Abstract: Managed aquifer recharge (MAR) is used worldwide in urban environments to replenish groundwater to provide a secure and sustainable supply of potable and non-potable water. It relies on natural treatment processes within aquifers (i.e., filtration, sorption, and degradation), and in some cases involves infiltration through the unsaturated zone to polish the given source water, e.g., treated wastewater, stormwater, or rainwater, to the desired quality prior to reuse. Whilst MAR in its early forms has occurred for millennia, large-scale schemes to replenish groundwater with advanced treated reclaimed water have come to the fore in cities such as Perth, Western Australia, Monterey, California, and Changwon, South Korea, as water managers consider provision for projected population growth in a drying climate. An additional bonus for implementing MAR in coastal aquifers is assisting in the prevention of seawater intrusion. This review begins with the rationale for large-scale MAR schemes in an Australian urban context, reflecting on the current status; describes the unique benefits of several common MAR types; and provides examples from around the world. It then explores several scientific challenges, ranging from quantifying aquifer removal for various groundwater contaminants to assessing risks to human health and the environment, and avoiding adverse outcomes from biogeochemical changes induced by aquifer storage. Scientific developments in the areas of water quality assessments, which include molecular detection methods for microbial pathogens and high resolution analytical chemistry methods for detecting trace chemicals, give unprecedented insight into the “polishing” offered by natural treatment. This provides opportunities for setting of compliance targets for mitigating risks to human health and maintaining high performance MAR schemes.

Keywords: managed aquifer recharge; microbial pathogens; metal mobilization; reclaimed water; water recycling; seawater intrusion

1. Introduction

1.1. Rationale and Examples of Large-Scale MAR in an Australian, Urban Context

Australia is a highly urbanised country with >75% of its population of 23.6 million people living in major cities [1]. According to the 2016 census data, 15.4 million people exist in Australia’s eight largest cities. Moreover, the Australian Bureau of Statistics predicts strong population growth into the future, predominantly in and around Australia’s capital cities [2]. Sydney, Melbourne, Brisbane and Perth,
the four biggest cities in Australia, are expected to accommodate 5.9 million more people (46% increase) by 2031, which is three-quarters of Australia’s total anticipated population growth [3]. The combined population of these four cities was 13.5 million according to the 2016 census.

Water security is of paramount concern, particularly in countries facing significant population growth and a drying climate. For Australia’s four biggest cities, climate projections for the next several decades show predominantly increased aridity, particularly in the southern winter wet-season, with the possible exception of Brisbane as confidence in projected rainfall changes are unclear; nevertheless, based on the fifth Climate Model Intercomparison Project Global Climate Models (CMIP5 GCMs), increased evapotranspiration is projected with a high level of confidence for each of these cities (Table 1) [4]. The projected increased intensity of extreme daily rainfall events has implications for stormwater runoff. High rainfall intensity can lead to flooding and less recharge to groundwater in some environments where the infiltration capacity of the soils is exceeded [5]. An additional concern in rapidly developing, coastal areas that rely on groundwater sources is intrusion of seawater into coastal aquifers and saltwater up-coning beneath pumping wells [6].

Table 1. Projected changes averaged across available CMIP5 GCMs for Comparison of projections for changes in temperature, rainfall, evapotranspiration, relative humidity, and the intensity of extreme daily rainfall events for 2030 and 2090 relative to the 1986–2005 average for the four largest cities in Australia from Webb and Hennessy [4]. The projections models shown are intermediate and high emission scenarios for greenhouse gases and aerosols, i.e., RCP4.5 and RCP8.5, respectively. For 2030, results for all RCPs are similar so only RCP4.5 values are shown [4].

| Climate Factor | Season | 2030 RCP4.5 | 2090 RCP4.5 | 2090 RCP8.5 | Confidence in Projection |
|---------------|--------|-------------|-------------|-------------|-------------------------|
| Sydney        |        |             |             |             |                         |
| Temperature (°C) | Annual | +0.9        | +1.8        | +3.7        | Very high               |
| Rainfall (%) | Annual | −3          | −2          | −3          | Not stated              |
|               | Summer  | +1          | 0           | +11         | Unclear                 |
|               | Winter  | −5          | −8          | −17         | Medium                  |
| Evapotranspiration (%) | Annual | +3.4        | +7.8        | +14.3       | High                    |
| Relative humidity (%) | Annual | −0.5        | −1          | −1.5        | Not stated              |
| Intensity of extreme daily rainfall events | − | Increased | High |
| Melbourne     |        |             |             |             |                         |
| Temperature (°C) | Annual | +0.6        | +1.5        | +3          | Very high               |
| Rainfall (%) | Annual | −2          | −7          | −9          | Not stated              |
|               | Summer  | −2          | −3          | −5          | Unclear                 |
|               | Winter  | −3          | −4          | −10         | High                    |
| Evapotranspiration (%) | Annual | +2.7        | +6.5        | +12.5       | High                    |
| Relative humidity (%) | Annual | −0.4        | −0.9        | −1.8        | Not stated              |
| Intensity of extreme daily rainfall events | − | Increased | High |
| Brisbane      |        |             |             |             |                         |
| Temperature (°C) | Annual | +0.9        | +1.8        | +3.7        | Very high               |
| Rainfall (%) | Annual | −4          | −9          | −16         | Unclear                 |
|               | Summer  | −5          | −5          | −6          | Unclear                 |
|               | Winter  | −5          | −12         | −17         | Unclear                 |
| Evapotranspiration (%) | Annual | +3.5        | +7.4        | +14.1       | High                    |
| Relative humidity (%) | Annual | −0.5        | −0.9        | −1.2        | Not stated              |
| Intensity of extreme daily rainfall events | − | Increased | High |
| Perth         |        |             |             |             |                         |
| Temperature (°C) | Annual | +0.8        | +1.7        | +3.5        | Very high               |
| Rainfall (%) | Annual | −6          | −12         | −18         | Not stated              |
|               | Summer  | −8          | −4          | −5          | Unclear                 |
|               | Winter  | −7          | −14         | −29         | High                    |
| Evapotranspiration (%) | Annual | +2.5        | +5.4        | +10.3       | High                    |
| Relative humidity (%) | Annual | −0.6        | −1.2        | −2.2        | Not stated              |
| Intensity of extreme daily rainfall events | − | Increased | Medium |
Faced with the prospect of less natural groundwater recharge, more stormwater runoff, degradation of coastal groundwater quality by seawater intrusion, and increased volumes of wastewater generated by the growing populous cities, Australia has a portfolio of options for sustainable urban water management to consider [7]. Among these options, managed aquifer recharge (MAR) plays a leading role and has come to the fore in several major Australian cities. In Perth, for example, the Groundwater Replenishment Scheme is intended for large-scale potable reuse [8]. This has followed international trends, especially in Europe where MAR is more commonly integrated in urban drinking water treatment [9–13]. Adoption for drinking water augmentation in Perth followed from several years of research trials conducted in aquifer conditions similar to the scheme [14,15]. At the Parafield Airport in Adelaide South Australia, a stormwater harvesting and aquifer storage and recovery system has been operating since 2003 [16]. The system was also investigated to determine if urban stormwater could be recycled via an aquifer and produce potable quality in conjunction with engineered treatments. More recent work has quantitatively demonstrated that this system offers a resilient source of non-potable water for the next several decades [17–19]. The planned Northern Adelaide Irrigation Scheme in South Australia is a recycled water scheme to use 12 million cubic metres per year of reclaimed water, mainly to support agricultural food production, and is intended to increase the use of recycled water by 60% annually [20].

