



GEOCHEMICAL TRANSFORMATIONS DURING ARTIFICIAL GROUNDWATER RECHARGE: SOIL–WATER INTERACTIONS OF INORGANIC CONSTITUENTS

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Abstract—Six soils from two vadose-zone injection wells were used in conjunction with three types of recharge waters (microfiltered reclaimed wastewater; reverse osmosis-treated reclaimed wastewater and membrane-filtered Colorado River water) to evaluate soil–water chemical processes that may alter water quality during recharge of these waters. Batch studies (soil–water slurries; 30-day contact time) and flow-through column studies (upflow mode columns; ~100 pore volumes over 30 to 100 days) showed that F, Ba and As were leached in appreciable concentrations, whereas leaching of B, Cr, Pb and Se was minimal. In the column study, concentrations often peaked during the first few days of operation (a “washout” phenomenon) and then declined. Precipitation and dissolution reactions may be important from a standpoint of sustained infiltration rates. © 1998 Elsevier Science Ltd. All rights reserved

Key words: aquifer storage and recovery, groundwater recharge, water quality infiltration, reverse osmosis, wastewater reclamation, F, As, Ba.

INTRODUCTION

Water scarcity is likely to become more problematic in the near future due to rapid population growth, increasing per capita water consumption and geographical disparities between centers of population growth and availability of water (Postel, 1997). Artificial recharge of groundwater with treated wastewater or excess surface water is gaining wide acceptance as a method to replenish overdrafted aquifers and provide sustainable water supplies (Bouwer *et al.*, 1990). Concentrations of BOD, suspended solids, pathogens and nitrogen generally decline as water infiltrates through the vadose zone (Gilbert *et al.*, 1973; Lance *et al.*, 1976; Bouwer *et al.*, 1980, 1990; Bouwer and Rice, 1984; Rice and Bouwer, 1984; Wilson *et al.*, 1995; Kopchynski *et al.*, 1996).

However, the nature and significance of abiotic geochemical processes that occur during recharge through the vadose zone have received little attention, although these reactions can have a major affect on the success of aquifer storage and recovery (ASR) systems (Pyne, 1995) and effluent recharge systems. Several geochemical processes may be important in ASR systems. First, many soils in arid

regions contain naturally occurring, easily leachable contaminants of relevance to drinking water quality, notably F, B, As, Cr, Pb and Ba (Hem, 1970; Faust and Aly, 1981). Naturally occurring As, Cr, F and total dissolved solids (TDS) can make groundwater unsuitable for drinking in Arizona (Baker and Bolitho, 1995; Baker *et al.*, 1998). Second, various reactions, including chemical precipitation [e.g. CaCO_3 , $\text{Fe}(\text{OH})_3$], dispersion of clays caused by the replacement of adsorbed divalent cations by Na^+ , swelling of expandable clays upon wetting, and soil “collapse” caused by dissolution of cementing materials (Houston *et al.*, 1988) may lead to reduced infiltration rates.

This paper describes experiments conducted to better understand geochemical transformations that occur as high quality wastewater effluent or surface water passes through the vadose zone at the City of Scottsdale, Arizona’s “Water Campus Project”.

STUDY SITE

Soil and water samples were obtained from the Scottsdale’s “Water Campus Project”, a state-of-the-art groundwater recharge and storage facility now in the pilot stage. Recharge water is injected to the vadose zone via wells drilled to a depth of 55 m. The water infiltrates through 100 m of vadose zone to the aquifer (Fig. 1). The Upper Alluvial Unit (UAU), from which soil samples were taken, consists of loose, unconsolidated sands and gravels

