil hydraulic properties. Chemosphere 142, 136-144. https://doi.org/10.1016/j.chemosphere.2015.06.069

Lima IM, Boateng AA, Klasson KT (2010) Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts. J Chem Technol Biotechnol 85(11), 1515-1521. https://doi.org/10.1002/jctb.2461

Liu Z, Dugan B, Masiello CA, et al. (2016) Impacts of biochar concentration and particle size on hydraulic conductivity and DOC leaching of biochar-sand mixtures. Journal of Hydrology 533, 461-472. https://doi.org/10.1016/j.jhydrol.2015.12.007

Lu H, Zhang W, Yang Y, et al. (2012) Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar. Water Research 46, 854-862. https://doi.org/10.1016/j.watres.2011.11.058

MARSOL (2016a) MAR to Improve Groundwater Quantity and Quality by Infiltration of River Water - The Llobregat Demonstration Site, Catalonia, Spain. Folch A, Barba C, Rodríguez-Escales P, Sanchez-Vila X. MARSOL project deliverable D6.4.

MARSOL (2016b) Llobregat Recharge Site - Water Quality. Barba C, Folch A, Sanchez-Vila X. MARSOL project deliverable D6.2.

Meyer S, Glaser B, Quicker P (2011) Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review. Environ Sci Technol 45, 9473-9483. https://doi.org/10.1021/es201792c

Mohan D, Pittman CU, Bricka M, et al. (2007) Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science 310, 57-73. https://doi.org/10.1016/j.jcis.2007.01.020

Mohanty SK, Valenca R, Berger AW, et al. (2018) Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. Science of The Total Environment 625, 1644-1658. https://doi.org/10.1016/j.scitotenv.2018.01.037

Murphy EM, Zachara JM, Smith SC, et al. (1994) Interaction of Hydrophobic Organic Compounds with Mineral-Bound Humic Substances. Environ Sci Technol 28, 1291-1299. https://doi.org/10.1021/es00056a017

Nartey OD, Zhao B (2014) Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants: An Overview. Advances in Materials Science and Engineering 2014, 1-12. https://doi.org/10.1155/2014/715398

Nunoura T, Wade SR, Bourke JP, Antal MJ (2006) Studies of the Flash Carbonization Process. 1. Propagation of the Flaming Pyrolysis Reaction and Performance of a Catalytic Afterburner. Ind Eng Chem Res 45, 585-599. https://doi.org/10.1021/ie050854y

Oguntunde PG, Abiodun BJ, Ajayi AE, van de Giesen N (2008) Effects of charcoal production on soil physical properties in Ghana. J Plant Nutr Soil Sci 171, 591-596. https://doi.org/10.1002/jpln.200625185

Omondi MO, Xia X, Nahayo A, et al. (2016) Quantification of biochar effects on soil hydrological properties using meta-analysis of literature data. Geoderma 274, 28-34. https://doi.org/10.1016/j.geoderma.2016.03.029

Park JH, Choppala GK, Bolan NS, et al. (2011a) Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil 348, 439-451. https://doi.org/10.1007/s11104-011-0948-y

Park JH, Lamb D, Paneerselvam P, et al. (2011b) Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. Journal of Hazardous Materials 185, 549-574. https://doi.org/10.1016/j.jhazmat.2010.09.082

Patnaik P (2004) Dean’s Analytical Chemistry Handbook. 2nd edn., McGraw-Hill Education.

Payne TE, Brendler V, Ochs M, et al. (2013) Guidelines for thermodynamic sorption modelling in the context of radioactive waste disposal. Environmental Modelling & Software 42, 143-156. https://doi.org/10.1016/j.envsoft.2013.01.002

Petit C, Kante K, Bandosz TJ (2010) The role of sulfur-containing groups in ammonia retention on activeted carbons. Carbon 48, 654-667. https://doi.org/10.1016/j.carbon.2009.10.007

Qiu Y, Zheng Z, Zhou Z, Sheng GD (2009) Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresource Technology 100, 5348-5351. https://doi.org/10.1016/j.biortech.2009.05.054

Rai RK, Singh VP, Upadhyay A (2017) Soil Analysis. In: Planning and Evaluation of Irrigation Projects, pp. 505-523, Elsevier.

Schaffer M, Kröger KF, Nödler K, et al. (2015) Influence of a compost layer on the attenuation of 28 selected organic micropollutants under realistic soil aquifer treatment conditions: Insights from a large scale column experiment. Water Research 74, 110-121. https://doi.org/10.1016/j.watres.2015.02.010

Suffet IH (1980) An Evaluation of Activated Carbon for Drinking Water Treatment: A National Academy of Science Report. Journal American Water Works Association 72, 41-50. https://doi.org/10.1002/j.1551-8833.1980.tb04461.x

Sun K, Keiluweit M, Kleber M, et al. (2011) Sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. Bioresource Technology 102, 9897-9903. https://doi.org/10.1016/j.biortech.2011.08.036

Tan X, Liu Y, Gu Y, et al. (2016) Biochar-based nano-composites for the decontamination of wastewater: A review. Bioresource Technology 212, 318-333. https://doi.org/10.1016/j.biortech.2016.04.093

Uchimiya M, Bannon DI, Wartelle LH, et al. (2012) Lead Retention by Broiler Litter Biochars in Small Arms Range Soil: Impact of Pyrolysis Temperature. J Agric Food Chem 60, 5035-5044. https://doi.org/10.1021/jf300825n