To date, there are no large-scale MAR projects operating in other Australian cities, as other options for sustainable urban water management are being embraced, e.g., desalination in Melbourne and non-potable recycled water for reticulation systems in Sydney, Melbourne and Brisbane [21,22]. A review of Sydney’s recycled water schemes by Chen et al. [23] documented many projects. There is also strong community support for increased wastewater recycling [24,25]. The Botany sand aquifer, south of Sydney, has been assessed as a potential target for large-scale MAR [26,27]; however, MAR does not play a leading role in Sydney’s water planning at this time [28]. Instead, the reuse options favour environmental releases that do not involve aquifers, e.g., the “Replacement Flows” project, involving advanced wastewater treatment and then release into the Hawkesbury Nepean River that feeds into Sydney’s major reservoir [29].

Given this background, the aim of this paper is to review the current status of MAR within the Australian context, highlight some of the key scientific and technological challenges that underpinned wider adoption of MAR in the last decade, and outline opportunities for developing MAR schemes. For a review of MAR policy development in Australia, which is not covered herein, see Parsons et al. [30].

1.2. Review of MAR Options

Several comprehensive reviews provide insight into the breadth of combined natural processes and engineered designs for MAR (see, for example, Dillon et al. [31]; National Research Council [32]; NRMMC-EPHC-NHMRC (Natural Resource Management Ministerial Council-Environment Protection and Heritage Council- National Health and Medical Research Council) [33]; and Maliva and Missimer [34]). Briefly, there is a wide range of methods for recharging water to meet a variety of local conditions, including infiltration techniques to recharge unconfined aquifers and well injection techniques, which are generally better suited to deeper, confined aquifers. In the summary of types of MAR (Table 2), benefits unique to each method are listed. Common benefits from those that involve infiltration of treated wastewater are that they offer a relatively low-cost alternative to other methods for wastewater disposal (especially nitrogen removal to meet environmental discharge requirements), and they promote nutrient and pathogen removal during passage through the unsaturated zone, which may reduce the levels of required treatment that is traditionally applied upstream.
Table 2. Summary of common types of MAR. Diagrams are modified after Dillon 2005 [31]. Reprinted by permission from Springer Customer Service Centre GmbH.

| Type of MAR                        | Description                                                                 | Unique Benefits of This Method                                                                                      | Examples                                                                 |
|-----------------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| Aquifer storage and recovery (ASR)| Injection of water into a well for storage and recovery from the same well  | Especially useful in brackish aquifers, where storage is the primary goal and water treatment is a minor consideration | Potable water supplies in the USA [35]; Reuse of treated sewage or urban stormwater in Australia, e.g., Rossdale, Australia [36]; Rainwater harvesting and storage in a confined aquifer in northeast region of India [37] |
| Aquifer storage, transfer and recovery (ASTR) | Injection of water into a well for storage, and recovery from a different well | Can be used to achieve additional water treatment in the aquifer by extending the residence time and allowing greater exposure to porous media and reaction sites than using a single well (ASR) | Parafield Gardens ASTR in Australia [38] |
| Infiltration pond or basin        | Water of impaired quality (e.g., urban runoff, treated wastewater) diverted into a basin or channel that allows water to soak through an unsaturated zone to the underlying unconfined aquifer | Relatively low cost method for disposal of treated wastewater as they are typically located adjacent to treatment facility and, thus, lessen pumping costs Sub-basins can be managed to handle inflow surges from seasonal rainfall runoff [39,40] | Kwinana managed aquifer recharge for non-potable purposes [41]; Basin infiltration to reduce seawater intrusion in the Burdekin Delta, Queensland [42] |
Table 2. Cont.

| Type of MAR                          | Description                                                                                                                                                                                                 | Unique Benefits of This Method                                                                 | Examples                                                                                      |
|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| **Soil aquifer treatment (SAT)**    | Treated sewage effluent, possibly mixed with urban runoff is intermittently infiltrated through infiltration ponds for recovery by wells after the required duration in the unconfined aquifer                                                                | Sub-basins can be managed to handle inflow surges from seasonal rainfall runoff [39,40]       | Montebello Forebay Groundwater Recharge Project [43]                                           |
|                                     |                                                                                                                                                                                                          |                                                                                                | Sweetwater Recharge Facility in Tucson, Arizona [44]                                          |
|                                     |                                                                                                                                                                                                          |                                                                                                | Alice Springs, Australia—Arid Zone Research Institute [45]                                   |
|                                     |                                                                                                                                                                                                          |                                                                                                | Combined sewer overflows and SAT in Germany [39,46]                                          |
| **Infiltration gallery**            | Covered, subsurface percolation trenches that contain a medium or supporting structure (e.g., polypropylene crates) and/or slotted pipes, in permeable soils that allow infiltration through the unsaturated zone to an unconfined aquifer | Below ground storage avoids evaporative losses, lessens surface footprint, which may be advantageous in urban areas with high costs of land and public health concerns over surface storage of recycled water near residential properties, and lessens clogging due to algal photosynthesis | Floreat infiltration galleries pilot trials using Atlantis™ crates [47,48]                      |
|                                     |                                                                                                                                                                                                          |                                                                                                | Trench infiltration using slotted pipes in permeable bedrock [49].                             |
| **Bank filtration**                | Extraction of groundwater from a well near or under a river or lake to induce infiltration from the surface water body                                                                                  | Groundwater abstracted from this system has a more consistent and improved quality than directly sourcing water from the river. | Berlin, Germany [50]                                                                           |
| **Rainwater harvesting (RWH)**      | Roof runoff is diverted into a well, sump or caisson (e.g., geofabric lined trench) filled with sand or gravel and allowed to percolate to the water table where it is collected by pumping from a well. A variation is a raingarden or bioretention/biofiltration system in an urban context, involving vegetation planted within a filter media to improve water quality | Below ground storage avoids evaporative losses, lessens surface footprint, which is advantageous in urban areas with high costs of land, and lessens clogging due to algal photosynthesis Reduces surface runoff and increases groundwater recharge Infiltration coupled with RWH can help modify urban microclimate and thus mitigate the heat island effect [52] | RWHR in Tel-Aviv, Israel [51] |
2. Scientific Challenges

