MARSOL

Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought

Guideline for Water Quality Requirements at MAR sites

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Summary: This report is part of the EU-funded MARSOL project (www.marsol.eu, grant agreement no. 619120). The objective of Deliverable 14.4 is to outline aspects most important to water quality in Managed Aquifer Recharge (MAR) and to provide an overview on recent regulations and frameworks incorporating these aspects.

MAR is an increasingly important and wide spread technique in water resources management. The combination of different MAR schemes including water sources and beneficial use and technical solutions provides a high degree of adaptation potential of MAR to nearly all types of local conditions. This high technological variability results in substantial difficulties to regulate MAR technologies with respect to water quality requirements, especially towards the infiltrated water (water source).

The Australian Guideline is a successful example that provides a generalized framework to assess potential risks to human health and environment posed by MAR. In this framework, water quality criteria of the water source are primarily based on beneficial use such as drinking water or water for irrigation. At the same time all environmental values that are met by native groundwater quality need to be protected. Quality requirements based on beneficial uses and environmental values are legally prescribed or subject to corresponding guidelines.

The framework lists potential hazards related to specific beneficial uses and their origin from source water for recharge, native groundwater, and aquifer minerals reacting with recharge water. Source water such as wastewater may include a multitude of pathogens and organic micropollutants such as pharmaceuticals depending on each water's origin and technical treatment. The Australian Guideline suggests that in the best case source water quality comply with quality requirements of the intended end use. If the source water does not meet water quality requirements the reliance on attenuation of hazards within the subsurface has to be analyzed based on risk assessment. The rigour of assessment shall commensurate with the level of risk posed by the respective MAR scheme.

In particular, the percolation through soil (unsaturated zone) in surface spreading methods is applied in MAR to reduce or remove dissolved and suspended contaminants as well as pathogens. However, attenuation capacity may vary considerably depending on site-specific conditions.

A mobilization of heavy metals may occur within the aquifer as a consequence of water recharge. Soil column and batch experiments are a good method to test natural attenuation and emission potential of soil and/or a potential destabilisation of the aquifer matrix under laboratory conditions. As general precaution measures pH and redox status of the infiltrated water should always be adjusted to conditions in the aquifer, and the concentration of labile organic carbon should be reduced.

A more holistic approach is given by the European Water Framework Directive WFD. The directive prescribes that surface bodies are required to meet "good ecological and chemical status" and groundwater bodies "good chemical and quantitative status". In this context, the WFD mentions

MAR as a possible supplementary measure to achieve these objectives. Artificial recharge and augmentation of groundwater require previous authorization and periodical controls ensuring that no deterioration in water status occurs. In this concept, water quality requirements of the water source are primarily oriented towards the status of the receiving environment and therefore, may vary considerably at different locations for one MAR Scheme. MAR schemes must be monitored to ensure that they are consistent with the intent of legislation.

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1 Introduction

1.1 Background

In the last decades water scarcity has become a severe problem not only in the Mediterranean Region but in all arid and semiarid regions. Climate change, irrigation of cropland, urbanization and an increasing water demand are stressors causing a degradation of groundwater resources not only in quantity but also quality. Especially in coastal regions of the Mediterranean Sea groundwater exploitation is closely connected to quality issues. Sea water intrusions are triggered by a negative water balance.

In this context, there has been an increasing interest in the use of alternative water resources. Managed Aquifer Recharge (MAR) represents a historically widespread applied alternative water resource by the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit. As the interest in MAR technologies increases, it is important to establish a framework that implies guidance to avoid potential risks of public health and environment, and enhance beneficial uses for future generations.

MAR is a technique to capture, (naturally) treat, and store excess water in aquifers for a specific purpose (value). However, MAR always has an impact on natural systems, i.e. on the groundwater flow or the water quality, or on both aspects. In particular, the artificial introduction of water, its chemical composition, and the introduction of pollutants as well as hydro(geo)chemical interactions with the aquifer and native groundwater may cause potential risks to public health and environment and therefore require a conjunctive management.

The application of MAR technologies is a wide and interdisciplinary field that brings together different groups of interests (Figure 1). Management strategies such as MAR technologies are primarily limited by environmental capabilities. In particular, the prediction of the storage and emission of potential pollutants is crucial for the design and planning of MAR. Technical solution can be addressed to eliminate, minimize or reduce potential risks to human health and environment, and thereby may support the feasibility of MAR.

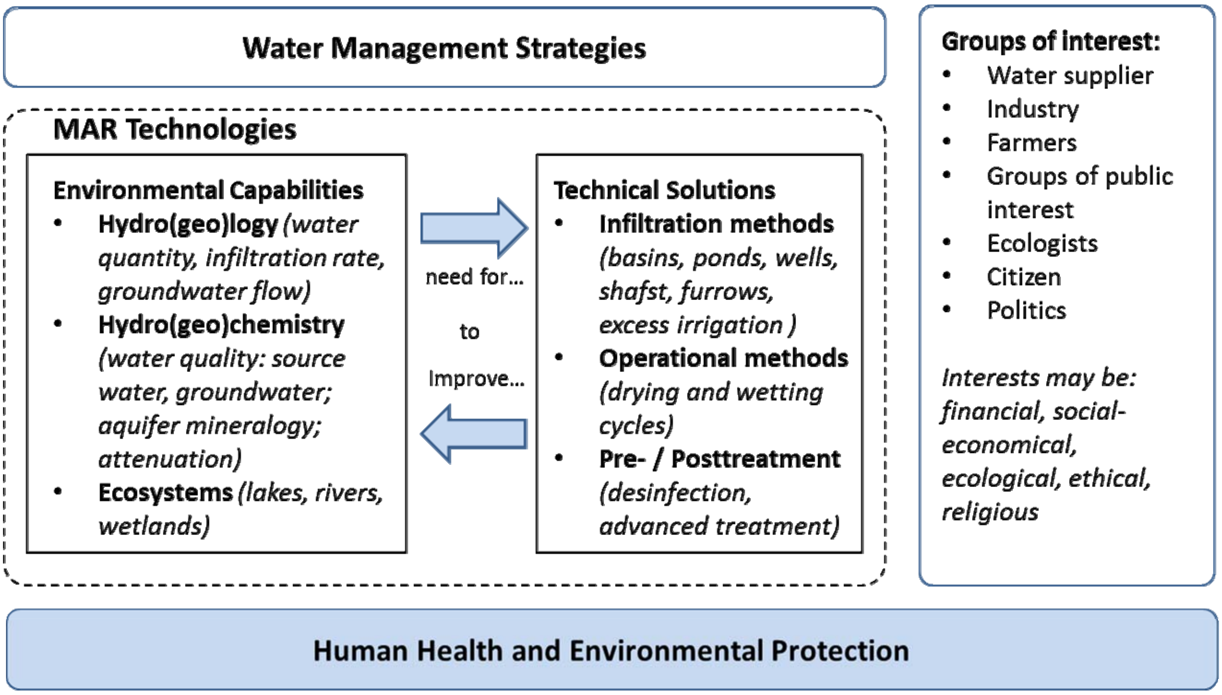

Figure 1: Water management strategies

1.2 Scope of Work

Managed aquifer recharge is defined as "the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit" (e.g. Dillon et al., 2009). This strongly generalized definition stands for a huge variety of MAR schemes encompassing different technical solutions, infiltration techniques, and receiving environments, as well as local and temporal variations. In this context, the quality of the water applied in MAR technologies varies with the water source; it is influenced by the infiltration method and its technical solutions and is subject to hydrochemical processes within the subsurface. Therefore, a generalized set of water quality requirements does not meet this large variety of factors and may lead either to an insurmountable obstacle for MAR when requirements are based on worst-case scenarios, or to high potential risks when related to best-case scenarios. Instead, this report shall give an introduction to aspects most important for water quality requirements, indicating how these are incorporated into recent regulations and what strategies are applied to handle water quality requirements. This approach requires the detailed description of a variety of areas of expertise such as technical solutions or legislative issues for which we refer to other activities within the MARSOL project:

- ✓ D13.1: MAR Technical Solutions (Escalante et al., 2015)
- ✓ D14.1: Recharge Water Constituents: Data base in compounds in different water sources used for MAR from literature and from MARSOL DEMO sites (Kübeck & Bergmann, 2015)
- ✓ D14.2: Risk Assessment report of water constituents for the aquatic environment (Nottebohm & Kübeck, 2016)

- ✓ D14.3: Column Experiment Results: Report on the results of accompanying bench-scale column experiments with soil and recharge water from the Lavrion and Menashe DEMO sites (Silver et al., 2016)
- ✓ D14.4: Water Quality Risks: Risk assessment report for water constituents and degradation products for the aquatic environment and for human health (Nottebohm & Kübeck, 2016)
- ✓ D17.1: Legislative Framework Review and Analysis (Capone & Bonfanti, 2015)

2 Water quality requirements – Definitions

Quality requirements are implemented into frameworks based on water quality criteria, water quality objectives, and water quality standards (Table 1). Water quality criteria establish numerical measures or statements on a designated water use such as drinking water or irrigation. They provide information about the effects of water parameters and pollutants on a specific water use as well as water quality requirements for environmental protection. Thus, quality criteria may be applied to

- ✓ set maximum levels for a substance concentration at which it will not be harmful if continuously applied for a specific use, or
- ✓ set a minimum acceptable concentration to maintain biological functions of biota or ecosystems (WHO 1997).