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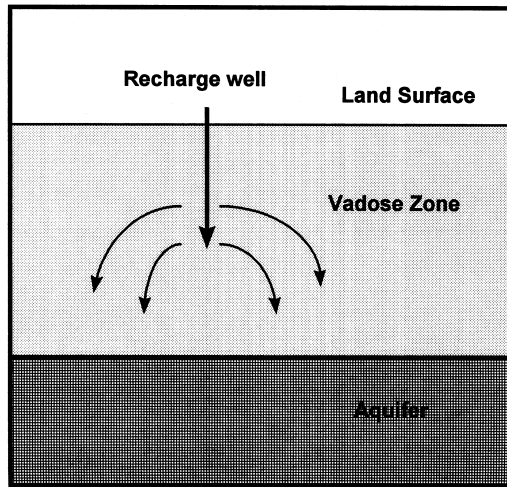


Fig. 1. Conceptual schematic of vadose-zone injection wells at the Scottsdale Water Campus.

interbedded with silts and clays (HydroSystems, 1995).

Soils were collected from three depth intervals in two pilot recharge wells (wells 1–3 and 1–4). These soils were chosen because they had a relatively high percentage of fines (3–23% clays) and were located near strata of high permeability (details in HydroSystems, 1995; Johnson, 1997). In all experiments, special attention was paid to the fines portion of each soil because this fraction is the most

geochemically reactive (Harmsen, 1977; Beek *et al.*, 1979; Forstner, 1990; Masscheleyn *et al.*, 1991; Allard, 1995). Batch experiments utilized fines that were dry-sieved (passing U.S. standard #200 sieve). Because of the need to maintain the flow of water through the flow-through columns, a coarser fraction (passing #10 mesh; 2 mm) was used to fill the columns.

Three types of water were used in these experiments. Microfiltered Colorado River water from the Central Arizona Project (CAP) canal had high levels of Na^+ , Cl^- and SO_4^{2-} and an average TDS of 649 mg/l. Two types of highly treated municipal wastewater effluent were also used. Microfiltered (0.2 μm nominal pore size) effluent (MF) had the highest TDS (919 mg/l) and also had high concentrations of SO_4^{2-} and Cl^- . The CAP and MF waters were well-buffered and circumneutral. Reverse-osmosis treated effluent (RO) was a portion of the MF effluent stream. The RO water had very low TDS (39 mg/l), almost no alkalinity and a pH of 6.5. Detailed analyses of the experimental waters are presented later (see “controls” in Table 1 and “inflow” in Table 2).

METHODS

Batch experiments

Batch experiments were conducted using the three source waters (CAP, MF and RO) and several blended waters (CAP + MF; CAP + RO) mixed with each of the

Table 1. Concentrations of major ions in the batch experiment

Source water	Constituent	Concentration in control, meq/l (mg/l)	Average change in concentration, meq/l (mg/l)	Standard deviation (meq/l)	% change
RO	calcium	0.25 (5)	0.76 (15)	0.16	304%
	magnesium	0.16 (20)	0.70 (9)	0.05	437%
	sodium	1.43 (33)	0.82 (19)	0.19	57%
	potassium	0.15 (6)	0.00 (0)	0	0%
	chloride	1.20 (41)	0.01 (0.5)	0.02	0.8%
	sulfate	0.11 (5.1)	0.05 (2.4)	0.05	45%
	carbonate	—	0.03 (0.8)	0.02	—
	bicarbonate	0.15 (9.3)	3.11 (190)	0.41	2070%
MF	calcium	2.59 (52)	−0.04 (−0.83)	0.43	−1.5%
	magnesium	1.65 (20)	0.93 (11)	0.13	56%
	sodium	6.20 (143)	0.07 (2)	0.10	1%
	potassium	0.46 (18)	−0.23 (−9)	0.00	−50%
	chloride	4.45 (158)	−0.33 (−12)	0.05	7%
	sulfate	4.04 (194)	−0.56 (−28)	0.07	−14%
	carbonate	0.00 (0.0)	−0.02 (−0.5)	0.00	−100%
	bicarbonate	0.44 (27)	0.19 (12)	0.66	43
CAP	calcium	1.89 (38)	−0.19 (−3.8)	0.38	−10
	magnesium	1.64 (20)	0.60 (7)	0.25	37
	sodium	3.47 (80)	0.19 (4)	0.24	5
	potassium	0.15 (6)	0.00 (0)	0.00	0
	chloride	1.86 (66)	−0.08 (−3)	0.05	−4
	sulfate	4.18 (201)	−0.43 (−21)	0.13	−10
	carbonate	0.02 (0.9)	−0.01 (−0.4)	0.01	−66
	bicarbonate	2.48 (151)	1.26 (77)	0.66	51