2.1. Quantifying Aquifer Treatment

Aquifers can polish or ameliorate the quality of the recharge water through natural processes: filtration, sorption, redox transformation (e.g., biological nitrification and denitrification), and degradation are key components of natural attenuation. However, MAR can also lead to the dissolution of the aquifer matrix and the mobilization of metals.

Physical heterogeneity plays an essential role in the straining or filtering of microorganisms and other particulate matter via a reduction in pore size. Theoretical and experimental studies have quantified the factors controlling the retention and release of colloid particles. Straining experiments conducted using laboratory analogues typically use carefully controlled surrogates for the aquifer matrix and/or the microbial pathogens to study the effects of grain size variability, surface roughness and other factors on transport [54]. Examples include flow cells packed with glass beads or carefully graded, clean sand. Alternatively, aquifer sediments are repacked into columns to represent field conditions. The structure of aquifer heterogeneity at an intermediate scale has been investigated using flow cells containing layered geometries of different-sized glass beads [55]. Intermediate scale structures in sedimentary deposits, such as fining-upward sequences, have also been investigated [56]. Nevertheless, the scale of observation using laboratory columns is limited as it relies on a one-dimensional interpretation of flow. Thus, larger scale pilot trials are needed to validate results obtained with column experiments [57].

The above-mentioned studies aimed to quantify filtration processes apart from the complexities of field conditions with the intent of developing quantitative models of the physical basis. In addition to the physical filtration or straining processes involved with reducing the concentration of contaminants in the source water, there have been major advances in measuring natural transformation and degradation with the intent of quantifying natural removal rates. These are reviewed in the following sections for specific constituents in MAR source water.

Documented cases of MAR are helping to build a knowledge base around the combinations of source water types, aquifer and MAR operational conditions that lead to specific changes in water quality. The ultimate goal is to have a matrix of conditions that allow proponents of MAR to predict or anticipate rates of natural attenuation for their site-specific conditions. In this section, we review several crucial studies that contribute to this knowledge base.

2.1.1. Total Organic Carbon (TOC) and Other Nutrients

The concentrations of total organic carbon and nitrogen are among the cursory level indicators of source water quality used to assess potential problems (e.g., clogging) at entry-level for new MAR schemes in Australia [33]. If necessary, pre-treatments are recommended prior to infiltration or injection. Nevertheless, significant improvements to water quality have been achieved as demonstrated in the following examples.

At the Floreat infiltration gallery site, near Perth, Western Australia, changes in the average concentrations of several constituents in the recycled water, including phosphorous (P) and total organic carbon (TOC), before and after passage through calcareous sand in the unsaturated zone were measured over a 39-month period [47]. The volumetric supply of recycled water to the infiltration galleries was carefully controlled and significant concentration reductions were observed for P and TOC, 30% and 51%, respectively. The authors caution that removal efficiencies are specific to the recycled water infiltration rate and aquifer conditions. Of particular note, phosphate sorption is dependent on the carbonate composition of the aquifer, and a maximum P adsorption capacity was reached during the trial, which prevented further removal below the threshold [47].

At the Bolivar ASR field site, near Adelaide, South Australia, removal rates for TOC and nutrients were monitored over an 11-year period to develop a probabilistic modelling approach for the validation of the water quality improvements from injecting recycled water into an anoxic carbonate aquifer [58].
The study documented median mass removal of TOC from 25% to 40% and total nitrogen (TN) from 46% to 87% over four cycles of ASR. The statistical method developed, however, could not quantify TP removal, due to the reversible removal of total phosphorus (TP) via adsorption and desorption in the anoxic, carbonate aquifer.

The Shafdan Reclamation Project in Israel uses six infiltration basins for SAT to produce up to 130 million m$^3$ of water annually for irrigation [59–61]. Optimal operation of the SAT system involves the carefully controlled timing of flooding/drying events to manage aeration of the upper vadose zone and exposure to the sunlight and temperature cycles. In this manner, efficient nitrification is achieved and there is less opportunity for Mn-oxide precipitation and the clogging of pipelines [61]. Recharge occurs through >40 m of sandy soil and the estimates of P breakthrough times in recovery wells are >400 years based on P sorption studies and monitoring data from the site over its 25 years of operation [62]. However, as the site has been in operation for such a lengthy period, there are concerns for maintaining high levels of performance. Pre-treatments prior to infiltration have been successfully trailed, which demonstrate the complete removal of ammonia, nitrate and phosphate using SAT with bio-filtered effluent [59].

Aquifers harbour diverse microbial communities which can facilitate the natural attenuation of nutrients through microbial metabolic processes [63,64]. Microbial processes that facilitate nitrogen removal include aerobic ammonia oxidation, denitrification and anaerobic ammonia oxidation (Anammox) [65,66]. Aerobic ammonia oxidation converts ammonia to nitrate (NO$_3^-$) via nitrite (NO$_2^-$) [67]. Denitrification is a stepwise reduction process involving a number of intermediates (NO$_3^-$ → NO$_2^-$ → NO$_3^-$ → N$_2$O → N$_2$) [67]. Anammox couples ammonia oxidation to the reduction of nitrite producing N$_2$ [66]. Smith et al. [66] used quantitative polymerase chain reaction (QPCR) to quantify genes responsible for denitrification and Anammox in a freshwater aquifer. Amo et al. [63] combined QPCR of functional genes to isotopic data to identify natural nitrate attenuation processes in groundwater.