In the last decades, there has been an increasing interest in developing water quality criteria for hazardous substances, in particular micropollutants such as pharmaceuticals, pesticides and Industrial chemicals. Although concentrations are low (ng/l to µg/l) for most of these compounds, many of them raise considerably concerns as a consequence of their toxicity, carcinogenic/mutagenic effects, potential to bio-accumulate and/or persistence in the environment. The regulation of micro-pollutants is complex due to their huge number and the diversity of chemical substances and their various entry paths into the aquatic environment (Schwarzenbach et al., 2006).

Water quality criteria are often used to establish water quality objectives in connection with information on water uses and site specific factors. Thus, water quality objectives provide allowable “limits or levels of water quality constituents or characteristics that are established for the reasonable protection of beneficial uses of water or prevention of nuisance within a specific area” (CalEPA, 1969). In contrast to water quality criteria, the establishment of water quality objectives is a political process that encompasses an assessment of national priorities and economic considerations. Water quality objectives can be applied as a planning or regulatory instrument in terms of water quality standards. In general three different approaches are applied to implement quality criteria into frameworks (CCME, 2003), based on:

- ✓ Technology: Limit values for hazardous discharges are based on the definition of what can be reasonably achieved in a technically and/or economic sense.

- ✓ Value-Protection: Limit values for hazardous discharges are established to ensure beneficial use or environmental values are not compromised.
- ✓ Non-Degradation: Discharge limits are established based on natural background levels of substances of concern at sites and has been adapted primarily to waters of high environmental value.

The development of quality criteria for hazardous substances is based on comprehensive laboratory studies assessing the impact on aquatic organisms, combined with literature studies. In addition to that, the precautionary principle allows taking action if a high risk of severe harm to public or environment is suspected. A scientific consensus or proof of harm is not necessary at this stage.

Table 1: Definitions related to water quality and pollution control (adapted from WHO, 1997)

Term	Definition
Water quality criterion	Recommendation of numerical measures or narrative statement for support and maintain of a designated water use (synonym: water quality guideline)
Water quality objective	Numerical measures or narrative statement established to support and protect the designated uses of water at a specific site (synonym: water quality goal or target)
Water quality standard	Objective recognised in environmental control laws or regulations of a level of government
Precautionary principle	Action to avoid adverse impacts of hazardous substances that scientific research has not fully proved a causal link between substances and potential adverse impact

3 Overview – Water Quality Guidelines

This section gives a general overview of water quality guidelines and their purposes. Guidelines in general represent a successful attempt to determine a course of action and enhance the regulation by a framework. Water quality guidelines are descriptive statements that may include numerical measures, e.g. concentrations. Although guidelines are not binding, they are often used as a basis for the establishment of regulations and standards on a national (or provincial) level. More specifically, water quality guidelines imply science-based levels of physico-chemical, biological and chemical parameters for the protection of human water uses (values) such as:

- ✓ Drinking water supply,
- ✓ Food related industry supply (e.g. irrigation, stock watering, food production),
- ✓ Non-food related industrial water supply and
- ✓ Recreational use (e.g. swimming and boating)

Each of these values requires specific guidelines since measures stated for one value may not be sufficient for another one. In example, water used for irrigation has to fulfil water quality criteria avoiding the accumulation of salt within the soil but do not necessarily meet criteria for drinking water. In some cases, criteria for chloride and sodium concentration may be even stricter for irrigation water than for drinking water (Annex 2).

Water quality guidelines for aquatic ecosystem protection and maintenance are more complex since natural variations such as water type, climate, topography and/or vegetation require ecosystem-specific indicators.

In literature, two approaches for the development of water quality guidelines are recommended, a) guidelines based on direct impact studies (assessment) and b) guidelines based on referential approach (EHP, 2009):

a) The direct impact study analyses the relationship between the indicator and the observed value in question (criteria). Based on this relationship the pressure of the indicator can be determined and level identified which is acceptably safe (objective).

b) The referential approach is applied for indicators that cannot be described by a simple direct impact approach as they are determined by the condition of that indicator or the acceptable departure from reference conditions (undisturbed conditions). This approach is often used for aquatic ecosystems.

Water quality requirements may be specified as maximum (e.g. concentrations of constituents) or minimum (e.g. acceptable concentration) or define an ideal status, often with inclusion of safety factors. As a consequence, water quality requirements of one specific parameter can vary by as much as ten times from one guideline to another (e.g. Drinking water: WHO (2011)/98/83/EC in Annex 2).

To be able to make a precise judgement on the suitability of water quality for protection value following information are essential (DWAF, 1996):

- ✓ characterisation of the water use or specific ecosystem from a water quality perspective,
- ✓ determine quality requirements of the intended use/ecosystem, and
- ✓ obtain key indicators that determine the suitability for its uses and/or health of aquatic ecosystems.

It is necessary to establish - but often not part of specific water quality guidelines - how and how much the intended use or aquatic ecosystem may be affected by the prevailing water quality or the change due to anthropogenic interventions such as MAR systems. In this context, undesired effects of water quality on particular uses have to be identified, and it has to be determined how these can be mitigated.

4 Managed Aquifer Recharge – Available Guidelines, Legislation and Studies

4.1 Available Guidelines – Australian Approach

In the last decade, Australian administration developed a series of guidelines to provide an authoritative framework for sustainable recycling of water (intended use for storm water, greywater and treated wastewater). The "Australian Guideline for Water Recycling: Managing Health and Environmental Risks" covers in document "Phase 1" water quality issues related to the application of water sources and adjacent uses in general. The additional document "Phase 2" extends the guidance provided in "Phase 1" on the use of recycled water to:

- ✓ augmentation of drinking water supplies (module 1; NRMMC-EPHC-NHMRC, 2008),
- ✓ storm water harvesting and reuse (module 2; NRMMC-EPHC-NHMRC, 2009), and
- ✓ **Managed aquifer recharge** (module 3; NRMMC-EPHC-NHMRC, 2009).

The guidelines are based on a risk management approach that involves three categories: a) assessing risks, b) managing risks, and c) monitoring and reviewing risks. The multi-barrier approach is included into the Australian Guideline covering the need to imply and continuously maintain robust and reliable barriers to prevent risks on a broader level.

4.2 EU – Legislative Framework

As part of the outcomes of EU Project MARSOL (Deliverable D17.1) the current legislative framework of different MAR technologies has been reviewed and analysed for Europe and extra-EU countries (Capone & Bonfanti, 2015). It could be clearly shown that despite being widely adopted in several countries, MAR technologies are not soundly regulated. The EU "Water Framework Directive" (2000) considers MAR technologies as a possible measure to achieve the "good status" objective for water bodies, but does not specify implementation strategies. MAR techniques are regulated marginally in laws that focus on water management and/or protection of environment. In particular, procedures of granting authorisations fall within environmental laws addressing water discharge, drilling, and groundwater abstraction.

In addition, it was found that community awareness and involvement regarding the implementation process of MAR technologies seems to be insufficient. However, the acceptance and support by the various stakeholders is vital for a successful introduction of MAR technology and adherent reuses (Dillon et al., 2009). Provision and transfer of information should be transparent in order to gain support from crucial sectors of the community and stakeholders including industry, commercial interests, landowner and developers. A comprehensive framework outlining the implementation procedure and potential risks of MAR could be beneficial to improve the awareness towards these technologies as it is still a sparsely developed field.

