Managed Aquifer Recharge with Advanced Treated Municipal Effluent: Modelling the Impact on Groundwater Chemistry and Native Microbial Ecology

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ABSTRACT

Managed aquifer recharge (MAR) using advanced treated municipal effluent (ATME) has become a viable solution to help replenish groundwater supplies in water-stressed areas. The coupled hydrogeochemical and microbiological responses of receiving aquifers are however underrepresented. An integrated field-monitoring and reactive-transport modeling approach is applied to evaluate the effects of ATME-based MAR on groundwater chemistry and native microbial ecology at a spreading-basin facility in the semi-arid southwestern United States. Groundwater samples were taken from 350 monitoring points over 24 months from twelve monitoring wells located at distances of 30–1200 m from the recharge basin. Major ions, trace elements, dissolved organic carbon (DOC), constituents of emerging concern (CECs) and stable water isotopes were measured in samples, while microbial communities were characterized by 16S rRNA gene amplicon sequencing (V3-V4 region) and functional profiling using PICRUSt2. A coupled MODFLOW/MT3DMS–PHREEQC model was used to simulate reactive transport. Mixing of ATME with native groundwater resulted in a chemical gradient that was dominated by a Ca–HCO_3–NO_3 facies within 300 m of the basin, and beyond 900 m a native Ca–Mg–HCO_3 signature was observed. DOC attenuation was pseudo-first-order ($k = 0.021\ d^{-1}$), and 68 % of the CECs monitored were reduced to below detection limits after 180 days of residence in the subsurface. Microbial α-diversity (Shannon index) rose by 22 % in the proximal wells compared to background, with enrichment of Proteobacteria, Nitrospirae and Planctomycetes, and a decrease in Firmicutes. The impact zone had significantly higher predicted numbers of functional genes involved in nitrogen cycling and xenobiotic biodegradation. Modeling using reactive transport was able to reasonably simulate the observed solute breakthrough, with a Nash–Sutcliffe efficiency of 0.87. The results offer a mechanistic approach to assessing water-quality trends and microbial risk in ATME-based MAR schemes, which can be used to guide residence-time requirements for potable-reuse applications.

Keywords—Managed aquifer recharge, advanced treated effluent, groundwater chemistry, microbial ecology, PHREEQC, MODFLOW, water reuse, PICRUSt2.

I INTRODUCTION

Freshwater scarcity is one of the major problems of the twenty-first century, affecting about 2/3 of the world's population and causing them to suffer from acute water shortages for at least one month a year [1]. In the southwestern United States, aquifer storage has continuously decreased in the Central Valley, California, the Colorado River Basin, and the Ogallala Aquifer due to long-term drought, groundwater overdraft, and rising demands from municipal, agricultural, and industrial uses [2, 3]. Water managers, in turn, have responded by implementing managed aquifer recharge (MAR) as a way to provide some buffer in water supply variability, to replenish storage, and to protect coastal aquifers from saltwater intrusion [4].

Advanced treated municipal effluent (ATME) is one of the many portfolios of source waters used in MAR, in particular due to the reliability of its supply and because it is not dependent on droughts, and because its production is linked to urban

population growth [5]. The advanced treatment usually involves the combination of microfiltration or ultrafiltration, reverse osmosis (RO), and ultraviolet-based advanced oxidation (UV/AOP), resulting in very low salinity, near-zero pathogens and significantly lower levels of most constituents of emerging concern (CECs) [6]. Full-scale ATME-based MAR schemes have been in operation for decades, including at the Orange County's Groundwater Replenishment System, West Basin Municipal Water District, and Scottsdale Water Campus [7, 8].

Although the ATME was widely deployed, the geochemical and microbiological evolution during its passage through the vadose zone and saturated aquifer is not well characterized. The composition of the infiltrating water can be significantly modified by reactive processes occurring at the recharge basin, such as cation exchange, calcite dissolution and precipitation, redox transformations, sorption of trace organics, and biodegradation [9, 10]. At the same time, a new source of dissolved organic carbon (DOC), residual nitrogen species, and trace organics can change the nature of the indigenous microbial community, leading to the proliferation of copiotrophs and specialized degraders and consequently to changes in important biogeochemical cycles [11, 12]. Subsurface microorganisms drive the majority of transformations that affect water quality, so understanding their response is critical to understanding long-term system performance and to designing regulatory frameworks that recognize the subsurface treatment [13].

