Natural Contaminant Attenuation During Reclaimed Water Aquifer Recharge in Destin

Robert G. Maliva, Monica Autrey, and Scott Manahan

Optimization of the reuse of reclaimed water often requires storage to balance variations in supply and demand. Aquifer storage and recovery (ASR) systems are increasingly being used for the seasonal underground storage of reclaimed water, as well as potable water and surface waters. Natural contaminant attenuation processes that occur in aquifers are being taken advantage of to provide additional treatment (polishing) of reclaimed water prior to potable and nonpotable uses.

Key technical issues for the direct subsurface recharge of reclaimed water are the fates of pathogens and disinfection byproducts (DBPs), such as trihalomethanes (THMs). Reclaimed water needs to be disinfected to meet applicable microbiological water quality standards for injection, while at the same time not exceeding applicable groundwater standards for DBPs. The leaching of arsenic into recharged water in concentrations exceeding groundwater standards has also occurred in numerous ASR systems.

The Destin Water Users Inc. (DWU) reclaimed water ASR system stores tertiary-treated reclaimed water in a sand-and-gravel aquifer located on a barrier island off the coast of northwest Florida. The storage zone contains anoxic freshwater that is restricted by local ordinance to nonpotable use. Chemical differences between the reclaimed water and native groundwater (e.g., chlorine [Cl] and fluorine [F] concentrations) provide accurate tracers for the presence of recharged reclaimed water in wells.

An exhaustive monitoring program (including in excess of 1,000 monitoring well samples since inception) provides an extensive database on the fate of THMs in the groundwater environment. The average measured total THM concentration of the injected water over the full-system operational period (starting in June 2012) was approximately 61 µg/L (n = 68), yet the concentration of THMs were below the detection limit (< 0.5 µg/L or less) in over 99 percent of the water samples from the storage-zone monitoring wells (SZMWs). The THMs were effectively removed by natural attenuation processes by the time the reclaimed water reached the SZMWs.

Arsenic leaching has occurred in the DWU ASR system, and other ASR systems globally, at concentrations exceeding the applicable groundwater standard of 10 µg/L. The source of the arsenic appears to be the oxidative dissolution of trace arsenic-bearing sulfide minerals. The concentrations of arsenic in recovered water have decreased over time as the amount of leachable arsenic near the ASR wells is progressively exhausted. Further from the injection and recovery wells, leached arsenic is being sequestered in the formation, as evidenced by low concentrations (generally below 10 µg/L) in most monitoring well samples.

Chlorination can be beneficial for reclaimed water recharge systems by providing pathogen inactivation, and a chlorine residual in injected water is desirable for minimization of biological clogging in recharge wells. The DWU ASR experience indicates that chlorination should not be avoided due to concerns over THMs, where anoxic aquifers are used as storage zones, as the THMs will be naturally attenuated. The DWU operational data demonstrate that natural contaminant attenuation processes can be highly effective in improving the quality of recharged reclaimed water and minimizing any residual risk to public health and the environment associated with its underground storage.

Florida: A Water-Rich State

Florida is blessed with abundant water resources, with a statewide annual average rainfall of about 53.6 in. (NOAA, 2019). The fundamental water management challenge in Florida is not that the state doesn't have enough water, but rather that there is a large seasonal disconnect in supply and demand: There is usually an overabundance of water during the summer wet season and inadequate water during the winter and spring dry season, which also coincides with a peak in tourism and seasonal resident populations.

The flat topography of Florida is suboptimal for large surface reservoirs, with only several notable exceptions (e.g., the Peace River Manasota Regional Water Supply Authority system in De Soto County, and the Tampa Bay Water C.W. Bill Young Regional Reservoir in Hillsborough County). It has been recognized in Florida for the past four decades that part of the solution to its water management challenge is to store water underground in ASR systems. Stormwater drainage wells have a much longer history in central Florida, where wells that have a primary water disposal function are also recognized to provide important aquifer recharge.