RO = reverse osmosis treated effluent; MF = microfiltered effluent; CAP = microfiltered Central Arizona Project water. The change in concentration is the difference between the concentration of the constituent in the control (source water without soil) and the corresponding soil–water slurry. The average and standard deviation for the six study soils are shown.

Table 2. Flow-weighted average concentrations (FWAC) of major ions in the column experiment, as computed from equation 1

Source water	Constituent	Concentration in inflow, meq/l (mg/l)	Flow-weighted average change, meq/l (mg/l)	Standard deviation (meq/l)	% change
RO	calcium	ND	0.29 (6)	0.03	N/A
	magnesium	ND	0.28 (3)	0.04	N/A
	sodium	0.23 (5)	0.28 (6)	0.07	118.5
	potassium	ND	0.05 (2)	0.01	N/A
	chloride	0.24 (9)	0.01 (0.4)	0.01	4.1
	sulfate	0.26 (12)	0.01 (0.5)	0.01	3.9
	carbonate	ND	0.01 (0.3)	0.05	N/A
	bicarbonate	0.19 (12)	0.80 (49)	0.00	420.7
MF	calcium	2.74 (55)	-0.38 (-8)	0.18	-13.8
	magnesium	2.06 (25)	1.52 (19)	0.20	74.0
	sodium	6.74 (155)	-0.22 (-5)	0.53	-3.3
	potassium	0.42 (19)	-0.05 (-2)	0.06	-10.5
	chloride	6.23 (216)	-0.10 (-4)	0.25	-1.6
	sulfate	3.83 (184)	0.68 (33)	0.26	17.9
	carbonate	0.03 (0.9)	0.03 (0.8)	0.41	83.3
	bicarbonate	4.27 (260)	0.25 (15)	0.02	5.9
CAP	calcium	1.92 (39)	0.11 (2)	0.14	5.7
	magnesium	2.56 (31)	0.58 (7)	0.16	22.7
	sodium	3.92 (90)	0.20 (5)	0.12	5.1
	potassium	0.15 (5)	0.05 (2)	0.01	32.6
	chloride	2.58 (92)	-0.01 (-0.4)	0.03	-0.4
	sulfate	5.41 (260)	-0.00 (-0)	0.03	0.0
	carbonate	0.01 (0.3)	-0.01 (-0.2)	0.08	-50.0
	bicarbonate	2.15 (131)	-0.07 (-4)	0.00	-3.2

RO = reverse osmosis treated effluent; MF = microfiltered effluent; CAP = Central Arizona Project water. The average and standard deviations for the six study soils are shown.

six soils. Soil-water slurries were made by adding 10 g of soil fines to 60-ml high density polyethylene bottles, which were then filled with the appropriate type of water. Bottles containing the soil-water slurries were continuously mixed at 40 rpm for 30 days in a homemade rotating mixer. This contact period should have allowed readily soluble minerals to reach equilibrium with water.

Column experiments

Experiments with small laboratory columns were conducted using all three waters and the six soils. The columns (25 × 5 cm, height × I.D.) were packed with each soil type (Fig. 2). Columns were operated in the upflow mode at a rate of 0.17 l/day (RO and MF water) for 100 days or

0.67 l/day for 30 days (CAP water). Assuming a porosity of 0.33, these flowrates and operation times correspond to about 100 exchanges of the void volume. The reservoir containing CAP water was stored at room temperature; reservoirs containing the two effluents were kept refrigerated in a cold room (5°C). Water was pumped through a hole in the cold room directly to the columns in the lab (~25°C) using a 20-channel peristaltic pump. Water entering the columns was assumed to be at room temperature. Inflow and outflow samples were collected throughout the experiment.