2.1.2. Microbial Pathogens and Antibiotic-Resistant Genes

Evidence of the natural attenuation of microbial pathogens during passage of wastewater through the sediments has been demonstrated at many MAR sites. For example, disinfection outcomes on par with chlorination in terms of log removals of pathogens have been achieved at the Shafdan/Soreq SAT system with no evidence of enteroviruses or faecal coliforms over the last decade [68,69]. The low survival of microbial pathogens through the Shafdan SAT system was attributed to the microbial diversity in the vadose zone, the low temperature, and long aquifer residence time (average of 960 days) [68].

The effects of aquifer heterogeneity on the natural attenuation and groundwater transport of viruses, bacteria and protozoa have been examined. The sizes of bacteria range from 0.2 to 10 µm, while viruses are much smaller (20–200 nm). Protozoa are larger in size than bacteria, and thus more readily filtered out during treatment. Bacteria and viruses are considered colloidal particles with effective diameters less than 10 µm [70], and some of the theories about the transport of bacteria via advection, hydrodynamic dispersion, and deposition (filtration) are similar to those for viruses [71,72]. Indigenous bacteria can multiply and grow in the subsurface, creating biofilms that affect the permeability of the aquifer [73], whereas human pathogenic viruses require host cells to replicate. Viruses are also less likely to block flow-paths and cause a reduction in permeability because of their small size and minor proportion relative to organic matter in wastewater. Some bacteria are motile and, although they rarely travel large distances [74], motility potentially affects their sorption and desorption [75]. There has been no consensus as to whether motility increases or decreases overall transport rate and the controlling mechanisms are not well understood [75].

Many of the early studies of pathogen inactivation in groundwater aimed to quantify survival rates relative to environmental factors in the aquifer [76–78]. Theoretical understanding of how microbial pathogens are removed has come about through extensive experimentation in the field and laboratory, and through modelling studies [79]. It is now well-recognized that decay rates for
microbial pathogens are likely to be highly site-specific, requiring field-validation at MAR sites [80]. Technologies developed for this purpose include using in situ diffusion chambers seeded with microbial pathogens and installed below the water table [81].

In addition to pathogen inactivation studies in relation to MAR, there is also research to quantify the retardation of microbes within the aquifer matrix due to adsorption. Modelling of microbial pathogen retardation during passage of recycled water through an aquifer has typically assumed an equilibrium adsorption approach; however, this has been shown to be inadequate [82], and new theoretical models have been developed to quantify adsorption [83].

Given the wide range of microbial pathogens which may exist in source water for MAR, more recently, a quantitative risk approach using reference organisms has been developed [84,85]. With the advent of this approach, research is now directed toward quantifying microbial inactivation targets for specific reference pathogens for different types of source waters [86]. The widespread and increasing use of antibiotics may contribute to the proliferation of antibiotic resistance in microorganisms, which can pose health risks to humans and animals [87]. A majority of antibiotics in the environment originate from sewage [87]. The growing interest in reusing treated urban wastewater for MAR calls for better understanding of the fate of antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARG) in aquifers. Several studies have reported the presence of ARB or ARG in surface waters, groundwater and reclaimed water [88–93]. Böckelmann et al. [90] monitored the presence of various ARGs with quantitative polymerase chain reaction in water extracted from groundwater recharge systems in Torreele, Belgium, Sabadell, Spain, and Nardò, Italy. The three aquifer recharge systems demonstrated different capacities for the removal of antibiotic resistance genes: genes encoding for the resistance of tetracycline resistance were detected at all three sites, erythromycin resistance genes were detected at Sabadell and Nardò, and ampicillin and methicillin resistance genes were detected only in reclaimed water from Sabadell. McLain and Williams [93] compared resistance patterns to 16 antibiotics in Enterococcus strains isolated from sediments of water storage basins containing either reclaimed water or groundwater in central Arizona. The study showed that high levels of resistance to certain antibiotics, including lincomycin, ciprofloxacin, and erythromycin, existed in sediments regardless of the water source (groundwater or reclaimed water). The reclaimed water sediments did not show higher antibiotic resistance than the groundwater sediments. Furthermore, resistance to multiple antibiotics was substantially reduced in isolates from reclaimed water sediments, compared to groundwater sediment isolates. Elkayam et al. [69] monitored antibiotic-resistant genes in a SAT system in Tel Aviv, Israel. Genes encoding for β-lactam resistance were detected by QPCR in the secondary effluent used for recharge, recovery wells, as well as in wells not impacted by effluent, suggesting that these genes are associated with native aquifer bacterial communities, whereas genes encoding for quinolones resistance were only detected in the secondary effluent used for recharge [69].

2.1.3. Metalloid Fate

Metalloid(s) can arise as a hazard in MAR operations due to their presence in the recharge water and also due to their potential for release from within the aquifer itself. Metalloids may be of geogenic origin, which means that concentrations may increase during aquifer storage. This mobilization is discussed in detail in Section 2.3.1.

In general, the mobility of metalloids will be influenced by their solubility, both initially in the recharge water and within the aquifer upon mixing of source water with native groundwater. Insoluble metalloids may be removed by filtration by the porous media, which may in turn contribute to a physical clogging of an infiltration basin or injection well. Soluble species concentrations may be controlled by aqueous speciation and subsequent solubility or propensity for sorption to available surfaces, such as metal oxides, clay minerals or organic matter.

Redox transformations play a key role in controlling the solubility and fate of metalloids in the subsurface [94], and are most relevant to MAR schemes where oxic recharge water is introduced to an anoxic aquifer. Notably, redox conditions can vary both spatially and temporally within the MAR
operation, for example oxic conditions will typically be limited to a zone around the point of injection while storage may result in increased microbial activity and more reducing conditions. As a result, the solubility and mobility of metalloids may fluctuate within an individual MAR operation [95]. Iron solubility is commonly modified by changing redox conditions in MAR [96]. Reductive iron (III) dissolution not only increases dissolved iron concentrations, but the reduction in sorption sites also leads to increases in other dissolved metalloid concentrations.

The fate of metals and metalloids were investigated in four, large-scale, stormwater ASR systems in South Australia located in a confined, anoxic, limestone aquifer [96]. Variations in source water concentrations and aquifer conditions complicated the process of attempting to use deterministic methods to estimate environmental risk. Instead, a probabilistic approach was used to estimate metal and metalloid removal efficiencies for long-term ASR operations and suggested for continual performance assessment. The fate of aluminium was thought to be consistently controlled by the insolubility of Al(OH)3 under the slightly alkaline conditions in the aquifer, filtration was important for insoluble lead, whereas redox processes and sorption to iron oxides were key influencing factors for the fate of arsenic, copper, nickel and zinc [96].