Originally, ASR was defined by Pyne (1995) as "the storage of water in a suitable aquifer through a well during times when water is available, and the recovery of the water from the same well during times when it is needed." The ASR is a subset of managed aquifer recharge (MAR), which is broadly defined as the "intentional banking and treatment of waters in aquifers" (Dillon, 2005) and includes other technologies in which water is recharged using either wells or surface spreading systems.

The advantages of ASR, and MAR in general, in Florida are compelling. Very large volumes of excess water can be stored underground during wet periods and later recovered during dry and high-demand periods. Indeed, ASR is being investigated as a key part of the Comprehensive Everglades Restoration Plan (CERP) for south Florida (USACOE and SFWMD, 2010).

Underground injection, including ASR, is regulated by the U.S. Environmental Protection Agency (EPA). The Safe Drinking Water Act (SDWA) of 1974 (and subsequent amendments) resulted in the establishment of the EPA underground injection control (UIC) program. Florida, and some other states, have obtained primary enforcement authority (primacy) for all or some types of injection wells. Individual states and Native American tribes that obtain primacy must still meet EPA UIC regulations, although they can establish more restrictive regulations.

The overriding objective of the EPA UIC program is to prevent endangerment of underground sources of drinking water (USDW), which are defined as nonexempt aquifers that contain less than 10,000 mg/l of total dissolved

Robert G. Maliva, Ph.D., P.G., is principal hydrogeologist with WSP USA Inc. in Fort Myers and is with the U.A. Whitaker College of Engineering at Florida Gulf Coast University. Monica Autrey, P.E., is operations manager at Destin Water Users Inc. Scott Manahan, P.E., is senior engineering manager with WSP USA Inc. in Fort Myers.

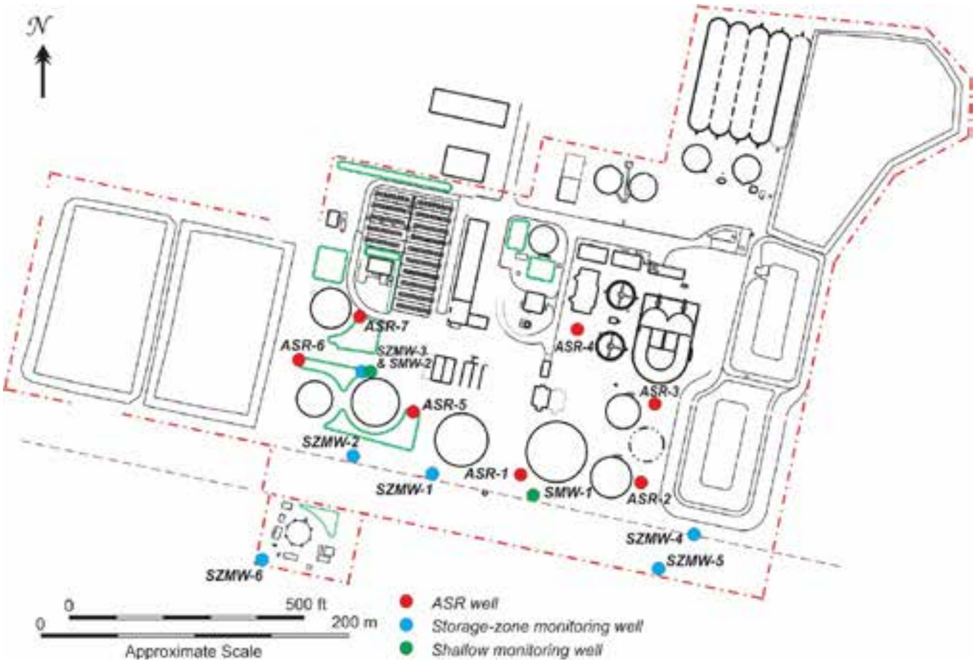

Figure 1. Site plan of Destin Water Users Water Reclamation Facility showing aquifer storage and recovery well locations.

solids. Endangerment is defined in the U.S. Code of Federal Regulations (40 CFR 144.3) as any "injection activity in a manner that allows the movement of fluid containing any contaminant into underground sources of drinking water if the presence of that contaminant may cause a violation of any primary drinking water regulation under 40 CFR part 142 or may otherwise adversely affect the health of persons."