Chemical analytical methods

In both experiments, DIC and pH were measured on unfiltered samples. Samples were then filtered through 0.2 µm membrane filters and refrigerated until analysis. Cation and trace metal samples were acidified with Ultra Pure[®] HNO₃ (details in Johnson, 1997).

Dissolved inorganic carbon (DIC) was measured using a Dohrman Model 180 Carbon Analyzer; DIC and pH were used to compute alkalinity. Major anions were measured using a Dionex DX-40 Ion Chromatograph. Major cations and iron were measured by flame atomic adsorption (Perkin Elmer Model 3100); trace elements (As, Ba, Cr, Pb and Se) were analyzed by graphite furnace (Perkin Elmer HGA-600) with an AS-60 Autosampler on the same AA spectrophotometer. Boron was measured by the carmine method (APHA, 1989).

Analytical bias, determined by analyzing a SPEX[™] trace metals reference standards after every 10th sample, ranged from 2–10%. The relative standard deviation for most analysis was < 10% for major cations and 6 to 17% for trace metals. Spike recovery ranged from 85 to 100% (Johnson, 1997). The error in charge balance (% error = $[\sum \text{cations} - \sum \text{anions}] / [\sum \text{cations} + \sum \text{anions}] \times 100$) was < 20% for 85% of the samples. The largest ion bal-

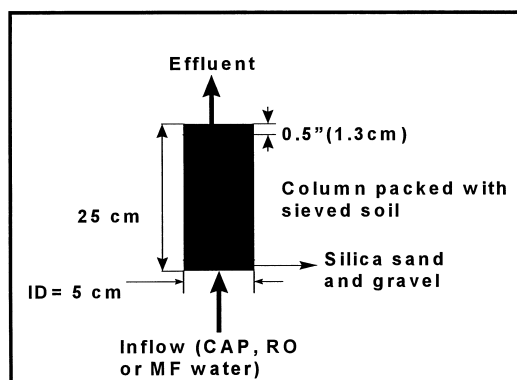


Fig. 2. Schematic of flow-through columns used in the column experiments. For each of three water types (RO, MF and CAP), six soils were tested for a total of 18 columns.