2.1.4. Trace Organic Chemicals

Trace organic chemicals (TORCs), which include pharmaceuticals, illicit drugs, corrosion inhibitors, pesticides, biocides, artificial sweeteners, personal care products, and industrial chemicals have been detected in wastewater worldwide [97,98]. In addition, the metabolites of certain trace organic compounds may be present. During MAR, the main attenuation mechanisms are dilution, adsorption and biotransformation, which can be enhanced by microbial activity, redox conditions and the presence of organic matter [97]. The rates of sorption and biodegradation of trace organics have been quantified using column studies that involve the passage of MAR source water through columns filled with field sediments in the presence and absence of microorganisms [99,100]. The fate of 11 pharmaceuticals was monitored in saturated column and batch experiments using sands of varying organic matter contents and secondary effluent for a riverbank filtration MAR project in South Korea [101]. The study identified biodegradation and sorption as the main mechanisms for the removal of pharmaceuticals. Whilst carbamazepine was recalcitrant, some of the sand media experiments revealed >80% removal efficiencies for the other tested pharmaceuticals (i.e., ioporomide, estrone, and trimethoprim [101]).

A comparison of trace organic pollutant data from five MAR sites (Shafdan in Israel, Nardo in Italy, Sabadell in Spain, Gaobeidian in China, and Torrell in Belgium) revealed that differences in local conditions, source water quality, pre-treatments, type of MAR (infiltration versus injection), and aquifer residence times were important [102]. In general, the removal of most trace organic compounds was favoured by aerobic conditions occurring in infiltration through soil as opposed to direct injection.

The removal of contaminants can vary by site and within the soil profile used for MAR infiltration. For example, at the Floreat infiltration galleries site, the sediment organic matter content and iron content vary with depth, which has implications for trace organic removal. Ying et al. [103] noted the decay of endocrine-disrupting chemicals (EDCs) was enhanced under aerobic conditions based on batch sorption experiments conducted with reclaimed water and sand from the vadose zone. The tested EDCs included oestrogen EE2 and bisphenol-A (BPA) [103]. Monitoring of nine trace organics under aerobic conditions at the Floreat MAR infiltration galleries site and in columns filled with aquifer sediments from below the water table revealed no evidence of degradation or retardation of some of the tested compounds, including the aforementioned EE2 and BPA [99]. The contrasting results from these studies were attributed to variable mineralogy within the soil profile with more iron oxide-coating on the quartz sand in the vadose zone to enhance sorption of trace organic compounds than in the saturated zone [99].

In Perth, Western Australia, secondary wastewater is pre-treated using ultrafiltration, reverse osmosis and ultraviolet radiation prior to the injection into the Groundwater Replenishment Scheme [98]. Despite the advanced levels of pre-treatment of reclaimed water prior to injection,
biodegradation is still a vital mechanism needed for removal of trace organic compounds, e.g., nitrosamines from wastewater disinfection and benzaltriazoles from detergents [100]. An active area of research is screening for residual micropollutants present in low ng L$^{-1}$ concentrations, particularly those which can be used as performance indicators [98].

Whilst there is a long-standing body of research on the biodegradation of pesticides under aerobic conditions in the vadose zone [104], there are relatively few studies on the anaerobic biodegradation of pesticides for Australian aquifers [105]. Kookana et al. [104] reviewed the degradation pathways for three herbicides commonly identified in ASTR (atrazine, simazine and diuron), as they may affect groundwater-dependent ecosystems downstream from MAR. Simazine has been shown to degrade under nitrate-reducing conditions which might occur in an aquifer receiving stormwater [105]. The laboratory study reports half-lives for simazine and diuron of up to 32 days and 92 days, respectively, which would allow sufficient degradation prior to recovery in the ASTR system [105].

2.2. Attenuation Zone, Predicting Aquifer Residence Times, Assessing Risks to Recycled Water Quality

MAR requires an attenuation zone or treatment barrier [84], i.e., the subsurface storage area surrounding the recharge zone where natural attenuation of contaminants occurs and, beyond which, the aquifer and other environmental values are not degraded by the system [33]. In planning new schemes for MAR, estimates of the size of the attenuation zone and the minimum aquifer residence time to allow for natural attenuation are obtained by quantitative modelling, performance monitoring, and/or tracer studies [106]. Residence time depends on flow rates within the aquifer, which may be natural or induced by the rates of recharge and/or recovery, depending on the type of MAR (Table 2). The estimation of travel times within an aquifer is complicated in heterogeneous strata. Although geophysical methods (e.g., flow metering and nuclear magnetic resonance) can help to elucidate changes in lithology to infer heterogeneity, tracer methods provide more direct measures [107].

The reuse of water poses risks to human health from contaminants. Microbial pathogens are the main health concern, as argued by Maliva and Missimer [107], on the basis that a single exposure may be sufficient to cause serious illness. Toze et al. [84] advanced the concept of using a quantitative microbial risk assessment (QMRA) for MAR, which involves using the estimate of aquifer residence time and the decay rates of reference pathogens to estimate the probability of infection to an individual in terms of disability adjusted life years (DALYs). The three reference pathogens—rotavirus, Cryptosporidium and Campylobacter—were recommended for representing viral, protozoan and bacterial hazards respectively [33]. At four MAR sites located in Mexico, South Africa, Australia, and Belgium, Page et al. [108] conducted a QMRA based on requirements for drinking water supplies and the estimates of average aquifer residence times, and then incorporated the results into a broader risk assessment to determine the human health burden. The results showed the aquifer treatment barrier was necessary for low risk [108].