The operation of ASR systems can endanger USDW if either the recharged water contains one or more contaminants at concentrations exceeding primary drinking water standards or if the concentration of a parameter increases to above a drinking water standard after recharge as the result of fluid-rock interactions.

In a number of ASR systems in Florida, endangerment of USDW occurred when recharged water containing dissolved oxygen (DO) caused the oxidative dissolution of arsenic-bearing iron sulfide minerals in the aquifer. The recharged water met the applicable arsenic maximum contaminant level (MCL) of 10 µg/L at the time of injection, but the released arsenic caused the MCL to be exceeded.

Avoiding endangerment of USDW is a fundamental operational and regulatory requirement for ASR systems in Florida and elsewhere in the United States. Endangerment can be avoided by treating the recharge water to drinking water standards and, in some cases, additionally pretreating the recharged water to avoid adverse-fluid rock interaction. The DO is being stripped from recharged water prior to injection in some ASR systems in Florida to prevent arsenic leaching. Where the recharge water will not be recovered for potable use (or otherwise enter the potable water supply), treating the recharge water to potable quality represents a large additional expense that could render ASR economically unviable.

The concentrations of pathogens and many chemical contaminants are naturally reduced in the groundwater environment. Natural contaminant attenuation processes can be taken advantage of as a less expensive alternative to (or also used in conjunction with) engineered treatment systems to improve the quality of water stored in ASR systems, or recharged in other types of MAR systems so as to meet the nonendangerment requirement. The compliance point for meeting applicable groundwater quality standards would be at the boundary of a zone of discharge (ZOD), rather than at the wellhead, which allows for an aquifer treatment zone around the ASR or recharge well.

There are considerable laboratory and field data on the natural contaminant attenuation processes active in the groundwater environment in general and associated with different types of MAR systems, which was recently reviewed by Maliva (2019). Two of the key issues facing ASR systems storing nonpotable water (e.g., reclaimed, storm, and surface waters) in Florida are simultaneously meeting bacteriological and disinfection products (particularly trihalomethanes) standards and managing arsenic leaching.

This article summarizes natural contaminant attenuation processes in groundwater and reports on the experiences of the DWU reclaimed water ASR system. Field data on water quality improvements during groundwater storage and transport are critical for guiding future incorporation of natural contamination attenuation processes in the design, operation, and regulation of ASR and MAR systems.

Natural Contaminant Attenuation Processes in Groundwater

The greatest health risk associated with the recharge and reuse of reclaimed and other impaired (nonpotable) waters is associated with pathogens. A one-time exposure to water containing even low concentrations of *Cryptosporidium* oocysts and some viral pathogens may be sufficient to cause serious illness, whereas drinking water standards for chemical contaminants are based on chronic, lifelong consumption of water. The EPA MCLs are based on lifetime ingestion of 2L of water per day for a 155-lb adult. The actual risk for long-duration potable consumption of water containing chemicals at concentrations of concern from an MAR system in Florida is insignificant due to the rigorous Florida Department of Environmental Protection (FDEP) permitting process and monitoring requirements. Injection of impaired water would not be allowed where it could enter a known well used for potable supply.

Because of their much greater heath risk, there has been considerable investigation of the fate of pathogens after groundwater recharge. Pathogen removal rates are commonly expressed as the $\log_{10}$ removal time (or just "log removal time; τ) defined as:

$$\tau = t/Log_{10}(C_0/C_t)$$

- where C_0 = initial number of organisms (at time t = 0) and C_t = number of organisms at time "t" (days).
- A 1-$\log_{10}$ removal is equal to a 90 percent reduction in concentration; a 2-$\log_{10}$ removal corresponds to a 99 percent reduction in concentration.

John et al. (2004) investigated the fate of microorganisms in aquifers for the Southwest Florida Water Management District and South Florida Water Management District. Benchtop testing was performed using two groundwater

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samples and two surface water samples from central Florida at temperatures of 72°F and 86°F. The protozoan parasites *Cryptosporidium parvum* and *Giardia lamblia*, and PRD-1 bacteriophage, were found to be more resistant than fecal coliform bacteria and enterococci with an estimated 10 to over 200 days required for the 99 percent (2-log) inactivation of *Cryptosporidium* and 24 to over 200 days required for the 99 percent removal of *Giardia*. The study did not consider the effects of filtration on the concentrations of the relatively large oocysts.