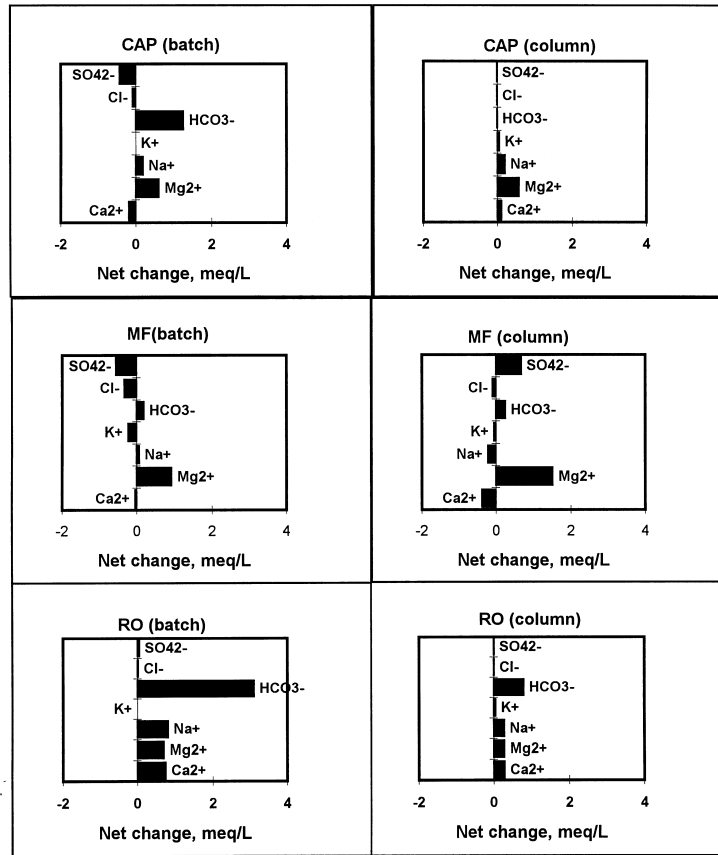


Fig. 3. Ion fingerprints showing changes in composition that occurred in the batch and column studies. For the batch study, the change in composition was the difference between the composition of the control (water but no soil) and the corresponding soil-water slurry, both analyzed at the end of the contact period. For the column study, the change in concentration was computed as the flow-weighted average change (FWAC; equation 1). For both studies, results are averaged for all six soil samples.

ance errors were associated with the RO water, which was extremely dilute.

Mineralogy

Clays from each soil were isolated by centrifugation of a sieved soil-water suspension, with Calgon added as a surfactant. The supernatant was then dripped onto plates and dried for X-ray diffraction (XRD) analysis. Parallel samples were glycolated to identify expandable clays and heated to destroy kaolinite. Non-clay minerals were prepared by grinding the soil in a mortar and pedestal. The XRD instrument was a Rigaku Model D/MAX-IIIB with a Cu X-ray tube and a monochromator in the diffracted beam. The instrument was operated with a continuous scan from 3 to 90° 2θ with sampling every 0.02° at a rate of 2° per min.

Data analysis

Because the composition of water exiting the soil columns varied over time and the sampling intervals varied, the change in ionic composition was computed as the flow-weighted average change (FWAC). The FWAC is the average change in flow-weighted concentration between influent and effluent over the course of the experiment:

$$FWAC = \frac{\sum_{i=2}^N \left(\frac{C_i + C_{i-1}}{2} \Delta t_i Q \right) - C_o Q \sum_{i=2}^N \Delta t_i}{Q \sum_{i=2}^N \Delta t_i} \quad (1)$$

where C_o = influent concentration; N = # of sampling period; Q = flowrate through columns; Δt_i = time interval between sampling periods i and $i-1$; C_i = concentration of outflow on sampling period i .

Changes in the composition of the water during these experiments were used to infer geochemical mechanisms (Baker *et al.*, 1991). From electroneutrality considerations it follows that:

$$\Delta Ca^{2+} + \Delta Mg^{2+} + \Delta K^+ + \Delta Na^+ = \Delta SO_4^{2-} + \Delta Cl^- + \Delta HCO_3^- + \Delta CO_3^{2-} + \Delta F^- + \Delta NO_3^- \quad (2)$$

where Δ = change in equivalent concentration (meq/l) of an ion over the course of the experiment. An increase in a cation must be balanced either by a decrease in another cation (implying cation exchange) or an increase in an anion (implying solubilization of a mineral).

Geochemical processes were further examined using a chemical equilibrium modeling program, MINEQA2

Table 3. Average saturation indices of selected minerals for batch test samples at the end of the 30-day contact period

Average SI							
water used	calcite, CaCO ₃	dolomite, CaMg(CO ₃) ₂	barite, BaSO ₄	fluorite, CaF ₂	aragonite, CaCO ₃	magnesite, MgCO ₃	halite, NaCl
RO	0.03	0.06	-0.28	-1.05	-0.1	-0.47	-7.2
MF	0.14	0.34	0.81	-1.08	0	-0.29	-6.3
CAP	-0.04	0.11	0.88	-1.29	-0.18	-0.35	-6.9

(Allison *et al.*, 1991). MINEQA2 was used to determine whether source waters and soil solutions were at equilibrium with various minerals. Oversaturated species were not allowed to precipitate in the model, allowing us to determine the degree of over- or undersaturation. For each mineral, the proximity to equilibrium was expressed as the saturation index (SI):

$$SI = \log \frac{Q}{K} \quad (3)$$

where Q = ion activity product for a certain mineral and K = equilibrium constant for the same mineral.