Most studies on MAR have focused on the chemical and biological aspects separately. Equilibrium and kinetic modeling software, e.g., PHREEQC and MIN3P, have been applied to simulate mineral dissolution, ion exchange, and mobilization of trace elements in soil-aquifer treatment (SAT) systems [14] and [15]. High throughput sequencing independently has identified unique microbial signatures in recharged aquifers such as increased abundance of Nitrospira, Comamonadaceae, and Sphingomonadaceae [16, 17]. Few studies, however, have combined chemistry, community structure, and reactive-transport modeling in a single study and have been applied over spatial and temporal scales that are large enough to capture the transition between recharge-dominated and native-groundwater zones [18].

The study aims to address this gap with three coupled objectives: (i) quantify the spatiotemporal evolution of major ions, trace constituents and CECs during ATME-based MAR in a semi-arid alluvial aquifer based on 350 groundwater samples collected over 24 months; (ii) characterize the concurrent changes in native microbial community composition, diversity and predicted function; and (iii) develop and validate a coupled reactive-transport model that simultaneously reproduces solute breakthrough and serves as a predictive tool for operational management. The incorporation of dense monitoring and next generation sequencing and process-based modeling is designed to shift the field from empirical performance descriptions to mechanistic prediction, especially as U.S. states move toward regulations for DPR and IDPR.

II MATERIALS AND METHODS

A. Study Site and MAR Facility

The study was carried out at a MAR facility in a spreading basin in a semi-arid alluvial aquifer system in the southwestern United States. The recharge basin has a total area of about 12 ha and is fed by ATME produced by a nearby water reclamation plant having a design capacity of 45,000 m³ d-1. The full-advanced-treatment (FAT) train consists of secondary-treated municipal wastewater, microfiltration (0.1 μm), two-stage reverse osmosis (85 % recovery), and UV/H_2O_2 advanced oxidation (UV dose 800 mJ cm^{-2}, H_2O_2 3 mg L^{-1}). Post-treatment stabilization includes decarbonation and lime addition to increase alkalinity and pH prior to transport to the basin. The receiving aquifer is composed of Quaternary alluvial sand and gravel with interbedded silty-clay lenses to a depth of about 90 m below ground

surface (bgs). Under the basin, the water table ranges from 6 to 9 m bgs. The estimated hydraulic conductivity from the pump tests ranges from 15 to 42 m d-1, with an average of 0.24. Groundwater velocities are generally southeastward with an average pore-water velocity of 0.28 m d^{-1}. The layout of the facility, monitoring network and the hydrogeological cross-section are presented in Fig. 1.

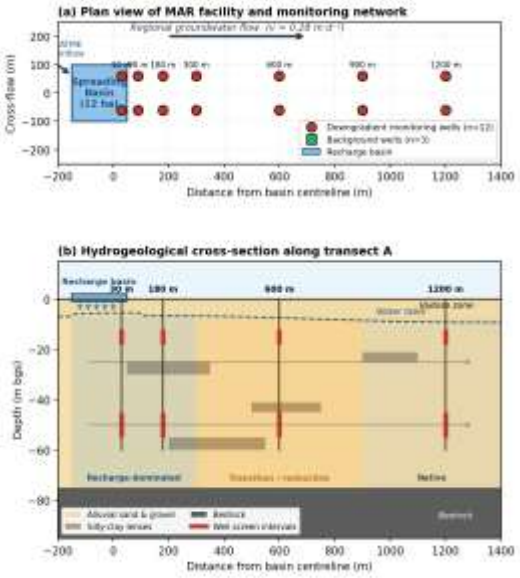

Fig. 1. Study site: (a) plan view of the MAR facility showing the 12-ha spreading basin, downgradient monitoring transects at 30–1,200 m, and upgradient background wells; (b) hydrogeological cross-section along transect A showing well screen intervals, water-table configuration under active recharge, and the delineation of recharge-dominated, transition/redoxcline, and native zones.

B. Sampling Design

Twelve monitoring wells were placed at 30, 90, 180, 300, 600, 900, and 1,200 m downgradient of the basin, and three were placed at 800 m upgradient of the basin for background conditions. To capture vertical variability, two depths (shallow: 12–18 m bgs; deep: 45–55 m bgs) were screened in the wells. The 350 samples were taken from January 2021 to December 2022, with monthly campaigns and four intensive weekly campaigns after planned changes in basin operations. Three well volumes were purged and field parameters (pH, electrical conductivity, dissolved oxygen, temperature, oxidation–reduction potential) measured in a flow-through cell. Cation and trace-metal samples were filtered (0.45 µm) and acidified with HNO_3; anion samples were filtered and refrigerated; DOC samples were filtered and preserved with H_3PO_4; and CEC samples were collected in pre-cleaned amber glass with sodium azide as a preservative. All samples for microbial analysis were filtered on site through Sterivex 0.22 µm filters and frozen at −80 °C within 4 hours.