4.3 Scientific Studies

Managed aquifer recharge requires a detailed understanding of chemical, biological and physical processes occurring in water treatment trains and aquifer. A fundamental contribution to understand these processes has been done by a growing number of MAR projects observing MAR for a very wide range of source water, infiltration/discharge methods, aquifer types and protection values. Since 2005 twelve projects including the MARSOL project have been funded by the EU:

- ✓ DESSIN: Demonstrate ecosystem services enabling innovation in the water sector (2014 – 2017)
- ✓ DEMOWARE: Innovation demonstration for a competitive and innovative European water reuse sector (2014 – 2016)
- ✓ DEMEAU: Demonstration of promising technologies to address emerging pollutants in water and waste water (2013 – 2015)
- ✓ NaWaTech: Natural water systems and treatment technologies to cope with water shortage in urbanized areas in India (2012 – 2015)
- ✓ PREPARED Enabling Change (2010 – 2014)
- ✓ SAPHPANI: Enhancement of natural water systems and treatment methods for safe and sustainable water supply in India (2011 – 2014)
- ✓ ENSAT: Enhancement of soil aquifer treatment to improve the quality of recharge water in the Llobregat river delta aquifer (2010 – 2012)
- ✓ TRUST: Tool for regional-scale assessment of groundwater storage improvement in adaptation to climate change (2009 – 2011)
- ✓ RECLAIM WATER: Water reclamation technologies for safe artificial recharge (2005 – 2008)
- ✓ GARBADINE: Groundwater artificial recharge based on alternative sources of water: advanced integrated technologies and management (2005 – 2008)
- ✓ AQUAREC: Integrated concepts for reuse of upgraded wastewater (2003 – 2006)

An important point of these projects is the ability to synthesise results across a variety of MAR sites and the use of laboratory methods such as batch and column experiments to fill in scientific gaps that cannot be easily observed under field conditions (Kazner et al., 2012, RECLAIM). The MARSOL project analyses at eight demonstration sites different MAR techniques applied under various geological, hydrological and hydrochemical conditions. An important part of work package 14 (Water Quality) of the MARSOL project was to gain insights into changes in hydraulics and water quality using different source waters and recharge conditions. In this context, column experiments were used as a model to simulate field conditions but have the advantage of being conducted under controlled conditions which can easily be changed. Results are summarized in MARSOL deliverable D14.3 (Silver et al., 2016).

Special attention in the MARSOL project as well as in the DEMEAU project was paid to the capability of infiltration methods to retain emerging pollutants (micropollutants). Within the DEMEAU project, it was pointed out that optimum MAR characteristics cannot be identified for trace organics and other pollutants as retention capacity of MAR technologies are depending on a suite of variables and therefore are strongly site-dependent (Vilanova et al., 2013). In this context, a generalized definition of water quality requirements – especially for micropollutants – is not possible.

Within the AQUAREC project (EU-FP5) a general guideline for water quality requirements for wastewater reuse in Europe has been developed (Salgot & Huertas, 2006). This report provides a set of microbiological and chemical limits and limit ranges based on regulations and developments. Limits are primarily related to direct application for irrigation purposes, impoundment, and discharge into surface water bodies. The authors recognise MAR technologies for two specific cases:

- ✓ aquifer recharge by direct injection into the soil for irrigation purpose, and
- ✓ aquifer recharge by localised percolation through the soil.

Microbial and chemical requirements for water sources used in MAR for irrigation purpose are most stringent (Annex 1). Sum parameters are applied for organic compounds including surfactants and mineral oil.

A more generalized approach is provided by Bixio & Wintgens (1998, in Kazner et al., 2012), suggesting quality goals of pre-treatment strategies with respect to MAR technologies. In this study the authors distinguish between:

- ✓ direct recharge of groundwater into the subsurface using recharge wells, shafts or dug wells, and
- ✓ indirect infiltration where groundwater is mainly augmented by means of ditches, pipes, or basins.

Quality requirements are listed in Annex 1.

5 MAR Technologies - Water quality requirements

The concept of MAR brings together different aspects of water quality requirements including:

- ✓ Operational MAR scheme
- ✓ Technical solutions including infiltration methods
- ✓ Receiving environment

Together these aspects determine the feasibility of MAR with respect to human health and environmental protection. In order to evaluate the feasibility of MAR technologies, the “Australian Guideline for Water Recycling” provides a water quality assessment of recycled water systems, which should be carried out before management risk assessment. In the following chapter water quality aspects addressed within the Australian Guidelines are summarised and extended by European legislation and recent studies.

5.1 MAR Schemes

According to the "Operational Policy 1.01 Managed Aquifer Recharge MAR" document (WHO, 2011b) MAR schemes are defined by a) water source and b) protection values (end-use).

5.1.1 Water sources

The Australian "Phase 2" Guideline covers all types of source water for MAR including:

- ✓ Water recycled from storm water, greywater and wastewater (see also "Phase 1"),
- ✓ Water from streams and lakes,
- ✓ Groundwater drawn from aquifers
- ✓ Water from the drinking water distribution system (e.g. desalinated seawater)

These water sources are characterized by the occurrence of a large number of organic and inorganic substances, dissolved gases and suspended particles. As described in the MARSOL deliverable D14.1 (Kübeck et al., 2015) the hydrochemical properties represent a fingerprint of each water source's origin, transport processes and/or technical treatment, which is very complex as many factors affect the composition of these waters. A principle flow chart is shown in Figure 2 which includes most important impacts and interactions on water composition of water sources used for MAR schemes. More complicating, a mixture of different water sources such as surface water and reclaimed water (storm water and wastewater) is often used in MAR schemes (Escalante et al., 2015).

Recycled Water

In particular, treated wastewater may obtain a wide range of harmful substances. However, water quality and treatment requirements differ as objectives/standards are not regulated in a uniform manner (see Chapter 2):

a) **Technological quality requirements** specify required technologies or processes such as biological treatment, however, do not establish water quality limits of the effluent.

b) **Effluent quality requirements** imply physical, biological and chemical criteria of the effluent. In general, allowance concentration of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), nitrogen and phosphorus concentration are established. **Uniform effluent criteria** are often applied, in which target concentrations of specific parameter are standardized. In contrast, **ambient or stream quality criteria** fix quality requirements of the (treated) wastewater depending on the receiving water body.

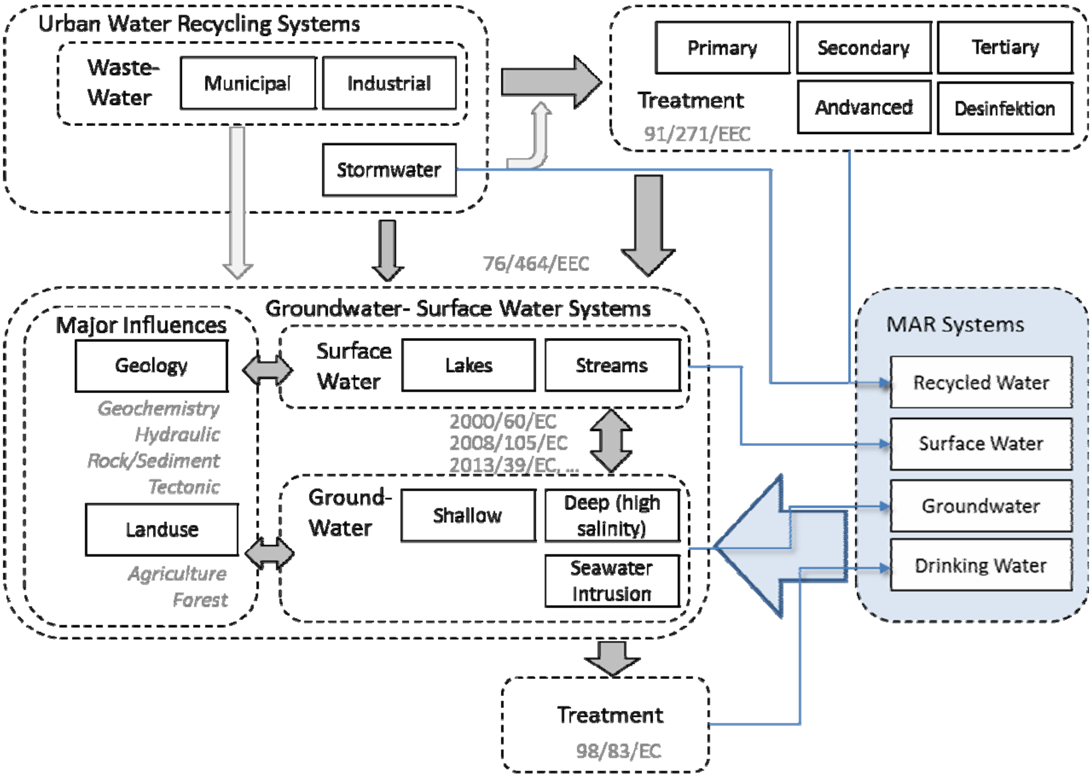

Figure 2: Potential water sources for MAR technologies as a part of the urban and rural water cycle including EU regulations on water quality requirements.

In Europe, collection, treatment and discharge of wastewater into the environment is regulated by the Council Directive 91/271/EEC concerning wastewater treatment. The regulation implies a reduction of nutrients and organics (Table 2); limit values are listed in Annex 1.

Table 2: Regulated quality parameters in treatment plant effluent and their influence on natural aquatic systems.