Subsequent review studies (Toze, 2005; Jones and Rose, 2005), and laboratory and in situ inactivation studies (Sidhu et al., 2006, 2012, 2015; Lisle, 2016), show variable removal rates between microorganisms and biogeochemical conditions. Most microorganisms had 2-log removal times of two months or less, although some viruses are more persistent (bacteria tend to have rapid removal rates). The available data strongly indicate that the health risks associated with pathogens in MAR systems can be naturally managed by ensuring sufficient aquifer residence time to achieve target removal rates based on the types and concentrations of organisms that might be present in recharged water.

The state of California recognizes natural attenuation of pathogens in groundwater replenishment reuse projects (GRRPs), with reduction credits granted per month of storage, depending on the method used to determine the travel time to the nearest downgradient drinking water well (California Code of Regulations 22 CCR § 60320.108). The greatest reduction credit (1 log per month) is granted for tracer tests using an introduced tracer, which are deemed to have the greatest accuracy.

In MAR systems in which the recharged water is treated by chlorination or chloramination, the challenge is optimizing the disinfectant dose so that bacterial (coliform) standards are met while not exceeding the drinking water standard for THMs, which is 80 µg/L for total THMs in Florida. Earlier studies on the fate of THMs in ASR systems focused on potable water storage systems, where the concern was that the THM standard would be exceeded upon recovery and redisinfection of the water (Miller et al., 1993; Singer et al., 1993; Pyne et al.,1996).

The results of these earlier studies and subsequent investigations indicate that THM formation may continue after injection through the interaction of residual chlorine, with organic compounds present in the recharge water and storage zone, and that THM removal occurs more rapidly under chemically reducing conditions. Haloacetic acids (another group of disinfection byproducts) and the more brominated THMs are more rapidly removed, and chloroform is the most refractory THM.

The fate of THMs was investigated in the intensely studied Bolivar (South Australia) reclaimed water ASR system in which treated wastewater was stored in an anoxic brackish-water aquifer. Operational data show both the initial formation of THMs and their subsequent biodegradation (Nicholson et al., 2002; Pavelic et al., 2005). Total THM concentration in the ASR well decreased from 145 µg/L at the end of recharge to <4 µg/L after 109 days of storage. The THMs were not detected at an observation well located 164 ft from the ASR well, even though the injected water had reached the well (Pavelic et al. 2005).