C. Chemical Analyses

Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and trace elements (As, B, Fe, Mn, Sr, U) were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900) with a method detection limit ranging from 0.01 to 0.5 µg L^{-1}. Ion chromatography (Dionex ICS-6000) was used for the measurement of anions (Cl^{-}, SO_4^{2-}, NO_3^{-}, F^{-}, Br^{-}). Alkalinity was determined by titrating to pH 4.5 with acid. The DOC and total dissolved nitrogen (TDN) were determined using a Shimadzu TOC-L analyzer. The stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$) were measured using cavity ring-down spectroscopy (Picarro L2130-i) with a precision of ±0.1 ‰ and ±1.0 ‰ respectively. A suite of 27 CECs has been analyzed using isotope-dilution ultra-high-performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS; Thermo TSQ Altis) with reporting limits of 1–10 ng L−1.

D. Microbial Community Analysis

Sterivex filters were processed for genomic DNA according to the manufacturer's instructions (Qiagen, DNeasy PowerWater kit) and included an extra bead-beating step. The integrity of DNA was evaluated by 1 % agarose gel electrophoresis and quantified fluorometrically (Qubit 4.0). Primers 341F/805R with Illumina overhang adapters were used to amplify the V3-V4 region of the 16S rRNA gene. Libraries were sequenced on an Illumina MiSeq platform (2 × 300 bp). Amplicon sequence variants (ASVs) were generated from raw reads using DADA2 pipeline in QIIME 2 (version

2022.11) [20]. Taxonomy was performed using the SILVA 138 reference database [21]. Alpha diversity indices (Shannon, Simpson, Chao1, observed ASVs) were calculated following rarefaction to 25,000 sequences per sample. Principal coordinates analysis (PCoA) was used to visualize beta diversity, and weighted UniFrac distances were used to calculate it. ANCOM-BC was used to test differential abundance. Functional gene profiles were predicted using PICRUSt2 [22] and pathways annotated with the MetaCyc database.

E. Hydrogeochemical and Reactive-Transport Modeling

The wateq4f thermodynamic database was used with PHREEQC version 3.7 [23] to calculate aqueous speciation and mineral saturation indices. A Gaines–Thomas convention was used to represent cation exchange and a bulk exchange capacity of 45 meq kg–1 was obtained from soil-column experiments conducted on site cores. Linear equilibrium partitioning model parameterized from batch experiments was used to describe sorption of trace organics to aquifer solids. A finite-difference, three-dimensional groundwater flow model was developed using MODFLOW-2005 with horizontal resolution of 10 m close to the basin (extending to 50 m at the model boundaries), 15 vertical layers, and a total area of 6 km². A Total-Variation-Diminishing (TVD) scheme was employed with MT3DMS to model the transport of solutes with a longitudinal dispersivity of 5 m and a transverse-to-longitudinal ratio of 0.1. The flow and transport models were connected to PHREEQC using the PHT3D interface [24] for the simulation of reactive transport of Ca, Mg, Na, K, HCO_3, SO_4, Cl, NO_3, DOC, and selected CECs. Inverse modeling (PEST) was used to estimate first-order decay rates for DOC and biodegradable CECs. The Nash-Sutcliffe efficiency (NSE), root mean square error (RMSE) and percent bias (PBIAS) were used to evaluate model performance.

F. Statistical Analysis

The statistical analyses were carried out in R (version 4.3.1) with the packages vegan, phyloseq, ANCOMBC and ggplot2. Permutational multivariate analysis of variance (PERMANOVA) was used to test differences in community structure between samples from the recharge area and background samples, and Mann–Whitney U tests or Kruskal–Wallis analyses were used for chemical variables. Canonical correspondence analysis (CCA) and Mantel tests were used to explore the relationship between chemistry and community composition. The threshold of statistical significance was set at $\alpha = 0.05$ and Benjamini–Hochberg false-discovery-rate correction was used for multiple comparisons.