Parameter	91/271/EEC Min. Reduction [%]	Treatment step
Suspended particles	70 - 90	Primary treatment (mechanical)
Biodegradable organics BOD_5 at 20°C COD	 70 - 90 75	Secondary treatment (biological)
Nutrients P total N total	 80 70 - 80	Advanced secondary treatment (chemical: flocculation, degassing, filtration)
Pathogenic bacteria and other disease-causing organisms		Third treatment (disinfection: ozonization, chlorination, filtration)

BOD_5 biochemical oxygen consumption after 5 days, COD chemical oxygen demand

Directive 76/464/EEC deals with the control and discharge of dangerous substances into the environment which are regarded due to their toxicity, persistence and bio-accumulation. Community controls including limit values are laid down in Daughter Directives listed in Table 3. As part of the ongoing restructuring of the EC water policy, Directive 76/464/EEC has been integrated into the Water Framework Directive (2000/60/EC) and has now been codified as 2006/11/EC water protection and management.

Table 3: Daughter Directives of 76/464/EEC and regulated substances.

Substance and related compounds	Council Directive	Emitter
Mercury	82/176/EEC	Chloralkali electrolysis industry
Cadmium	83/513/EEC	
Hexachlorocyclohexane	84/491/EEC	
1,2-Dichloroethane Trichloroethylene Perchloroethylene Trichlorobenzene	86/280/EEC Amended by: 88/347/EEC 90/415/EEC	

Surface Water and Groundwater

In terms of MAR schemes, surface water and groundwater act as potential water sources as well as protection value. Thus, environmental laws such as “Clean Water Act” (US EPA, 1972) provide national controls to protect water bodies. In Europe, quality parameters of surface water and groundwater are regulated by “Water Framework Directive” 2000/60/EC and discussed in Chapter 5.1.4.

The physico-chemical composition of surface water and groundwater may vary considerably since surface waters in rivers, streams (and lakes) provide a mixture of diffuse surface run-off intake, and point sources such as the discharge from wastewater treatment plants (municipal and industry). Emitted pollutants are expected to be more rapidly diluted and decomposed due to constant mixing and oxygen supply, respectively. However, the input of pollutants can be immense since major sources such as cities and industry have been located historically along rivers and streams. In addition, agricultural activities are often concentrated near rivers due to fertile soils of floodplains and easy access to water.

The interaction between surface water and groundwater systems results in an exchange between both compartments. Thus, the infiltration of shallow groundwater into surface water may lead to an inflow of water with high nutrient concentrations. The other way round surface water may introduce anthropogenic micropollutants into the groundwater system.

During transport, surface water and groundwater react with solid phases that occur in the rock and sediment of the riverbed and aquifer, respectively, and dissolve a wide range of substances leading to a sequential alteration of water quality depending on geological and morphological conditions.

Drinking Water

The application of water from the drinking water distribution system represents a special case applied, e.g., in Israel (s. MARSOL deliverable D14.3). Water for drinking purposes do not pose a risk to human health, but may imply different risks to specific ecosystems due to the lack of agents (e.g., salinity in salt water ecosystems).

Nowadays, for drinking water international standards do not exist which are universally accepted. Many developed countries established water quality standards for drinking water enshrined in directives such as:

- ✓ **Europe: European Drinking Water Directive (98/83/EC, put into national legislation)**
- ✓ USA: Safe Drinking Water Act (US EPA, 1996)
- ✓ China: Environmental quality standards for surface water (GB3838-2002 Type II)
- ✓ Russia: Sanitary hygienic rules and norms SanPin

Guidelines provide an authoritative reference to the communities and water supply industry on safe and good drinking water quality and how it can be achieved/assured:

- ✓ Canada: Guideline for Canadian Drinking Water Quality (Federal-Provincial-Territorial Committee in Drinking Water (CDW))
- ✓ Australian Drinking Water Guideline (Australian Government)
- ✓ Guideline for Drinking-water Quality Management for New Zealand (New Zealand Government)

The World Health Organization (WHO) provides international guidelines on water quality and human health used as a basis for the world-wide establishment of regulations and standards: Guideline for Drinking water quality (WHO 2011).

5.1.2 Protection Values

Protected values of a MAR scheme refer to the beneficial use/end-use of water. In current recharge applications different goals (and purposed endpoints) are envisaged such as (Figure 3):

- ✓ Water for domestic use (drinking water) (=> Humans)
- ✓ Industrial use and fire control (=> Industry, Infrastructure)
- ✓ Irrigation supply (=> Plants *(Biota)*)
- ✓ Wetland restoration and maintenance (=> Biota)
- ✓ Recreational purposes (=> Biota, Humans)

Water quality requirements have to be defined for the protection value of water based on national regulations, guidelines, or best practice. Therefore, the end-use of water has to be characterized and requirements defined in detail (see example Info-Box 1).

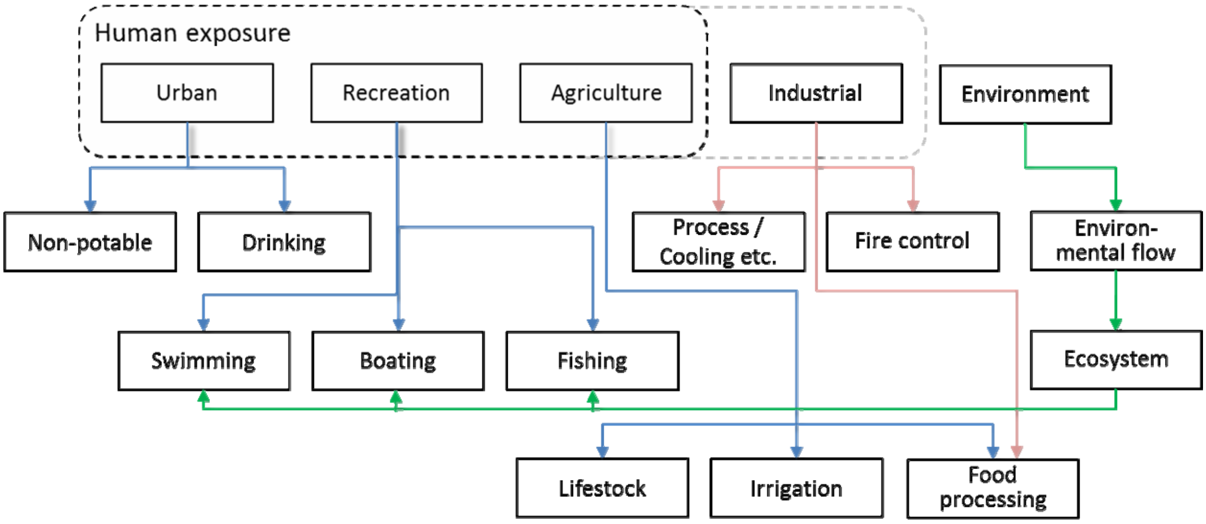

Figure 3: Protection values (adapted from WHO 1997).

Although water may be used for a wide range of activities, regulation should follow the end-use of most stringent quality requirement. However, goals such as:

- ✓ improvement of the groundwater quality (=> Groundwater)
- ✓ environmental flow (e.g. seawater barrier) (=> Groundwater)

are more complicated and depend on local issues. Especially MAR technologies used to improve groundwater quality should be viewed in a critical light as it may obscure actual problems posed, e.g., by intensive agriculture but do not offer a solution to environmental issues.

Info-Box 1: Example: Water for Domestic Use and Water for Irrigation

Domestic Use

The supply of water for domestic use is common to all consumers and provides the widest experience of effects of water quality. In the domestic environment water is used for:

- ✓ Drinking purpose
- ✓ Preparation of food
- ✓ Bathing and personal hygiene
- ✓ Cleaning purpose (e.g. dish and laundry)
- ✓ Gardening and animal care (fish ponds)

Although domestic water is used for a wide range of activities, it follows most stringent quality requirement for drinking water. An exception are households with a separate greywater or rainwater system used to supply water of a less high quality for purposes such as toilet flush or cleaning. Here water quality requirements are determined in guidelines for recycled water schemes.

Irrigation

Poor water quality may impact agricultural cultivation due to an accumulation of salt in the root zone or contamination with pathogens or contaminants which may be directly toxic to plants or those consuming them. An accumulation of salt or contaminants in the soil may render the soil unfit for agriculture after a period of years (WHO, 1997). Guidelines about water quality criteria for irrigation water are available for many countries but differ considerably due to different annual application rates. Annex 2 shows a direct comparison of water quality criteria posed for agricultural irrigation by DWAF (1996) for South Africa and drinking water standards of the EU and proposed by WHO. For metals considerably higher concentrations are allowed, however, reference was made to clogging caused by high iron and manganese concentration. A restriction for micropollutants is not provided.

5.1.3 Routes of Exposure

The assessment of potential exposure "is the determination if the emissions, pathways and rates of movement of a substance and its transformation or degradation, in order to estimate the concentrations/doses to which human population or environmental compartments (water, soil, air) are or may be exposed" (EC, 1996). An expose of people to recycled water may occur via ingestion, inhalation or contact with skin. The greatest risk is represented by ingestion of pathogens and chemical contaminants. Potential environmental effects are site-specific and may include factors such as:

- ✓ Hydrochemical characteristics and proximity of receiving waters (surface water and groundwater)
- ✓ Geochemical characteristics of soils and aquifer at point of application
- ✓ Site hydrology (soil/aquifer permeability, groundwater flow direction)
- ✓ Climate conditions and evaporation

Although MAR technologies focus on intended uses, the Australian guidelines point out that an inadvertent or unauthorised use cannot be excluded and should be considered in risk assessment.