With regard to health and environmental risks posed by inorganic chemicals, there is insufficient data to develop a DALY approach; instead, a definition of tolerable risk is used based on guideline concentrations and risk quotients [33]. In the case of the large-scale Groundwater Replenishment Scheme in Perth, Western Australia, water quality guidelines were set for the point of recharge and for monitoring groundwater within the aquifer. For this project, the Department of Health (DoH) undertook a comprehensive study of the potential public health risks from pathogenic micro-organisms, chemical contaminants and radioactive compounds to establish water quality guidelines for reverse osmosis treated wastewater for drinking water purposes [15,109]. Given the large number of chemicals that can potentially exist in wastewater, the study involved a prioritization process based on health risks [109]. The DoH study identified 254 water quality guidelines that the recycled water must meet to protect human health prior to recharge and 292 recycled water quality parameters, which must be measured, and, of these, selected 18 recycled water quality indicators to demonstrate the safety of the system [15,109].
As described earlier (Section 2.1), a probabilistic modelling approach is one method used to assess nutrient and organic carbon removal for ASR [58]. This approach has seen further application in studies involving metalloid fate to improve upon deterministic methods for estimating environmental risk [96]. In a study by Gonzalez et al. [110], a methodology was advanced for managing risks not only to human health, but also to the environment and to system operations in association with any type of MAR scheme. The method was applied to a case study which addressed the 12-element, risk-based framework for water safety consistent with Australian and international drinking water guidelines [111,112] and the Australian Water Recycling Guidelines for MAR [33,110]. The framework applied the hazard analysis and critical control point (HACCP) principles to prevent hazards or reduce them to an acceptable level. Critical limits are prescribed tolerances beyond which system performance is unacceptable, e.g., health-based regulatory criteria. Alert limits can be used to provide advanced warning of system failures triggering preventative action to avoid reaching critical limits. A probabilistic approach provides a way of setting limits based on historic trends to flag when a system strays from normal function. Distributive functions are very useful when dealing with highly variable parameters and where non-detects are frequent, e.g., microbial water quality. A decision tree for systematically determining critical and alert level criteria was developed by Gonzalez et al. [110] and is reproduced in Figure 1.

![Decision Tree Diagram](image)

**Figure 1.** Methodology based on a decision-tree approach for determining critical limits for water quality and setting alert limits from Gonzalez et al. [110] with permission from ASCE.
2.3. Understanding Biogeochemical Changes in MAR-Affected Aquifers

The injection or infiltration of source water into aquifers of contrasting water quality can give rise to a variety of biogeochemical changes, e.g., microbial-mediated redox reactions. These may affect the quality of water recovered from MAR and affect the hydraulic properties of the aquifer to affect the flow paths and residence times. Understanding the nature of recharge-induced biogeochemical reactions and their impacts on recovered water quality and clogging are key operational issues for MAR systems. Examples are provided in the Australian Water Recycling Guidelines for MAR [33]. This section explores three examples: (1) microbial-mediated redox reactions affecting metal mobility; (2) changes to the metabolic function and population ecology of microbes indigenous to aquifers that act upon pathogens in source water; and (3) mitigation of clogging which may develop due to biogeochemical changes.

At the fore of research in this area are combining experimental approaches and kinetic modelling [113], as well as developing a quantitative model of biogeochemical changes and their impacts on water quality and aquifer porosity. For example, Greskowiak et al. [114] successfully developed and tested a numerical model of biogeochemical response, mainly focused on dissolved organic carbon (DOC) mineralization and bacterial growth/decay, to ASR with reclaimed water into an anaerobic limestone aquifer. The study also estimated porosity increase due to calcite dissolution in the vicinity of the injection/extraction well, and porosity loss due to biomass growth [114]. More recently, modelling of microbially-catalysed reactions in relation to MAR has advanced to focus on incorporating isotope fractionation processes caused by biochemical reactions: Seibert et al. [115] combined stable sulphur isotope analysis with reactive transport modelling to trace pyrite oxidation during ASR and used $\delta^{34}$S signals as model calibration constraints.

2.3.1. Altered Aquifer Geochemistry and Metal(loid) Mobilization

While the aquifer can polish or ameliorate the quality of the recharge water, it can also lead to decrease in water quality due to the mobilization of geogenic constituents. Aquifer storage during MAR can induce rock–water interactions that increase the concentrations of arsenic, iron, manganese, and a host of trace ions in groundwater, depending on the pH, redox state, mineralogy, organic matter and microbial activity in the aquifer [33]. Among the list of possible metal(loid)s mobilized by MAR, naturally-occurring arsenic is the most problematic as it is common in sedimentary aquifers, relatively mobile over a wide range of redox conditions, and poses a health issue for potable supplies [116,117]. Iron is commonly mobilized during MAR, but is typically an aesthetic water quality concern rather than a health issue [96]. Table 3 reviews common processes leading to the mobilization of arsenic and the triggers for these.

| Mobilizing Processes | Triggering Factors |
|----------------------|--------------------|
| Release due to the oxidation of pyrite (FeS$_2$) and arsenopyrite (FeAsS) | High redox potential, temperature; microbial activity |
| Release due to the dissolution of arsenic-sulphide minerals | Changes in pH; increased presence of carbonates |
| Desorption due to the reduction of iron hydroxides | Decreased redox potential; microbial activity |
| Desorption due to changes in mineral surface chemistry | Increased pH |
| Desorption of arsenite/arsenate from minerals due to presence of competing species | PO$_4^{3-}$, HCO$_3^-$, H$_2$SiO$_4$, DOC, SO$_4^{2-}$ |

In natural waters, arsenic is mostly found as anions of arsenite (As(III)) and arsenate (As(V)). The latter is the more stable form of As under oxidizing conditions and can adsorb onto clays, iron oxides, and organic matter, while As(III) is dominant under reducing conditions [119].

Vanderzalm et al. [120] showed the importance of iron oxyhydroxides for controlling As concentrations at an ASR injection site in South Australia where microbial activity stimulated by the injection of organic matter caused increased As mobility. The results from this study were used to guide management decisions to reduce the potential for As release, e.g., pre-treating source water to
lower organic matter concentrations [120]. Arsenic mobilization and geochemical conditions in the MAR-affected, shallow aquifers of Orange County, California are quite different: despite the use of highly purified source water for injection, there is a need to minimize the potential for As release and the recommended strategy involves the use of water amendments (Ca\(^{2+}\) and Mg\(^{2+}\)) to promote As adsorption to phyllosilicate clay minerals of the aquifers [116].

The spatial- and temporal-variability of hydrochemical changes accompanying MAR injection and the implications for arsenic mobilization and adsorption were investigated using reactive transport simulations by Wallis et al. [121] for the Langerak ASTR system in Netherlands. The ASTR involved the injection of oxygenated water into a deep anoxic aquifer at the site, which led to the oxidation of pyrite and mobilization of significant amounts of arsenic, as well as nickel and zinc [121]. For the trial site used for the then-proposed Groundwater Replenishment Scheme in Western Australia, Seibert et al. [115] used reactive transport modelling to analyse pyrite oxidation in relation to proposed injection of aerobic injectant into an anaerobic aquifer. Reactive transport models for this Scheme involved obtaining experimentally-derived kinetic data for pyrite oxidation [113], using samples from the heterogeneous stratigraphy [113,115].

These studies highlight the variability in aquifer conditions, stratigraphic heterogeneity, and source water hydrochemistry, which reactive transport models are tailored to address for different MAR sites. They also emphasize the need for high quality experimental and field data to support and validate these models.