III RESULTS

A. Physicochemical Composition of ATME and Native Groundwater

The ATME source water was consistently of very low mineral content (mean electrical conductivity 145 ± 22 µS cm^{-1}), slightly alkaline (pH 7.6 ± 0.3), oxic (dissolved oxygen 7.2 ± 0.8 mg L^{-1}), and characterized by low DOC (0.6 ± 0.2 mg L^{-1}) and residual nitrate (2.4 ± 0.9 mg N L^{-1}). By contrast, native groundwater at background wells exhibited higher salinity (mean EC 810 ± 95 µS cm^{-1}), a Ca–Mg–HCO_3 facies (Ca 78 ± 12 mg L^{-1}, Mg 22 ± 4 mg L^{-1}, HCO_3 285 ± 30 mg L^{-1}), sub-oxic conditions in deep zones (DO 1.1 ± 0.4 mg L^{-1}), and elevated dissolved arsenic (7.8 ± 2.1 µg L^{-1}) and manganese (215 ± 62 µg L^{-1}) relative to ATME. Stable-isotope compositions of ATME ($\delta^{18}O$ = −6.9 ‰; $\delta^{2}H$ = −49 ‰) were substantially heavier than native groundwater ($\delta^{18}O$ = −10.2 ‰; $\delta^{2}H$ = −72 ‰), providing a robust conservative tracer of recharge mixing.

B. Spatial Evolution of Groundwater Chemistry

Mixing calculations based on $\delta^{18}O$ indicated that recharge-water fractions decreased systematically from 92 ± 4 % in wells 30 m downgradient of the basin to 71 % at 300 m, 38 % at 600 m, 14 % at 900 m, and less than 5 % at 1,200 m. Corresponding shifts in major-ion composition are summarized in Table I and illustrated in Fig. 2. Wells within 300

m displayed a Ca–HCO_3–NO_3 facies with pronounced enrichment of nitrate (mean 4.8 mg N L^{-1}), consistent with residual nitrate in the ATME plus partial nitrification of trace ammonia. Sulfate concentrations declined from 62 mg L^{-1} at background wells to 34 mg L^{-1} in proximal wells, indicating dilution rather than reduction, as ORP values remained above +150 mV. Calcite saturation indices calculated in PHREEQC ranged from −0.4 near the basin (undersaturated) to +0.2 at background wells (near equilibrium), suggesting minor calcite dissolution during infiltration and repartitioning of exchangeable calcium.

TABLE I
Summary of Groundwater Chemistry Along the Downgradient Transect (n = 350)

Parameter (units)	Background (n=62)	30–300 m (n=148)	600–900 m (n=96)	1,200 m (n=44)
pH	7.4 ± 0.2	7.6 ± 0.2	7.5 ± 0.2	7.4 ± 0.2
EC (µS cm^{-1})	810 ± 95	260 ± 45	520 ± 82	745 ± 88
DO (mg L^{-1})	1.1 ± 0.4	6.4 ± 0.9	3.8 ± 1.1	1.6 ± 0.5
Ca (mg L^{-1})	78 ± 12	41 ± 8	58 ± 10	72 ± 11
Mg (mg L^{-1})	22 ± 4	8 ± 2	15 ± 3	20 ± 3
HCO_3 (mg L^{-1})	285 ± 30	128 ± 22	205 ± 28	268 ± 30
NO_3-N (mg L^{-1})	1.2 ± 0.4	4.8 ± 0.9	3.1 ± 0.7	1.4 ± 0.4
DOC (mg L^{-1})	0.9 ± 0.3	0.4 ± 0.2	0.7 ± 0.2	0.9 ± 0.2
As (µg L^{-1})	7.8 ± 2.1	3.2 ± 1.0	5.4 ± 1.5	7.1 ± 1.9
Mn (µg L^{-1})	215 ± 62	44 ± 15	128 ± 38	198 ± 55

In particular, dissolved arsenic was reduced from the background concentration of 7.8 µg L^{-1} to 3.2 µg L^{-1} within 300 m of the basin, which is consistent with (co-)precipitation on freshly formed Fe(III) oxyhydroxides in the oxic recharge zone, and a similar attenuation trend was observed for manganese. In water beyond 600 m, both trace metals were restored to background levels with the return of native suboxic conditions.