5.1.4 Key Hazards

The Australian Guideline for Water Recycling (NRMMC-EPHC-NHMRC, 2006/2009) gives an overview of "key hazards" posed by different water sources applied in MAR schemes. Key hazards that are associated with MAR are agents (biological, chemical, or physical) that have the capacity of adverse consequences to human health or the environment (endpoints, DSE-VIC, 2006) (NRMMC-EPHC-NHMRC 2009):

- ✓ Pathogens (bacteria, viruses, protozoa)
- ✓ Inorganic chemicals (i.e. nutrients, salinity, hardness, metals)
- ✓ Organic chemicals (detergents, industrial chemicals, biologically active compounds, pharmaceuticals, disinfection by-products)
- ✓ Turbidity and particles
- ✓ Radionuclides.

A more detailed description for hazards potentially occurring in water sources is given in Info-Box 2. Potential variations in concentration due to seasonal and event changes (extreme and infrequent events such as droughts or floods) including occurring peak concentrations should be considered. Therefore, historical data of water source quality should be collected and analysed by evaluating the reliability of data and identifying data gaps. If needed additional analyses have to be conducted. Based on this, trends in water quality should be identified.

Info-Box 2: Key hazards – introduced by source water (Nottebohm & Kübeck, 2016)

Pathogens: The highest amounts of pathogens can usually be found in (treated) wastewater and greywater, but also in surface waters pathogens may be present.

Inorganic Chemicals: In terms of key hazards only such ions are considered that may pose an effect on human health and the environment.

Nutrients: Highest concentration of nutrients such as nitrogen, phosphorus and dissolved organic carbon are present in (treated) wastewater. However, high concentration can be also found in shallow groundwater in agricultural dominated areas. Nutrients such as nitrogen are problematic, as specific nutrient species present at defined *redox potential* (ammonium, nitrite) show toxic effects at relatively low concentrations, whereas others (nitrate) can be tolerated at higher concentrations. However, *redox conditions* of surface water should be clearly oxidic. Exceptions may be organic rich waters with low flow velocities or stratified surface waters.

Salinity: The use of ion exchange reagents (water softeners) in households and industry can cause high concentrations of chloride in (treated) wastewater. Deep groundwater or groundwater bodies affected by seawater intrusion my also show high salinity. In coastal areas storm water may be influenced by an airborne discharge of salt from sea water spray.

Metals and metalloids: In particular industrial wastewater may show high concentration of heavy metals. High amounts can be also allocated to specific geological regions. Whether metals are dissolved or precipitated depends on *pH and redox conditions*.

Gases: The occurrence of gases in the water is mainly influenced by the *redox conditions*. Thus, gases such as methane and hydrogen sulfide arise at strongly reducing conditions in the presence of organic compounds. During treatment municipal wastewater undergoes the process of degradation of organics where methane and hydrogen sulfide may be formed. An adjacent aeration should establish oxidic conditions eliminating these gases.

Organic chemicals: There is a vast number of naturally occurring and artificially introduced organic compounds that have the potential to harm human health and the environment, including pesticides, pharmaceuticals, and industrial agents. A list of the micropollutants and their measured environmental concentrations in different source water is given in MARSOL deliverable D14.1 (Kübeck & Bergmann, 2015).

In particular the elimination of micropollutants in current wastewater treatment plants including primary, secondary and advanced secondary treatment is often incomplete. As a consequence, the effluent of treatment plants may contain a variety of micropollutants with concentrations ranging from ng/L to µg/L. Therefore, additional treatment steps including ozonation, filtration, UV disinfection, coagulation-flocculation etc. are in discussion for many wastewater treatment plants.

Turbidity and particulates: Treated wastewater may show a high turbidity depending on treatment processes. In surface water, the turbidity level may be caused by growth of phytoplankton. In addition, human activities that disturb land such as construction, mining, and agriculture as well as natural erosion can lead to high sediment levels in storm water and surface waters.

Radionuclides: Radionuclides (e.g. uranium, potassium-40) occur naturally in the environment and can as well be released by human activity such as industrial and medical use of radioactive materials.

6 Water Pollution Control

Regulatory frameworks apply different approaches of water pollution control such as:

- ✓ Control of discharge at source (emission approach)
- ✓ Managing the receiving environment (ambient water quality approach)

Initially water pollution control was focused on the emission approach applying uniform emission or discharge requirements. Recently, emphasize is shifting to an integrated approach where specific emissions are set in individual permits based on pertinent ambient water quality requirements. Since discharge requirements are determined by the receiving environment, the ambient water quality approach may lead to different regulatory conditions for similar MAR schemes in different environmental conditions.

However, for pollutants that accumulate within the environment an emission control is essential. Thus, regulations such as European Water Framework Directive imply both approaches: emission level and ambient water quality approach.

6.1 Australian Guidelines

For key hazards, the Australian Guidelines propose an entry level assessment based on the water quality requirements of the protection value (emission approach) to evaluate the feasibility of MAR schemes. If the quality requirements of the entry level assessment are not fulfilled, further research on risk assessment and preventive or protective efforts during MAR operation has to be realized. In this context, water quality requirements of protection values should be reached prior to infiltration which neglects potential treatment capacity of the underground passage as an important barrier for microbial and chemical constituents. In this case, water quality requirements for MAR are primarily based on current guidelines or regulations for specific protection values such as drinking water abstraction or irrigation (Annex 2). In this context, water quality requirements may vary considerably for different MAR schemes independently from natural conditions of the receiving environment.

6.2 Europe Water Framework Directive

In Europe, the Water Framework Directive (WFD) has a central role for environmental protection, and therefore, the application of MAR technologies. The framework does not adopt the limit value approach, but provides strategies to establish good qualitative (ecological and chemical) and quantitative status of all water bodies. The ecological and chemical status are assessed according to a) biological aspects such as the abundance of fish, benthic invertebrates, and aquatic flora; b) hydro-morphological conditions such as quantity and dynamics of water flow and the interaction between surface and groundwater bodies; c) physicochemical properties of the water including temperature, salinity, oxygen, and nutrient concentrations; and d) chemical status referring to all identified priority substances being discharged into the water body. An initial characterization shall be conducted by the EU member states to assess the degree of which water bodies are at risk and on potential changes in their status. In these analyses existing hydrogeological, geological and pedological aspects, land use, discharge and abstraction shall be identified. In order to evaluate the magnitude of chemical stressors, priority substances and other significant pollutants shall be monitored. The directive assigns the following set of core parameter for monitoring groundwater bodies: oxygen content, pH, conductivity, nitrate and ammonium. In Table 4 EU regulations are listed for different protection values.

The Water Framework Directives sets the objectives for protection and sustainable use of all water ecosystems in a more holistic manner by setting ambient water quality and source specific emission objectives. For chemical status, a procedure has been established by:

- ✓ Identification of priority hazardous substances for which zero emission are targeted for 2020 (emission approach)
- ✓ The EU Council identifies a list of priority substances and proposed ambient quality objectives, based on the protection of aquatic ecosystems and human health
- ✓ The EU member states set ambient quality standards based on aquatic ecotoxicity

In the Environmental Quality Standard Directive 2008/105/EC, European Parliament and Council identify 33 substances or groups of substances of prior concern including plant protection products, biocides, metals and other groups such as polyaromatic hydrocarbons (PAH) and biphenylethers (PBDE) used as flame retardants. This list has been extended by 12 substances (2013/39/EC) and existing standards have been deepened. The issue of nitrate from agricultural sources is covered by the Nitrates Directives 91/676 and 1882/2003. In this context, the WFD provides a general framework to assess and monitor MAR technologies in terms of potential stressors to water bodies.

Under Article 5 of the WFD, member states of the EU are requested to develop a risk assessment for groundwater bodies. A review of the reported risk assessment has been done in the CIS Guidance Documents (EC 2004/2010). Here groundwater pollution risk is defined by "the actual/potential consequence on the health of a specific receptor" (protection value) "arising from a specific source via defined subsurface pathways" (EC, 2004).

Table 4: Protection values and EU regulations.