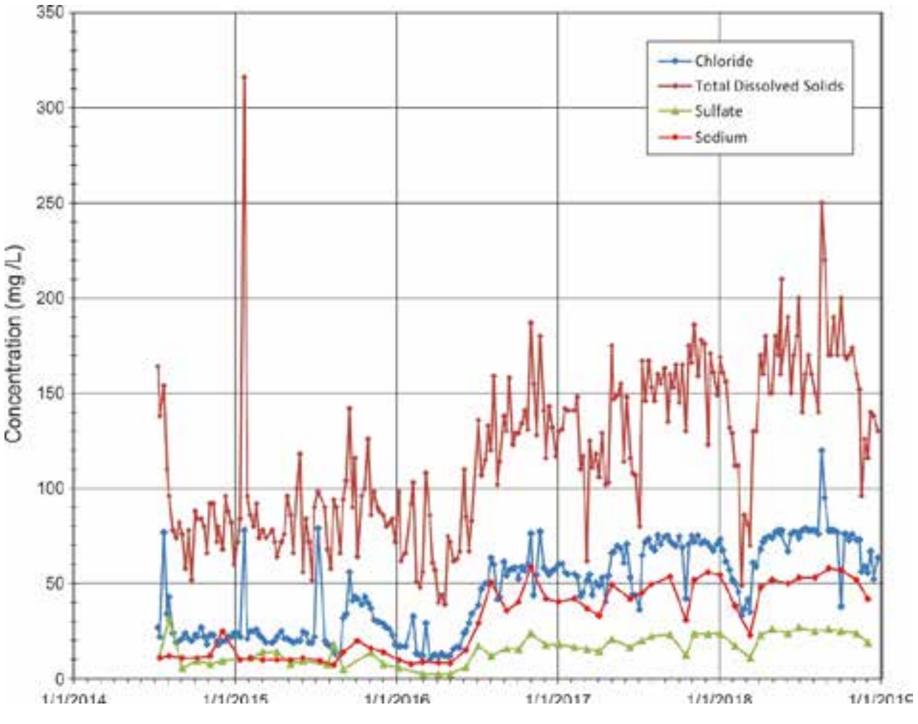

Figure 2. Plot of salinity parameter concentration data for Storage-Zone Monitoring Well 6.

The causes of arsenic leaching in ASR systems have received considerable study because it's a violation of a regulatory standard and thus potentially impacts the ability of the affected systems to legally operate. Arsenic leaching has also cast a cloud over the technology, which has slowed its implementation in Florida. The amount of leachable arsenic in most formations is quite limited, and over time, will be exhausted.

Two main strategies have been employed to manage arsenic leaching: pretreatment and source removal. Recharge water can be treated by different physical and chemical processes so that it reaches chemical equilibrium with arsenic-bearing minerals in the storage zone. Pretreatment can potentially result in immediate compliance with the arsenic standard, but it has the disadvantages of additional costs and that it will be continually required over the operational life of the system. The alternative is to allow for the supply of labile arsenic in the formation to be exhausted over multiple injection and recovery cycles. The advantage of the arsenic source removal process is low cost and finality, but it has the disadvantage of a long and uncertain time requirement, and requires regulatory approval.

The fate of leached arsenic is less uncertain. Released arsenic either remains in solution or is subsequently removed from solution by mineral precipitation and/or sorption processes. Two main arsenic removal models have been proposed: under oxic conditions, arsenic may be sorbed onto newly formed iron (oxy) hydroxides (Mirecki, 2006); and under anoxic conditions, such as may be established after recharge of organic-rich reclaimed and surface waters, released arsenic may be sequestered by coprecipitation with iron sulfides (Mirecki et al., 2013).

Destin Water Users Reclaimed Water Aquifer Storage and Recovery System

The DWU reclaimed water ASR system, located at the George F. French Water Reclamation Facility (WRF) in northwestern

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Florida, stores tertiary-treated reclaimed water in the main-producing zone of the sand-and-gravel aquifer. The main-producing zone is located between approximately 115 and 165 ft below land surface (ft bls) at the WRF site. The storage zone is hydraulically well-separated from the Upper Floridan aquifer, which is used on the barrier island for potable water supply and the surficial zone of the sand-and-gravel aquifer, which is very widely used in Destin for domestic irrigation wells.

The ASR system consists of seven ASR wells (ASR-1 through ASR-7), six SZMWs (SZMW-1 through SZMW-6), and two shallow monitoring wells (SMW-1 and SWM-2), as shown in Figure 1. The DWU ASR system has a design capacity of 2.125 mil gal per day (mgd) or 210 gal per minute (gpm) per well.

The DWU ASR system was constructed in two phases. The initial system, constructed in early 2009, consisted of a single ASR well (ASR-1), two SZMWs (SZMW-1 and SZMW-2), and one shallow monitoring well. After completion of the initial operational testing of well ASR-1, the remaining wells were constructed in late 2011.

The main-producing zone contains anoxic freshwater that is restricted by local ordinance to nonpotable use. Chemical differences between the reclaimed water and native groundwater (e.g., salinity parameters and fluoride concentrations) provide accurate tracers for the presence of recharged reclaimed water in wells. Recharged reclaimed water has a higher salinity than the native groundwater and its breakthrough in a monitoring well can be detected by an increase in the concentration of the salinity-related parameters. For example, the arrival of the recharged reclaimed water in SZMW-6 in middle 2016 is evident by increases in the concentrations of total dissolved solids (TDS), chloride, sodium, and sulfate (Figure 2).