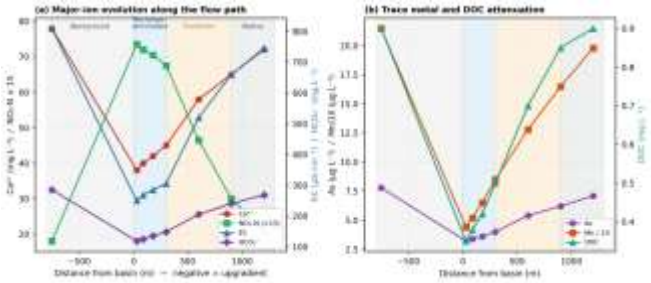

Fig. 2. Spatial evolution of groundwater chemistry along the downgradient transect. (a) Major-ion trends showing depletion of Ca^{2+}, HCO_3^- and EC and enrichment of NO_3-N within the recharge-dominated zone; (b) attenuation of dissolved arsenic, manganese, and DOC in proximal wells followed by rebound in transition and native zones.

C. Attenuation of Dissolved Organic Carbon and CECs

The average concentration of DOC in ATME was 0.6 mg L^{-1}, but decreased further down the flow path, reaching 0.3 mg L^{-1} after 90 m and then remaining constant. The pseudo-first order removal rate constant k was determined by fitting concentrations against apparent subsurface travel times (based on isotope mixing and MODFLOW-derived flow paths) which resulted in a value of k = 0.021 ± 0.004 d^{-1} or a half-life of 33 days.

Of the 27 CECs monitored, 18 (67 %) were detected at levels below reporting limits after 180 days of sub-surface residence, including sulfamethoxazole, trimethoprim, atenolol, gemfibrozil, DEET and 1,4-dioxane. Persistent compounds were the recalcitrant tracer's sucralose, primidone, TCEP, PFOA, PFOS, and PFHxS, which only decreased in concentration as they were diluted. Per- and poly-fluoroalkyl substances (PFAS) were found throughout the recharge-impact zone at low ng L^{-1} concentrations, indicating trace persistence during RO and near-conservative subsurface behavior. The decrease of carbamazepine (CBZ) was modest, at 34 % and

was greater than the conservative-mixing predictions, indicating slow biotransformation or sorptive retardation.

D. Microbial Community Structure

A total of 12.4 million high-quality reads were obtained from the 350 samples, with 8,942 amplicon sequence variants (ASVs) identified. Rarefaction curves were all asymptotical, suggesting adequate sequencing depth. Alpha diversity was found to be significantly different between zones (Kruskal–Wallis, $p < 0.001$). The Shannon index increased from a background mean of 5.8 ± 0.4 to 7.1 ± 0.5 in wells 30–90 m downgradient of the basin—a 22 % enrichment—before declining to 6.3 ± 0.4 at 600 m and returning to 5.9 ± 0.4 at 1,200 m. The same trend was observed for Chao1 richness. The spatial trend suggests that the addition of oxygenated, low salinity, DOC-bearing water increases the niche space for aerobic heterotrophs and nitrifiers, and brings about a dilution of salinity and redox constraints found in the native aquifer.

Proteobacteria was predominant in all zones, and there were distinct differences in abundance at the finer taxonomic levels (Fig. 3a). The abundances of Betaproteobacteriales (notably Comamonadaceae and Rhodocyclaceae), Nitrospirae (Nitrospira), and Planctomycetes (Pirellulaceae) significantly increased ($\log_2$ fold change 1.4–2.8, ANCOM-BC $q < 0.05$), whereas the abundances of Firmicutes (Clostridia) and Chloroflexi (Anaerolineae) decreased. Proximal wells were enriched by 2.1 times with Sphingomonadaceae, which are known to degrade xenobiotics. PCoA analysis of weighted UniFrac distances (Fig. 4) divided the samples into three distinct clusters that closely followed the geochemical zones, with samples from the recharge-dominated zone (<300 m) grouped together, the transition zone (300–900 m) grouped together, and the native zone (>900 m) grouped together. The distance from the basin had a significant effect on community structure ($R^2 = 0.41$, $p < 0.001$) as shown by PERMANOVA, and Mantel tests showed high correlation between the community and geochemical dissimilarity matrices ($r = 0.62$, $p < 0.001$).