Protection values	Regulation on water quality requirement
Water Framework Directive (WFD 2000/60/EC)	A framework for the protection of inland surface water, transitional waters, coastal waters and groundwater has been established by WFD to prevent and reduce pollution, promote sustainable water use and protects aquatic environment and improve the biological and chemical status of aquatic ecosystems. The framework does not provide standards and limit values, however, describes steps to establish good qualitative (biological and chemical) status of all water bodies and sets a time schedule to achieve this goal.
Drinking water	Directive 98/83/EC defines the basic standards for water intended for human consumption. Member States of the EU may include additional quality standards specific to regional conditions as long as this results in higher standards.
Bathing water	The Bathing Water Directive (2006/7/EC) was adopted to enhance public health and environmental protection.
Groundwater	Directive 2006/116/EC provides specific criteria for assessing the good chemical status of groundwater bodies and identifying trends. Pollutant limitations are set by Member States of the EU. Exceptions to this are nitrates and pesticides which are set by the EU legislation. The Nitrates Directive (91/676 and 1882/2003) covers the protection of waters from nitrates from agricultural sources. It is extended by regulation 2004/648/EC that restricts phosphates in detergents.
Surface water and aquatic ecosystems	Legislations for the protection of surface water from 1970's have been replaced by WFD. Directive 2008/105/EC presents a list of 33 priority substances and 8 other pollutants which is extended by Directive 2013/39/EU that introduces additional 12 substances to the current list.
Irrigation	No specific regulation.

The WFD recognises that greatest protection would be achieved by defining criteria values at the level of the environmental quality standard for the receptor or a relevant protection value. However, criteria might not be in all cases so strict due to dilution and natural attenuation processes that occur between recharge zone and the receptor (EC, 2000).

6.3 Risk Assessment

Water quality requirements can be expressed by health based criteria (WHO, 2011) or environmental protection criteria that are established based on judgement of safety and on risk assessment of water borne hazards. The description of the level of, e.g., health risks in terms of water quality are expressed by specific health outcomes. Thus, the impact of water of an inadequate quality on human health can have various severities and clinical significances, ranging from asymptomatic infections to acute or chronic illnesses and death. In order to assess the risks MAR pose it is necessary to apply appropriate statistics, depending on the types of effects that are likely. Recently, there is no international standard to define or measure health risks, whether related to drinking water consumption or other factors. Most risk measures applied in quantitative risk assessment primarily analyse probabilities of impacts and do not consider diversity of nature and magnitude of adverse health consequences (Havelaar & Melse, 2003).

The disability-adjusted life years (DALY) approach is a measure of years of healthy life lost due to premature death (YLL) and poor health or disability (YLD). The YLD measures the number of years enduring a disability weighted in terms of severity of the disability. Thus, the DALY characteristic of a hazard provides a basis for risk assessment defining a tolerance level. In order to calculate DALYs caused by water contaminants or any other agents, the number of people experiencing each outcome is required based on medical registration or surveys. The number can also be obtained by combining exposure risk or dose-response relation with data of adverse health outcome. By using DALYs, reference levels of different risks can be obtained. Thus, microbial risks are mostly expressed by annual individual probability of infection for a given exposure. In contrast, chemical risks related to genotoxic cancerogens are described as an increase of cancer incidence to lifetime exposure.

The identification of environmental targets is more complex since hazards may be biological, chemical or physical agents as well as situations that may lead to harm or specific conditions under which agents may cause adverse effects. A guideline for risk assessment and management is given by Gormley et al. (2011). Environmental risk assessment for chemicals is generally based on comparing exposure with an effect threshold (predicted no-effect concentration: PNEC). Exposure assessment of micropollutants such as pharmaceuticals and industrial agents introduced by wastewater ("down-the-drain") is commonly based on the calculation of predicted environmental concentration (PEC; EC Directive 93/67 and Regulation 1488/94). This approach is based on a simple ratio of per capita consumption and per capita domestic water use, adjusted by removal during sewage treatment and dilution in the receiving environment (using a generic dilution factor, e.g. 10). This approach is adequate to calculate average concentrations of substances at a large scale but do not consider local and temporal variations. Therefore, measured environmental concentrations (MEC) are compared with PNEC data at specific sites. This approach was also applied for the demonstration sites of the MARSOL project, in the frame of project deliverable D14.2 (Nottebohm & Kübeck, 2016).

7 Receiving Environment and MAR Technologies

MAR technologies involve an artificial introduction of water into the underground that impacts the receiving environment. On the other hand, the receiving environment may influence a planned MAR scheme and its feasibility with respect to water quality aspects. Type, intensity and likelihood of impacts may differ between various infiltration methods.

A general overview of infiltration methods is given by NRMMC-EPHC-NHMRC (2009). In the MARSOL project, technical and operational solutions are described in deliverable D13.1 and are summarised for the most important categories in terms of water quality requirements in Info-Box 3.

All infiltration methods involve the aquifer (saturated zone) as the "targeted" receiving environment, but show differences in the inclusion of additional environmental compartments such as air, soil (unsaturated zone), and surface water systems (ecosystems) primarily for the spreading methods. An exception to this is irrigation which is applied to plants, but can also be used in terms of excess irrigation for replenishment of groundwater bodies. Similarly, MAR technologies appear as point or diffusive source. In particular, the diffusive discharge due to irrigation or flooding may pose a high environmental risk as source water – and, with this, pollutants – is spread over a large area of land (Table 5).

Table 5: Characterisation of infiltration/recharge methods

Method	Point/Line/ Diffusive	Vegetation	Receiving environment		Evaporation/ Transpiration
			targeted	inadvertent	
Surface Spreading Method (Direct Method)					
Irrigation	Diffusive	Yes	Soil (plants)	Air, groundwater, surface water	Yes (high relevance)
Ditch/Furrow Systems	Line	Yes	Groundwater	Soil	Yes
Flooding	Diffusive	Yes	Groundwater	Soil	Yes
Basin (natural)	Point	Yes	Groundwater	Soil	Yes
Basin (constructed)	Point	No	Groundwater	--	Yes
Subsurface Spreading Method (Direct Method)					
Well (ASR)	point	No	Groundwater	--	No
Well (ASTR)	point	No	Groundwater	--	No
Pits / Shafts	Point	No	Groundwater	--	Yes
Induced Recharge (Indirect Method)					
Well Galleries	Diffusive	Yes	Groundwater	--	(Yes)
Dams	Diffusive	Yes	Groundwater	--	(Yes)

Info-Box 3: Infiltration / recharge methods applied in MAR technologies

Spreading Method

One of the oldest and most widely applied technique is the spreading method where groundwater is augmented using a system of ditches, furrows or basins. In agricultural dominated areas artificial recharge can be obtained by excess irrigation. Areas with a flat topography are favourable for flooding techniques. These spreading methods require a large surface zone with unconfined aquifers and without impervious layer above it. Thus, the most favourable method is basin infiltration as this allows efficient use of space, infiltrate of large quantities of water at low costs, and requires only simple maintenance.

The rate of infiltration depends on the hydraulic properties of the top soil. At the water surface evaporation occurs which decreases the amount of infiltrated water. As long as the infiltration rate is high the water loss due to evaporation at the water surface is small. However, water sources with high loads of suspended particles may cause clogging and increase evaporation due to long residence times. Thus, specific construction techniques are being used to reduce clogging.

During the passage of water through the soil, most dissolved and suspended contaminants as well as pathogens are reduced or completely removed due to a combination of physical, chemical, and biological processes. Thus, spreading methods are favourable to improve the water quality of water containing a considerable pollution such as recycled water or surface water. Limitations are given by the geochemical and geological composition of the subsoil.

Sub-Surface Method

This method implies a direct recharge of groundwater below the surface using recharge wells, shafts or dug wells. This method can be applied using existing operational structures designed to withdraw groundwater from an aquifer as these structures can also be used to recharge the groundwater. Within areas with impervious layers at shallow depth, pits and shafts are suitable structures to directly recharge the groundwater.

Generally, groundwater recharge through wells is distinguished by the depth of the aquifer that is being recharged into a) injection wells where water is pumped in and b) recharge wells where water flows under gravity. Injection wells are suitable to recharge single aquifer or multiple aquifer systems in the deep ground. In comparison with most spreading methods this technique is costlier as specialized techniques of tube well construction and maintenance is required to protect the well from clogging.

In comparison to most spreading methods, sub-surface methods show a high efficiency in space, are not restricted to unconfined aquifers, and show practically no losses of water in form of evapotranspiration and evaporation - but the infiltration rate in most sediments is relative slow. Exceptions with a high infiltration rate are very coarse sediments or fractured and karstified bedrocks. Especially within these aquifers the risk of a groundwater contamination is high as the attenuation capacity is very low. Thus, the availability of water sources of an adequate quality may be an important limitation factor for such sub-surface methods.

Induced Recharge

Induced recharge is a widely used indirect technique involving the abstraction from aquifers that are hydraulically connected with surface water bodies such as river, perennial streams or lakes. This scheme commonly consists of a gallery or a line of wells at a short distance from, and parallel to the surface water body. Pumping of the wells causes a decrease of water table adjacent to the river or lake inducing this water to replenish the groundwater. This method is efficient where stream beds or lake bottoms are hydraulically connected to the aquifer by permeable, unconsolidated deposits. The applicability mainly depends on quality issues of the water source, geochemical reactions during underground passage, and final use of the water. Like spreading methods this technique is also restricted to areas with surface water of an adequate quality and with an unconfined aquifer.