An exhaustive monitoring program (including in excess of 1,000 monitoring well samples since inception) provides an extensive database on the fate of THMs in the groundwater environment at the DWU WRF site. The average measured total THM concentration of the injected water over the full-system (seven wells) operational period (starting in June 2012) was approximately 61 µg/L (n = 68). The concentration of THMs were below detection limit (< 0.5 µg/L or less) in (remarkably) over 99 percent of the water samples from the SZMWs, including samples consisting of recharged reclaimed water, as indicated by salinity parameters. The THMs were effectively removed by natural attenuation processes by the time the reclaimed water reached the SZMWs.

The main-producing zone consists mainly of quartz sand and gravel and no potential arsenic-bearing minerals were observed in samples collected during well drilling. Nevertheless, arsenic leaching did unexpectedly occur. A source attenuation strategy was employed in the DWU ASR system. The arsenic concentrations in the recovered water from each well have progressively decreased over time and, with the exception of one well (ASR-6), now meet the 10 µg/L MCL (Figure 3). After early 2016, arsenic concentrations in the four SZMWs have consistently met the 10 µg/L MCL (Figure 4). The low concentrations of arsenic in the more-distal monitoring wells (SZMW-5 and SZMW-6), in which recharged reclaimed water has broken through, indicate that leached arsenic is either being removed via recovery or is being sequestered in the storage zone in a stable form. Arsenic is not staying in the solution and is being pushed away from the ASR well.

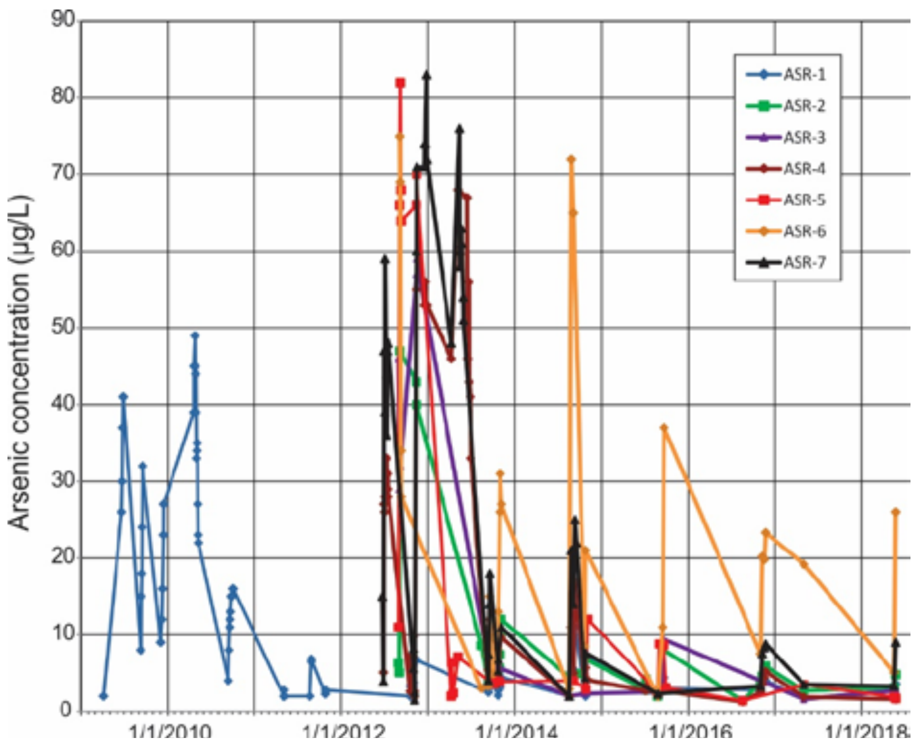

Figure 3. Recovered water arsenic concentrations.