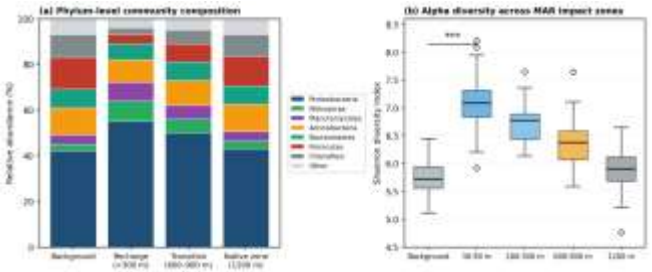

Fig. 3. Microbial community response to ATME-based MAR. (a) Phylum-level relative abundance in background, recharge-dominated, transition and native zones showing enrichment of Nitrospirae and Planctomycetes and suppression of Firmicutes and Chloroflexi in the proximal zone; (b) Shannon α-diversity indices across the five downgradient bins showing a ~22 % increase in 30–90 m wells (*** $p < 0.001$).

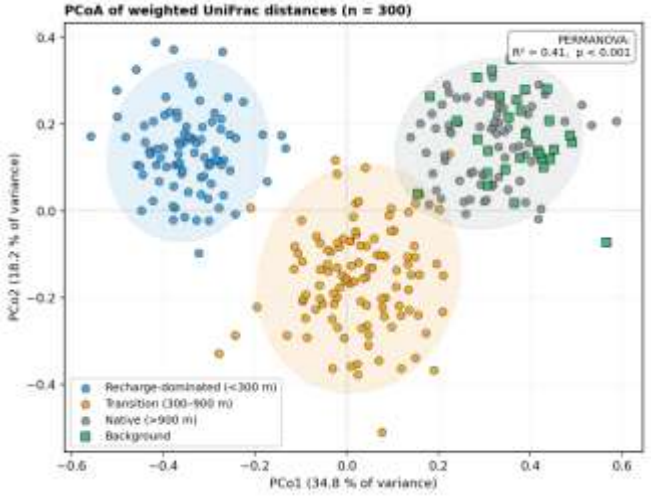

Fig. 4. Principal coordinates analysis (PCoA) of weighted UniFrac distances for 300 groundwater microbial community samples. Clusters correspond to recharge-dominated (<300 m), transition (300–900 m), native (>900 m) and background zones. PERMANOVA confirmed a significant zonal effect ($R^2 = 0.41$, $p < 0.001$).

E. Predicted Functional Profiles

PICRUSt2-inferred functional profiles showed distinct zonation in the predicted metabolic potential. The 30–300 m zone had a significant enrichment of genes involved in nitrification (amoA, hao, nxrB), aerobic heterotrophic metabolism (TCA cycle, glyoxylate shunt), and xenobiotic biodegradation pathways (benzoate,

aminobenzoate, atrazine, xylene) by Wilcoxon ($q < 0.01$). The anaerobic pathways (dissimilatory sulfate reduction, methanogenesis and denitrification) were inhibited near the basin and were restored in the deep, native zone (> 900 m). The relative abundance of predicted denitrification genes (narG, nirK, nosZ) was 2.4-fold higher in transition-zone wells than in either the recharge-dominated or fully native zones, which suggests a mid-plume redoxcline with residual DOC and pre-existing nitrate under intermediate DO levels.

F. Reactive-Transport Modeling

The calibrated coupled MODFLOW–MT3DMS–PHREEQC model successfully reproduced observed spatiotemporal patterns of major-ion and $\delta^{18}O$ breakthrough at all 12 monitoring wells (Table II, Fig. 5). The overall performance of the models was good with NSE values between 0.79 and 0.91 for the constituents (mean 0.87), RMSE of 6.4 mg L-1 for chloride and PBIAS values in the range of ±11 %. The timing of the arrival of the recharge front at 300 m (around 340 days after continuous recharge began) and 900 m (around 1,050 days after continuous recharge began) was correctly captured by the model.

TABLE II

Calibrated Reaction Parameters and Model Performance Statistics

Process / Constituent	Rate constant / Parameter	NSE	RMSE
$\delta^{18}O$ (conservative tracer)	—	0.91	0.28 ‰
Chloride	—	0.90	6.4 mg L^{-1}
Nitrate	1st-order denitrification $k = 0.006\ d^{-1}$	0.85	0.5 mg N L^{-1}
DOC	$k = 0.021\ d^{-1}$	0.87	0.09 mg L^{-1}
Calcite dissolution	SI-driven, log $k = -8.4$	0.83	12 mg L^{-1}
Sulfamethoxazole	$k = 0.034\ d^{-1}$	0.79	4 ng L^{-1}
Carbamazepine	$k = 0.0018\ d^{-1}$	0.82	6 ng L^{-1}