2.3.2. Changes to Subsurface Microbial Ecology

As the activity of indigenous microbes are relied upon in MAR systems to ameliorate the quality of recharging source waters, for example, by removing viral pathogens [77], mediating redox reactions affecting metalloid mobility [122,123], and affecting the fate of TOrCs [97,124], there is growing interest in quantifying the composition, diversity and change of microbial communities. At two pilot MAR sites in Perth and Adelaide, Reed et al. [125] evaluated changes in the sulphate reducing bacterial populations in relation to nutrient inputs in the source water by characterising sulphate-reducing enrichment cultures using denaturing gradient gel electrophoresis of polymerase chain reaction amplified 16S rRNA genes. The culturable bacterial communities responded to the migrating chemical gradient and aquifer geochemistry. The diversity of the culturable sulphate reducing bacteria was restored at the Adelaide MAR site, after aquifer geochemistry returned to ambient conditions.

Li et al. [124] used 16S rRNA gene pyrosequencing to investigate the change in microbial community structures in laboratory-scale soil columns to simulate MAR in relation to concentrations of biodegradable dissolved organic carbon. Bacterial and archaeal abundance was quantified using QPCR. Total microbial biomass was positively correlated with biodegradable dissolved organic carbon (BDOC) concentrations and bacterial populations dominated the community over archaea which represented only 1% of the overall community. The availability of BDOC had a clear impact on the microbial community structure and higher BDOC availability correlated with lower microbial diversity. The results were consistent with observations from field MAR sites at Taif River, Taif, Saudi Arabia and South Platte River, Colorado, which showed that DOC correlated positively with microbial numbers and negatively with microbial diversity [126].

As part of Perth’s Groundwater Replenishment Scheme, Ginige et al. [64] characterised the bacterial community within the anaerobic Leederville aquifer being recharged with aerobic reclaimed water using culture-independent molecular methods (clone library and QPCR of 16S rRNA genes) and flow cytometry. The study revealed that bacterial numbers increased and diversity decreased as a result of the aquifer recharge. The changes were proposed to reflect the increased numbers of denitrifiers and sulphur oxidisers as a result of increased concentrations of nitrate, oxygen, and residual organic matter in the receiving aquifer. Geochemical data suggested that denitrification and pyrite oxidation occurred after the commencement of the aquifer recharge.
2.4. Optimal Performance of MAR and the Science behind Siting New MAR Schemes

Siting new MAR schemes has typically focused on the hydrogeology and the limitations and cost-benefit considerations imposed by the existing infrastructure, and environmental and engineering constraints. The feasibility of MAR for the Kwinana Industrial Area in Western Australia was evaluated by modelling multiple scenarios at different locations in view of engineering constraints and methods for extracting, treating, and adding reclaimed water through infiltration basins and galleries in the coastal aquifer [127]. Understandably, a barrier to implementing new MAR projects is the uncertainty of performance and technological costs. A recent study by Drumheller et al. [128] developed an advanced algorithm to generate optimal control decisions for MAR operations that uses real-time sensors embedded within the aquifer to monitor water pressure and water quality. Although conducted at a laboratory scale, the proof-of-concept study paved the way for validation using field scale demonstration.

A range of conventional and advanced methods (e.g., borehole and surface geophysics, and reservoir modelling) are available for aquifer characterization, which can also aid in optimizing the design and future performance of systems given the existing constraints of the hydrogeology [129]. Groundwater flow and transport modelling is another tool for assessing MAR systems and minimizing hazard risks (e.g., low recovery efficiency, clogging and geochemical processes). Different models for this purpose were reviewed by Ringleb et al. [130] based on 216 studies dealing with MAR from 37 countries.

This section deals with some of the complex issues of siting MAR in catchments compromised by existing pollutant sources or hydraulically up-gradient from ecologically sensitive areas.

2.4.1. Pollutant Release and Transfer from Existing Contamination Sites

A potentially confounding issue for siting MAR is the uncertainty of mobilizing contaminants in the aquifer. For the MAR feasibility and groundwater modelling study for Kwinana, Bekele et al. [41] described the existing point or diffuse sources, including nutrients, petroleum hydrocarbons, metals, pesticides, phenols and solvents from industrial and commercial properties in the catchment proposed for MAR. In addition, there are areas within the coastal aquifer mapped for acid sulphate soil risk [41]. National registries for substance emissions from industries to the environment are crucial for siting new MAR schemes. In Australia, the National Pollution Inventory is a government database that provides this information which can be used to assess the potential for leaching of contaminants from soil into groundwater. This can be incorporated into groundwater models for optimal placement of new MAR schemes or to effectively manage recharge volumes to assist with the dilution of existing contaminants. In South Korea, the risks posed by siting new ASTR in two urban locations were assessed: Ji and Lee [131,132] highlighted that Pollutant Release and Transfer Registry (PRTR) data from selected sites are vital to planning new MAR and further develop a hazard analysis and critical control points methodology for river water used for ASTR. A promising area for future research is applying newly developed theoretical methods to predict pollutant release history and source location in groundwater to properly constrain placement of new MAR schemes. Butera et al. [133] presented several theoretical case studies using a new geostatistical method for this purpose, but medium scale laboratory tests and field validation of the approach are needed.

2.4.2. Clogging Management in MAR

Clogging is one of the most serious operational problems in MAR since it restricts the volume of water recharged, thereby increasing the effective unit price of stored water. Clogging develops with time as a result of the interaction between the source water (including its constituents), and the native groundwater and the porous media. This can lead to a reduction in the permeability of the infiltration basin, well screen or the surrounding aquifer. Clogging-induced permeability reductions cause a decline in injection rate and/or hydraulic head increase. Comprehensive reviews of these processes
have been previously well documented (e.g., [134,135]), and are not repeated here. Multiple forms of clogging (physical, chemical or biological) can occur simultaneously or separately and over similar or different intervals of time and space. Examples are from filtration of suspended solids, microbial growth, geochemical reactions, and air entrainment. In many cases, the processes responsible for clogging are very difficult to interpret and conclusions must be drawn from indirect evidence.

In Australia and elsewhere, opportunities to enhance groundwater resources through ASR have been foregone due to a limited and site specific knowledge of water quality requirements for injection into unconsolidated aquifers [136,137]. ASR operations in Australia have largely focused on limestone or fractured rock aquifers and the results have generally been successful (e.g., Page et al. [136]). From a well clogging perspective, limestone aquifers are the more tolerant of poorer source water quality due to the offsetting effect of matrix dissolution. Although fractured rock aquifers are more complex to characterize in terms of their permeability structure and storativity, detailed studies have not yet been conducted systematically across Australia. Unconsolidated, fine-grained aquifers present challenges to maintain adequate rates of injection in ASR wells.