Uchimiya M, Chang S, Klasson KT (2011) Screening biochars for heavy metal retention in soil: Role of oxygen functional groups. Journal of Hazardous Materials 190, 432-441. https://doi.org/10.1016/j.jhazmat.2011.03.063

Valhondo C, Carrera J, Ayora C, et al. (2015) Characterizing redox conditions and monitoring attenuation of selected pharmaceuticals during artificial recharge through a reactive layer. Science of the Total Environment 512-513, 240-250. https://doi.org/10.1016/j.scitotenv.2015.01.030

Valhondo C, Carrera J, Martínez-Landa L, et al. (2020) Reactive Barriers for Renaturalization of Reclaimed Water during Soil Aquifer Treatment. Water 12, 1012. https://doi.org/10.3390/w12041012

Valhondo C, Martinez-Landa L, Carrera J, et al. (2018) Evaluation of EOC removal processes during artificial recharge through a reactive barrier. Science of The Total Environment 612, 985-994. https://doi.org/10.1016/j.scitotenv.2017.08.054

Valhondo C, Martínez-Landa L, Carrera J, et al. (2019) Six artificial recharge pilot replicates to gain insight into water quality enhancement processes. Chemosphere 240, 124826. https://doi.org/10.1016/j.chemosphere.2019.124826

Viswanathan P, Muralidaran Y, Ragavan G (2017) Chapter 7 - Challenges in oral drug delivery: a nano-based strategy to overcome. In: Andronescu E, Grumezescu AM (eds), Nanostructures for Oral Medicine, pp. 173-201, Elsevier.

Wang B, Gao B, Fang J (2017) Recent advances in engineered biochar productions and applications. Critical Reviews in Environmental Science and Technology 47, 2158-2207. https://doi.org/10.1080/10643389.2017.1418580

Weber K, Quicker P (2018) Properties of biochar. Fuel 217, 240-261. https://doi.org/10.1016/j.fuel.2017.12.054

Wei L, Li S, Noguera DR, et al. (2015) Dissolved organic matter removal during coal slag additive soil aquifer treatment for secondary effluent recharging: Contribution of aerobic biodegradation. Journal of Environmental Management 156, 158-166. https://doi.org/10.1016/j.jenvman.2015.03.049

Xiang W, Zhang X, Chen J, et al. (2020) Biochar technology in wastewater treatment: A critical review. Chemosphere 252, 126539. https://doi.org/10.1016/j.chemosphere.2020.126539

Xiao X, Chen B, Chen Z, et al. (2018) Insight into Multiple and Multilevel Structures of Biochars and Their Potential Environmental Applications: A Critical Review. Environ Sci Technol 52, 5027-5047. https://doi.org/10.1021/acs.est.7b06487

Xu K, Lin F, Dou X, et al. (2018) Recovery of ammonium and phosphate from urine as value-added fertilizer using wood waste biochar loaded with magnesium oxides. Journal of Cleaner Production 187, 205-214. https://doi.org/10.1016/j.jclepro.2018.03.206

Xu R, Xiao S, Yuan J, Zhao A (2011) Adsorption of methyl violet from aqueous solutions by the biochars derived from crop residues. Bioresource Technology 102, 10293-10298. https://doi.org/10.1016/j.biortech.2011.08.089

Yan Y, Ma M, Liu X, et al. (2017) Effect of biochar on anaerobic degradation of pentabromodiphenyl ether (BDE-99) by archaea during natural groundwater recharge with treated municipal wastewater. International Biodeterioration & Biodegradation 124, 119-127. https://doi.org/10.1016/j.ibiod.2017.04.019

Yang HI, Lou K, Rajapaksha AU, et al. (2018) Adsorption of ammonium in aqueous solutions by pine sawdust and wheat straw biochars. Environ Sci Pollut Res 25, 25638-25647. https://doi.org/10.1007/s11356-017-8551-2

Yao Y, Gao B, Inyang M, et al. (2011) Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. Bioresource Technology 102, 6273-6278. https://doi.org/10.1016/j.biortech.2011.03.006

Yu H, Zou W, Chen J, et al. (2019) Biochar amendment improves crop production in problem soils: A review. Journal of Environmental Management 232, 8-21. https://doi.org/10.1016/j.jenvman.2018.10.117

Yu X-Y, Ying G-G, Kookana RS (2009) Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 76, 665-671. https://doi.org/10.1016/j.chemosphere.2009.04.001

Zhang H, Lin K, Wang H, Gan J (2010) Effect of Pinus radiata derived biochars on soil sorption and desorption of phenanthrene. Environmental Pollution 158, 2821-2825. https://doi.org/10.1016/j.envpol.2010.06.025

Zhang P, Sun H, Yu L, Sun T (2013) Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: Impact of structural properties of biochars. Journal of Hazardous Materials 244-245, 217-224. https://doi.org/10.1016/j.jhazmat.2012.11.046

Zhang Y, Chen P, Liu S, et al. (2017) Effects of feedstock characteristics on microwave-assisted pyrolysis – A review. Bioresource Technology 230, 143-151. https://doi.org/10.1016/j.biortech.2017.01.046

Zhu X, Chen B, Zhu L, Xing B (2017) Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: A review. Environmental Pollution 227, 98-115. https://doi.org/10.1016/j.envpol.2017.04.032