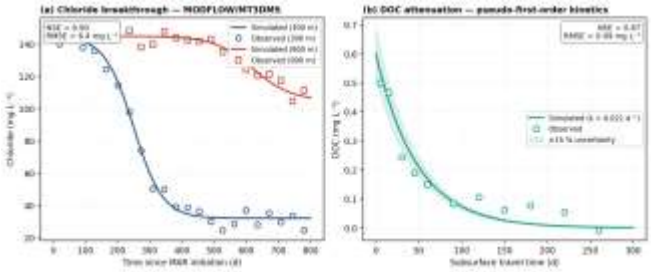

Fig. 5. Reactive-transport model performance. (a) Observed versus simulated chloride breakthrough at wells located 300 m and 900 m downgradient of the recharge basin; (b) DOC attenuation as a function of subsurface travel time fitted to a pseudo-first-order decay model ($k = 0.021\ d^{-1}$). Shaded area indicates ±15 % parameter uncertainty envelope. The parameters that had the greatest effect on solute breakthrough were identified through sensitivity analysis as the longitudinal dispersivity, DOC decay rate, and the cation-exchange selectivity coefficient for Ca–Na exchange. A one-year predictive scenario with 25 % recharge rate increase showed that the front edge of the recharge plume would move an additional 180 m in 18 months and that trace-metal attenuation would not be affected within the first 300 m if the DO in the ATME was kept above 6 mg L^{-1}.

IV DISCUSSION

A. Geochemical Evolution and Water-Quality Implications

The geochemical gradients observed illustrate that recharge from ATME creates a well-defined and spatially organized mixing zone and that the extent of this mixing zone can be quantitatively constrained using stable-isotope tracers and reactive-transport modeling. The proximal Ca–HCO_3–NO_3 facies within 300 m of the basin is a reflection of the low-mineral, oxic, nitrate-bearing character of the source water that overlies the native Ca–Mg–HCO_3 facies. The engineered recharge with well-oxygenated ATME has resulted in the persistence of oxic conditions and a sharp decrease in dissolved concentrations of As and Mn

in proximal wells, consistent with significant in-situ attenuation of naturally occurring trace metals, probably through co-precipitation onto Fe(III) oxyhydroxides and sorption onto Mn(IV) oxides freshly formed at the redox front [25], [26]. This result is similar to previous observations at both the Orange County and Wulpen sites where recharge with high-quality reclaimed water resulted in net reductions in As and Mn concentrations in shallow monitoring wells [8, 27].

However, the occurrence of arsenic and manganese above 600 m suggests caution in extrapolating short-distance benefits to the entire aquifer. The transition zone seems to act as a redoxcline, where the remaining DOC in the recharge water supports the microbial consumption of oxygen and subsequent nitrate reduction, creating conditions that allow for reductive dissolution of Fe/Mn oxides. Redoxcline behavior is similar to that reported for SAT systems in Israel and the western United States [28, 29]. Although the nitrate concentrations in the proximal wells have not exceeded the U.S. MCL of 10 mg N L-1, they are of interest because they are a long-term legacy of nitrogen residuals in the ATME. Therefore, optimization of upstream nitrogen removal, especially partial biological denitrification before RO, is recommended for future upgrades to the facility.

B. Trace Organic Attenuation

The high removal efficiencies (68 %) for the monitored CECs after 180 days of subsurface residence further support the significant polishing capabilities of the aquifer even for compounds that enter the full-advanced-treatment train at trace levels. The removal was most rapid for compounds with moderate biodegradability and hydrophobicity, as would be expected from mechanisms involving both sorption and aerobic biotransformation, which have been observed in laboratory columns and pilot studies [30].The recalcitrance of PFAS is an important issue, as it is essentially not removed by either RO rejection or subsurface residence beyond conservative dilution. This is consistent with the increasing evidence that PFAS management will need source control and improved treatment (e.g., granular activated carbon, ion exchange, foam fractionation, and/or destructive technologies like supercritical water oxidation) and not natural attenuation [5]. The 34 % excess loss of carbamazepine compared to conservative mixing indicates that slow biological or sorptive processes are still at work even with this well-known persistent tracer, in line with recent studies with compound-specific isotope analysis.