In an effort to better understand limits to infiltration in unconfined aquifers using treated wastewater for MAR in Australia, Vanderzalm et al. [138] and Bekele et al. [57] conducted two field-based studies, involving the characterization and monitoring of a range of soil and water quality parameters to document how clogging develops and how it can be prevented. At the Alice Springs SAT site in the Northern Territories, the study determined that heterogeneous soil characteristics had a major impact on clogging, but treatment upgrades involving sand filtration and ultraviolet disinfection prior to recharge increased the average infiltration rate, nominally less than 1 m/day, per basin by 40% to 100% [45]. At the infiltration galleries site in Western Australia, the study involved the infiltration of treated wastewater in medium-grained sand deposits at rates of up to 4 m/day, but maintaining hydraulic performance largely depended on reducing total suspended solids below a target level (i.e., 5 mg/L) to reduce the potential for clogging [57].

2.4.3. Coastal MAR to Prevent Seawater Intrusion and Dealing with Potential Nutrient Outflows

In the coastal aquifers adjacent to Monterey Bay, California, an investigation was conducted of nutrient loading in relation to MAR operations at the Harkins Slough, to better understand the effects of using recharge ponds with an average infiltration rate of >1 m/day [139]. The study showed significant nitrate load reduction (7 kg/day/ha) during infiltration due to the presence of high dissolved organic carbon in the recharge water and variations in soil texture, which promote local redox conditions conducive to denitrification [139]. While denitrification was highest within the first meter of subsurface soil below the pond, concentration reductions observed in the underlying aquifer were mainly due to dilution [139]. Submarine groundwater discharge (SGD) of nutrients stimulates the phytoplankton blooms in the area [140]. The most toxic algal bloom ever recorded in the bay was due to elevated levels of nitrate relative to silica stimulating the production of a biotoxin by the diatom, *Pseudo-nitzschia australis*. Toxicity production by this species has a nitrogenous preference for urea [141,142]. *P. australis* exists in other parts of the world, including the east and south coasts of Australia where it forms extensive blooms [143].

In the beginning of 2017, Pure Water Monterey near Monterey Bay commenced the construction of a large-scale, groundwater replenishment project that will inject 3.4 GL/year of advanced treated wastewater into the Seaside Groundwater Basin [144]. The source waters will include municipal and industrial wastewater, stormwater, surface water and agricultural tile drain water. The scheme is primarily to replenish the Seaside Groundwater Basin, but it will also assist in preventing seawater intrusion and reduce the amount of secondary effluent currently discharged via ocean outfall [144].

In Western Australia, the feasibility of augmenting groundwater and preventing seawater intrusion using MAR and recycled water was investigated throughout a 290 km$^2$ section the coastal plain near the Kwinana Industrial Area adjacent to the Cockburn Sound [127]. Groundwater modelling revealed that recharging the aquifer with 1.7 to 3.5 GL/year could reduce the threat of
seawater intrusion in the coastal aquifer; however, the input of nitrogen to Cockburn Sound via submarine groundwater discharge (SGD) and enhanced marine plant productivity are a concern. Additional measurements are needed to reduce uncertainty in the existing nitrogen budget to accurately assess whether further wastewater treatment prior to infiltration is required [127,145].

3. Conclusions and Future Research

Groundwater depletion and quality improvement, water scarcity, a drying climate, and seawater intrusion of coastal aquifers are global concerns which MAR can readily address. In an urban setting where land is a premium cost, MAR typically requires a much smaller areal footprint compared to equivalent surface water storages while also avoiding some of the problems associated with above-ground storage such as evaporative losses, algal blooms and mosquitos. Increased water availability for urban greenspace irrigation through MAR can also mitigate urban heat island effects and increase amenity value. Infiltration-based MAR using reclaimed water is a relatively low-cost alternative to other methods of wastewater disposal, especially considering nutrient removal costs to meet environmental discharge requirements to freshwater or marine environments. This review summarizes the current understanding of natural attenuation processes of aquifer storage to reduce the concentrations of nutrients, microbial pathogens, and trace organic chemicals. It also highlights some of the hazards and risks accompanying the implementation of MAR, namely the mobilization of contaminants, either pre-existing within the aquifer or released through biogeochemical reactions and the dissolution of the aquifer matrix, and nutrient export downstream to ecologically-sensitive environments, i.e., via submarine groundwater discharge.

MAR-related research breakthroughs have been increasingly reported in the scientific literature in the last decade. Specific conclusions are:

- Many of the early studies of potential water quality improvements were obtained using laboratory-scale, column studies of rock–water interactions designed to replicate MAR-conditions using different source waters and sediment and/or aquifer matrix materials. These remain a fundamental approach, accompanying the planning stages for new MAR opportunities. In addition, groundwater modelling is used in the planning stages to predict changes in water levels and pressures to quantify potential supply augmentation and examine possible deleterious effects such as aquifer over-pressurization or raised water tables, or contaminant transport.

- The state-of-science in MAR is to embark on field-scale demonstrations, documenting the changes in permeability changes, water pressure and water quality in real-time and to use theoretical algorithms to manage MAR operations for optimal performance. After several decades of research in this area, operators are now much better equipped to understand the combinations of source water types, aquifer and MAR operational conditions that lead to specific changes in water quality.

There remain opportunities to further advance the state-of-science in MAR. These include documented field trials of permeable reactive barriers or groundwater amendments that alter the biogeochemical environment to further ameliorate the quality of groundwater prior to recovery. In addition, there remain opportunities for greater adoption of science in regulation, and a standardized approach to assess natural treatment so that aquifer is incorporated within a treatment train, especially with regard to drinking water systems. Furthermore, there could be greater use of pollutant release and transfer registry data to plan and model the impacts of MAR. In particular, source water chemistry data can be matched to point source or diffuse contamination in aquifers to allow beneficial geochemical reactions or dilution to occur. With the advent of new technologies for screening for micropollutants and molecular methods for microbial pathogens and antibiotic resistant genes in microorganisms, there are now more data to underpin ecotoxicology studies, establish trigger values for selected indicators, and to guide environmental risk assessments. These can be used to fine-tune MAR operations to allow greater compliance with water quality regulations.
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