7.1 Natural Attenuation

Natural attenuation is a large benefit to MAR, however, often raises strong objections related to environmental protection goals. The reason for this controversy is mainly the definition of "natural attenuation" that does not identify end-point objectives or occurring processes that can achieve these objectives. The U.S. National Research Council (NRC 2000) compares different approaches: the US EPA released a policy directive that describes natural attenuation as a variety of physical, chemical, or biological processes that are at work in-situ, under favourable conditions, acting without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater. The American Society for Testing and Materials (ASTM) extend this definition by the reduction of contaminants over time and distance from their source.

More specifically, the US National Research Council (NRC 2000) points out that destruction and strong immobilization are the only processes that may achieve a realistic objective. The strategies to obtain evidence that the objective is achieved are measurements that establish a cause-effect relationship between contaminant emission and destruction or immobilization reactions.

The concept of natural attenuation is an important segment of the multi-barrier strategy of MAR. However, different infiltration methods and site-specific conditions result in a site-specific expression of in-situ processes and attenuation capacity. In particular, the percolation of water through soil (unsaturated zone) in surface spreading methods is applied to reduce or remove dissolved and suspended contaminants as well as pathogens due to a combination of filtration, sorption, chemical reactions, biotransformation, die-off, and predation (Kanarek & Michail, 1996). These methods are favourable to improve the quality of source water containing a considerable pollution such as treated wastewater. Limitations are given by the hydraulic and geochemical composition of the soil. For example, preferential flow paths may reduce the effectiveness of natural attenuation due to locally high flow rates and a low filter effect. Favourable conditions for pathogens removal may be given by a high clay and organic matter content in the soil since clay minerals and organic matter are good sorbents for some pathogens (Kazner et al., 2012). In particular physico-chemical conditions may influence attenuation processes in the subsoil. Thus, degradation of pathogens is promoted at aerobic conditions (Sidhu et al., 2015). Abel et al. (2012) could show an increase of DOC removal at higher temperatures and under aerobic conditions. Removal rates of DOC are described in Kazner et al. (2012) for primary, secondary and tertiary wastewater effluent achieving a large range of 10 to 60%, 12 to 94% and 19 to 80%, respectively, after percolation. In turn, DOC and its ratio to nitrogen, redox conditions, and detention time influences the nitrogen removal. The removal of organic compounds such as pharmaceuticals shows a high sensitivity to redox conditions (Maeng et al., 2011). Some organic compounds are most effectively removed under aerobic conditions, whereas the removal of other organic compounds is more favourably under anaerobic conditions (Vilanova et al., 2013).

As a consequence, the definition of “favourable conditions” for natural attenuation differs for different pollutants and may be mutually exclusive. The ideal is to have different zones in the aquifer to achieve the best water quality improvement (Dillon et al., 2009).

In comparison to most surface spreading methods, sub-surface methods show a high efficiency in land use, are not restricted to unconfined aquifers, and show practically no losses of water due to evaporation. However, the risk of groundwater contamination is comparably higher since the removal of hazards may be very low especially in karstic and hardrock aquifers with a high permeability through conduits and fractures. Thus, quality goals for sub-surface methods need to be revisited and given greater prominence. Bixio and Wintgens (2006, in Kazner et al., 2012) primarily postulate higher water quality requirements for microbiological contamination and chemical oxygen demand in sub-surface schemes independently from aquifer properties. Concentrations of micro-pollutants should be lower than 0.1 µg/l.

Australian Guideline

The Australian Guidelines (Appendix 5; NRMMC-EPHC-NHMRC, 2009) provide models for water flow and substance transport to estimate present concentrations in ambient groundwater and impact zone in the aquifer. First-order exponential decay is assumed for chemicals subject to degradation. Redox conditions are considered by defining half-life data depending on the presence or absence of oxygen.

Seis & Sprenger (2015) criticize the application of models based on point estimates. Especially in early stage the risk assessment would pretend a level of certainty which does not exist. In addition, first-order rate coefficients provide a strongly simplified description of removal mechanisms during sub-surface passage without considering spatial and temporal dynamics of the specific physico-chemical conditions.

Water Framework Directive

The European Community provides a guidance document on “Risk Assessment and the Use of Conceptual Models for Groundwater” (EC, 2010). This document encourages to start thinking about (ground)water management with all available knowledge, focus on what are environmental or human risks, and finally collect information required to improve the understanding. Models may be applied at different stages of this process and developed to a different degree of complexity. This approach gives the chance to develop a site-specific concept close to the needs of the specific system but, however, does not allow a comparison between different sites as it is implemented in the Australian Guideline.

7.2 Emission Potential of the Receiving Environment

The potential of the receiving environment to emit substances is primarily caused by the application of waters in MAR that differ in (physico-)chemical properties from the natural conditions (equilibrium state) on the receiving environment, i.e. the (typically) sediments of the aquifer (saturated zone). Source waters interact with phases of the receiving environment resulting in a mobilisation of hazards due to desorption or dissolution, or flush out. In particular, the mobilisation of metals is an important issue in MAR technologies. Thus, the infiltration of oxidized water into an aquifer containing, e.g., pyrite may result in a mobilization of iron as well as incorporated trace elements such as manganese, arsenic, cadmium, copper, and uranium. The introduction of a reducing water or the change to reducing condition due to the degradation of dissolved organic matter (DOC) in an oxidized aquifer may lead to the dissolution of iron- and manganese oxides/hydroxides from the sediment.

A major concern in karstic aquifer is the pH-driven dissolution of rock matrix and destabilisation of the well and aquifer systems. The dissolution capacity of calcite is affected by different processes changing the pH and/or the calcium and CO_2 concentrations, such as pyrite dissolution or the degradation of organic carbon (e.g. DOC).

Australian Guideline

The Australian Guideline (NRMMC-EPHC-NHMRC 2009) points out that there is a risk of an emission of hazards from the receiving environment as a consequence of MAR and provides different strategies to minimize adverse impacts:

- ✓ Adjust pH and redox status of the infiltrated water to conditions within the aquifer
- ✓ Reduce the concentration of labile organic carbon in water
- ✓ Deplete the aquifer of offending minerals within the active storage zone

These strategies require reliable information about the geochemical composition of the soil/aquifer.

Water Framework Directive

Article 5 of WFD provides the necessity to analyse pressures and impacts on the basis of river basin catchment areas including a characterisation of the impact of human activity on the status of surface water and groundwater and on protection values. The WFD adopts the widely-used DPSIR model to represent environmental pollution and measures for protection. The DPSIR describes the causal relationship between:

- ✓ ***Driving Force***: anthropogenic activities that pose an effect on environment

- ✓ ***Pressures***: resulting environmental effect
- ✓ ***State***: condition of the environmental compartment (water body) resulting from both natural and anthropogenic factors
- ✓ ***Impacts***: specific environmental effect of the *pressure*
- ✓ ***Response***: measures taken to improve the state of environmental compartment (water body)

7.3 Dilution and Mixing

As water flows through the saturated zone hazards are diluted by mixing of water in different flow paths and flowing at different velocities in the aquifer. Although the concentrations of hazards decrease, dilution is not a reliable remedy for pollution or may be in some cases misinterpreted as natural attenuation. Therefore, an understanding and precise description of dilution and mixing is required for the evaluation of natural attenuation and the implementation of groundwater management strategies. As a consequence of mixing two different waters, dissolution capacity of the resulting water may change which may lead to dissolution or precipitation processes. Dilution factors can be calculated location- and time-dependent based on tracer technologies or isotopic signatures.

7.4 Investigation Methods - Column and Batch Experiments

Soil column and batch experiments are a good method to test natural attenuation and emission potential of soil and/or a potential destabilisation of the aquifer matrix under laboratory conditions. These experiments aim to simulate very different processes or a combination of processes that may lead to changes in

- ✓ hydraulic properties due to clogging, dissolution or precipitation within the soil and
- ✓ water quality due to dissolution, precipitation, sorption and microbiological processes

when using different source waters, infiltration methods, and recharge conditions.

Simplest technique is the batch experiment where source water and soil react in a specific ratio and time. A variation of key parameters, such as reaction time, provides information on kinetic effects of the processes. The water to soil ratio should be defined according to equilibrium status. Batch experiments are also suitable to investigate quality changes due to the mixing of source water with ambient groundwater in the presence or absence of soil matrix.

Column experiments are more complex. However, they may provide a wide range of information including on groundwater flow and reactive transport. However, experimental goals require a careful adaptation of the experimental set-up. For example, variations in flow velocity have an impact on the reaction time as well. A guideline protocol for soil column experiments to investigate the fate of organic compounds in MAR is given in DEMEAU's project deliverable D12.3 (Gibert et al., 2014). In the frame of the MARSOL project, Silver et al. (2016) describe the experimental set-up and operational mode for two different MAR schemes. In this study it could be shown that wetting and drying cycles increase the range in redox conditions, not only by raising the redox potential during drying, but also by lowering it during the wetting periods beyond the most reducing extent of conditions when operating under continuous infiltration.