Conclusions

The operational data from the DWU ASR system provide valuable insights into the behavior of THMs and arsenic during reclaimed water ASR and demonstrate the viability of relying on natural contaminant attenuation processes to protect public health and the environment. Pathogens inherently pose a greater health risk than THMs because of the potential for illness from a one-time exposure to some pathogens. Chlorination can be beneficial for reclaimed water recharge systems by providing pathogen inactivation, and a chlorine residual in injected water is desirable for minimization of biological clogging in recharge wells. Hence, when recharging reclaimed or other nonpotable waters, chlorination should be considered to provide an additional barrier against pathogens, in addition to the natural inactivation of pathogens that occurs in groundwater environments.

The DWU ASR experience indicates that chlorination should not be avoided over concerns about THM formation, where anoxic aquifers are used as storage zones, as the THMs will be naturally attenuated.

The DWU ASR system also demonstrates how arsenic leaching can be successfully managed by source attenuation. Over operational time (injection and recovery), the amount of leachable arsenic in the DWU ASR storage zone has been progressively depleted, and arsenic concentrations in the recovered water and SZMWs have either reached or are approaching concentrations below the 10 µg/L MCL.

Natural contaminant attenuation processes are one element of a multiple-barrier approach to ensuring that the MAR does not endanger USDW and impair public health. The DWU operational data demonstrate that natural contaminant attenuation processes can be highly effective in improving the quality of recharged reclaimed water and minimizing any residual risk to public health and the environment associated with its underground storage. The reduced need for often cost-prohibitive engineered treatment would make more ASR and MAR systems economically viable, allowing society to capture their water management benefits.

Key elements for successful utilization of natural contaminant attenuation are a sound technical understanding of the biogeochemical processes involved, regulatory policies that allow for a ZOD (in essence, a geographically delineated aquifer treatment zone), and a right-sized monitoring program to ensure that contaminants are not approaching potable supply wells (and other sensitive receptors) and that anticipated water quality improvements are indeed occurring.

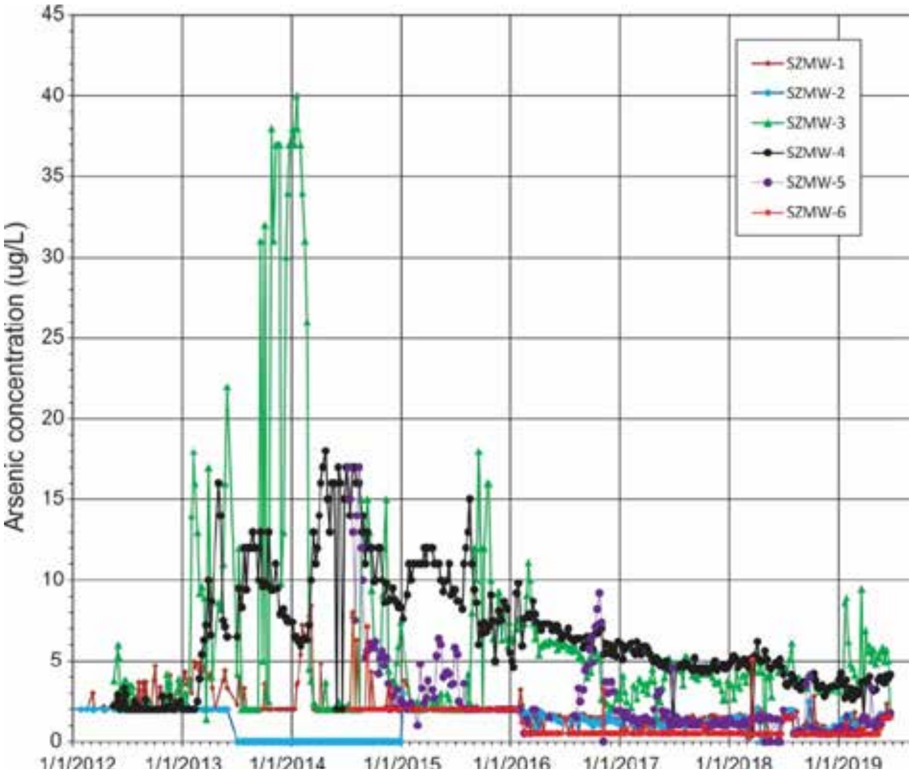

Figure 4. Storage-zone monitoring well arsenic concentrations.

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