C. Restructuring of the Native Microbial Community

The 22 % increase in α-diversity in proximal wells and the high zonation detected by PCoA together indicate that ATME recharge is a significant ecological disturbance that has a spatial signal of at least 900 m. The enrichment of Nitrospira and Comamonadaceae in the recharge-impacted zone is consistent with the increased nitrification potential, with comammox Nitrospira becoming a growing recognized group of nitrifiers in drinking-water and MAR systems with low ammonia concentrations [8]. The enrichment of Sphingomonadaceae and Rhodocyclaceae is also associated with the biodegradation of xenobiotic and aromatic compounds [7]. The suppression of anaerobic groups (e.g., Anaerolineae and Clostridia) near the basin reflects the transition to oxic conditions, and their partial recovery in the transition zone reflects the re-establishment of suboxic conditions.

Importantly, the microbial-community response was significantly related to the geochemical gradients (Mantel r = 0.62), showing that community structure is a sensitive integrator of hydrogeochemical state. This is of practical importance for MAR monitoring: sequence a set of indicator taxa or functional genes in addition to traditional chemistry-based surveillance, especially to identify incipient redox transitions prior to their expression in trace-metal remobilization. The same arguments have been proposed for the use of microbial ecology as an early warning system in aquifer storage and recovery [11].

D. Modeling Integration and Predictive Utility

The coupled MODFLOW–MT3DMS–PHREEQC framework simulated observed solute breakthrough with high fidelity (mean NSE 0.87) and was able to capture both conservative and reactive behaviors, including calcite dissolution, cation exchange, and pseudo-first-order attenuation of DOC and biodegradable CECs. Similar results have been obtained in previous modelling studies of MAR sites in Australia and the Netherlands [15] but the present integration with a dense microbiological data set is a step forward: predicted functional-gene profiles (nitrification, denitrification, xenobiotic degradation) qualitatively match the redox and CEC-attenuation zones simulated by the reactive-transport model, providing an independent validation of the underlying biogeochemical process representation. The moderate recharge-rate increase (25 %) predicted by the predictive-scenario is consistent with limited expansion of the plume without compromising the trace-metal attenuation, if oxygen delivery is maintained. This highlights the usefulness of the calibrated model as an operational decision support tool. Future research should consider expanding the framework to include a more explicit representation of biomass dynamics and biogeochemical feedbacks, e.g., Monod-type kinetics, with community composition to improve prediction of response to loading and climate change.

V LIMITATIONS

There are some limitations to be noted. First, the study took place at one site, with one hydrogeological setting; extrapolation to fractured, karstic or coastal aquifers would require further site-specific characterization. Second, functional predictions made using PICRUSt2 are necessarily only approximate and should be verified in future studies by metagenomic or metatranscriptomic analyses, which would also allow for direct quantification of antibiotic-resistance genes and virulence factors. Third, the sorption of trace organics was modeled as linear equilibrium partitioning; nonlinear or kinetic behavior may be significant for compounds with slow desorption. Last, long-term monitoring (5–10 years) is needed to determine if the capacities of attenuation observed during short-term use are maintained during long-term operation, including possible sorption-site exhaustion and biofilm dynamics.

V CONCLUSION

This study is an integrated field-monitoring and modeling evaluation of a full-scale spreading-basin managed aquifer recharge facility (MARF) that receives advanced treated municipal effluent in the semi-arid southwestern United States. We measured the co-evolution of major-ion chemistry, trace constituents, constituents of emerging concern, microbial community structure and predicted function in 350 groundwater samples collected over 24 months in a 1,200 m transect, and validated a coupled MODFLOW–MT3DMS–PHREEQC reactive-transport model. The key findings are: (i) the presence of a spatially structured mixing zone with a distinct Ca–HCO_3–NO_3 facies extending 300 m from the basin and a redoxcline centered near 600–900 m; (ii) significant in-situ attenuation of naturally occurring arsenic and manganese in the proximal oxic zone, but rebound beyond the redoxcline; (iii) rapid removal (>68 %) of most monitored CECs within 180 days of subsurface residence, but essentially conservative behavior of PFAS; (iv) enrichment of microbial α-diversity in the recharge-impacted zone by 22 % with distinct enrichment of nitrifiers and xenobiotic degraders; and (v) strong congruence between geochemical zonation, microbial community structure, and reactive-transport model predictions (mean NSE 0.87).

Overall, these data help to validate the use of ATME-based MAR as an effective component of drought-resilient water portfolios and highlight the need for source-control measures for PFAS, careful monitoring of nitrogen residuals, and design of residence-time criteria to protect against trace-metal remobilization at the redoxcline. A scalable

framework for supporting the regulatory advancement of indirect and direct potable reuse in the United States and similar areas globally involves integration of dense chemistry, next-generation microbiological analysis, and process-based modeling.

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