8 Conclusions

This report presents two strategies to develop water quality requirements for MAR. The Australian Guideline provides water quality objectives based on the beneficial use or environmental value, however, also incorporates measures to prevent the mobilization of contaminants from aquifer body. Water quality objectives proposed by the WFD refer to the groundwater body as the receiving environment independent from other beneficial uses such as drinking water extraction, but does not clearly defined measures to achieve these objectives.

The Australian Guideline provides detailed information about water quality aspects in MAR and offers important assistance to evaluate the viability and degree of difficulty of MAR at an entry-level assessment. In contrast, the WFD does not provide a clearly defined approach to assess the risks posed by MAR but encourages developing site-specific concepts close to the needs of the specific system.

In this context, we consider the Australian guidelines as a good approach which, however, should be complemented by the concepts of the WFD and recent studies in particular about the fate of micropollutants in MAR. The focus of Australian Guideline on beneficial use may lead, for water uses with low quality requirements such as irrigation, to a deterioration of the groundwater body which is not consistent with European legislation. On the other hand, the Australian Guideline provides a more comprehensive list of potential hazards including organic micropollutants.

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Annex 1: Overview of microbiological and chemical limits for reclaimed water reuse in MAR.

		91/271/EEC (98/15/EC)	Salgot & Huertas (2006)		Bixio & Wintgens (2006)	
Parameter		Treated wastewater	into the soil for irrigation purpose	localised percolation through the soil	Indirect infiltration via ditches, pipes or basins	Direct injection into the subsurface
Pathogens						
Total bacteria	cfu/ml	-	1,000	100,000	-	-
Faecal coliforms	cfu/100ml	-	abs	Abs - <10,000	10,000	0
Faecal streptoc.	cfu/100ml	-	-	-	-	0
Clostridium perfrigens	cfu/100ml	-	Abs - 20	100	-	-
Legionella	cfu/100ml	-	<100	-	-	-
Enterococci	cfu/100ml	-	abs	10,000	-	-
Salmonella	cfu/ml	-	Abs – 1,000	0.1	-	-
Enteroviruses	pfu/ml	-	Abs - 10	-	-	-
Coliphages	pfu/ml	-	1	-	-	-
Cryptosporidium and Gardia	cyst/50ml	-	1	-	1	0
Nematode eggs	eggs/l	-	<1 - 10	1	-	-
T. saginata	eggs/l	-	-	1	-	-
T. solium	eggs/l	-	-	1	-	-
Physico-Chemical Parameter						
pH	-	-	>6.0 – >9.5	>7.0 – <9.0	>6.0 – <9.5	>6.5 – <9.5
El. conductivity	µS/cm	-	3,000	1,400	700	700
BOD	%	-	10 - 20	-	-	-
COD (TOC)	%	125	100	70 – 100	70 – 100	5
Dissolved oxygen	mg/l	-	>0.5	>8	-	-
AOX	mg/l	-	-	25	-	-
TSS	mg/l	35	10 - 20	-	-	-
Active chlorine	mmol/l		0.2 – 1.0	-	-	-
Inorganic Chemicals						
Nutrients						
Total N	mg/l	15	15 - 25	-	25	25
Ammonium-N	mg/l	<0.2	2 - 20	0.2	0.2	0.5
Total P	mg/l	2	2 – 5	-	-	-
Total F	mg/l	-	1.5 – 2.0	-	-	-
Sodium	mg/l	-	150	-	-	-
Nitrate	mg/l	-	-	25	25	25
Chloride	mg/l	-	250	100	100	250
Sulphate	mg/l	-	500	100	30	250
Metals						
As	mg/l	-	0.1 – 0.02	0.005	0.005	0.010
B tot	mg/l	-	0.4	0.2	0.2	1.0
Cd	mg/l	-	0.005	0.003	0.003	0.005
Cr tot	mg/l	-	0.1 – 0.01	0.025	0.025	0.050
Cr III	mg/l	-	0.1	-	-	-
Cr VI	mg/l	-	0.005	-	-	-
Hg	mg/l	-	0.001 – 0.002	0.0005	0.5	1
Pb	mg/l	-	0.1	0.005	0.005	0.010
Al	mg/l	-	1 – 5	-	-	-
Ba	mg/l	-	10	-	-	-

		91/271/EEC (98/15/EC)	Salgot & Huertas (2006)		Bixio & Wintgens (2006)	
Parameter		Treated wastewater	into the soil for irrigation purpose	localised percolation through the soil	Indirect infiltration via ditches, pipes or basins	Direct injection into the subsurface
Be	mg/l	-	0.1	-	-	-
Co	mg/l	-	0.05	-	-	-
Cu	mg/l	-	0.2 – 1.0	-	-	-
Fe	mg/l	-	2	-	-	-
Li	mg/l	-	2.5	-	-	-
Mn	mg/l	-	0.2	-	-	-
Mo	mg/l	-	0.01	-	-	-
Ni	mg/l	-	0.2	-	-	-
Se	mg/l	-	0.01 – 0.02	-	-	-
Sn	mg/l	-	3	-	-	-
Th	mg/l	-	0.001	-	-	-
V	mg/l	-	0.1	-	-	-
Zn	mg/l	-	0.5 – 2.0	-	-	-
Organic Chemicals						
Surfactant tot	mg/l	-	0.5 – 1.0	-	-	-
Mineral oil	mg/l	-	0.05	-	-	-
Micropollutants	µg/l		-	-	<0.1	depending on compound

Annex 2: Comparison of drinking water and irrigation standards (not complete).

Parameter		Drinking Water		Water for agricultural irrigation	
		WHO (2011)	(98/83/EC)	(DWAF 1996) Target / max. acceptable for long term irrigation	
Pathogens					
Colony count (22/ 37°C)	/ml	100	100 / 20	--	
Escherichia coli (E. coli)	/250ml		0	--	
Coliforme bacteria	/100ml	0	0	1 / 1000	>1000 no contact with humans acceptable
Enterococci	/250ml		0	--	
Inorganic Compounds Nutrients					
Ammonium	mg/L		0.5	--	
Calcium			--	--	
Chloride	mg/L	-	250	100 / 175 (350)	
Fluoride	mg/L	1.5	0.8 / 1.5	2 / 15	
Magnesium		--	--		
Nitrate	mg/L	50	50	21 / 130	
Nitrite	mg/L	3	0.5		
Phosphor (tot)	mg/L		6.7		
Potassium			--		
Sodium	mg/L		200	70 / 230	SAR: 2 / 8
Sulphate	mg/L		250		
Metals					
Aluminium	µg/L	100	200	5000 / 20000	
Arsenic	µg/L	10	10	100 / 2000	
Beryllium	µg/L	--		100 / 500	
Boron	µg/L	2400	1000	500 / 4000	
Cadmium	µg/L	3	5	10 / 50	
Chromium	µg/L	50	50	100 / 1000	
Cobalt	µg/L	--		50 / 5000	
Copper	µg/L	--	2	200 / 5 000	
Iron	µg/L	--	200	5000 / 20 000	Clogging: <1500
Lead	µg/L	10	10	200 / 2000	
Lithium	µg/L	--		2500	
Manganese	µg/L	400	50	200 / 10000	Clogging: <1500
Molybdenum	µg/L	--		10 / 50	
Mercury	µg/L	6	1	--	
Nickel	µg/L	70	20	200 / 2000	
Selenium	µg/L	40		20 / 50	
Uranium	µg/L	30		10 / 100	
Vanadium	µg/L	--		100 / 1000	
Zinc	µg/L	--		1000 / 5000	
Organic Compounds					

Pesticides	µg/L µg/L	--	0.1 0.5 (tot)	--	
Acrylamide	µg/L	0.5	0.1	--	
Benzene	µg/L	10	1	--	
Benzolpyrene	µg/L	0.7	0.01	--	
1,2-Dichlorethan	µg/L	30	3	--	
Epichlorhydrin	µg/L	0.4	0.1	--	
PAH	µg/L		0.1	--	
Tetrachlorethene, Trichlorethene	µgLl	40	10	--	
Total Trihalomethane	µg/L	<1	100	--	
Vinylchloride	µg/L	0.3	0.5	--	
Physico-chemical Parameter					
pH	--	8.2 – 8.8	6.5-9.5	6.5 – 8.4	
Electrical Conductivity (20°C)	mS/m	--	2 500	3 000	FAO 1985 (slight to moderate degree of restriction)
Turbidity	NTU	1.5	1	--	
Redox potential	mV	--	--	--	
TDS/TSS	mg/L	--	--	40 / 270 (540)	
Salinity	ds/m	--	--	3	FAO 1985 (moderately sensitive)

SAR – Sodium adsorption rate