A SI of zero indicates that the solution is in equilibrium with a particular mineral. A SI < 0 indicates that the solution is undersaturated with respect to a particular mineral and a SI > 0 indicates oversaturation. Inputs to the model were measured concentrations of major ions and trace elements, pH, and DIC (input as alkalinity). The model was run at 25°C (room temperature); ion activities were adjusted by the Davies equation.

Finally, the sodium adsorption ratio (SAR) was determined, where

$$SAR = \frac{(Na^+)}{[(Ca^{2+} + Mg^{2+})/2]^{1/2}} \quad (4)$$

where all values are in meq/l. The SAR and TDS are good indicators of the tendency of infiltrating water to reduce permeability (Tchobanoglous and Schroeder, 1987).

RESULTS

XRD analysis showed that predominant clays in the study soils were montmorillonite, illite and kaolinite. Primary minerals included several feldspars (plagioclase and orthoclase), quartz, calcite and halite. All of the clay and primary minerals were found in all five analyzed samples, confirming our visual impression that the well soils were quite similar in their makeup, except for variations in particle size.

Tables 1 and 2 summarize key results regarding the aqueous chemistry of major ions. For the column and batch studies, all six soils yielded similar results (see standard deviations in Tables 1 and 2), so our discussion focuses on average results for the six soil types. "Ion fingerprint" diagrams (Fig. 3) show the net change in composition of the source waters in the batch and column experiments. Temporal trends in the composition of effluent leaving the soil columns are shown in Fig. 4.

There was no evidence of anaerobic conditions in either the batch or column studies. Concentrations of H₂CO₃* computed from alkalinity and pH in MINEQA2 showed that the source water and column effluents were slightly oversaturated with respect to atmospheric CO₂, but we never detected

iron in any samples and there was never any blackening or odor that would indicate the presence of H₂S. We therefore conclude that oxidizing conditions were maintained in both experiments.

Batch study

Major ions.

RO. The composition of the RO-treated effluent changed markedly during the 30-day contact period, as would be expected. Increases in Ca²⁺, Mg²⁺ and Na⁺ were balanced by an increase in HCO₃⁻ (Fig. 3), implicating dissolution of carbonate minerals as the source of these ions. RO water at the end of the contact period was very close to equilibrium with respect to several carbonate minerals (Table 3). Cl⁻ and SO₄²⁻ concentrations remained nearly unchanged during the experiment. The TDS increased from 120 to 217 mg/L.

MF. The composition of the MF effluent changed little in the batch experiments: TDS decreased by only 0.34%. The only ions which changed significantly were Mg²⁺ (slight increase), SO₄²⁻ (slight increase) and NO₃⁻ (large increase). NO₃⁻ concentrations increased from 0.2 meq/l (3.1 mg NO₃-N/l) to 1.6 meq/l (22.5 mg NO₃-N/l), presumably reflecting nitrification of ammonium during the batch experiment. Despite the apparent nitrification, average pH declined only slightly (from 7.91 to 7.51) and the alkalinity actually increased slightly (+0.25 meq/l). The H⁺ produced by nitrification apparently was exchanged with adsorbed Mg²⁺, resulting in a 1.5 meq/l increase in Mg²⁺ concentration in solution. There was little or no change in Ca²⁺, Na⁺, K⁺, Cl⁻ or HCO₃⁻ during the 30-day contact period. At the end of the experiment, the MF water was slightly oversaturated with respect to calcite and dolomite and at equilibrium (SI = 0) with aragonite.

CAP. The major ion composition of CAP was also changed very little during the batch study. TDS increased by 11%, but the only ion to increase significantly was Mg²⁺, which increased by 37%. Changes in ions were too small to make inferences regarding processes, but equilibrium modeling showed that the CAP-soil slurries were very close to equilibrium with respect to common carbonate minerals (Table 3).

Trace elements

Concentrations of F, Ba and As increased substantially in all soil and water combinations used in

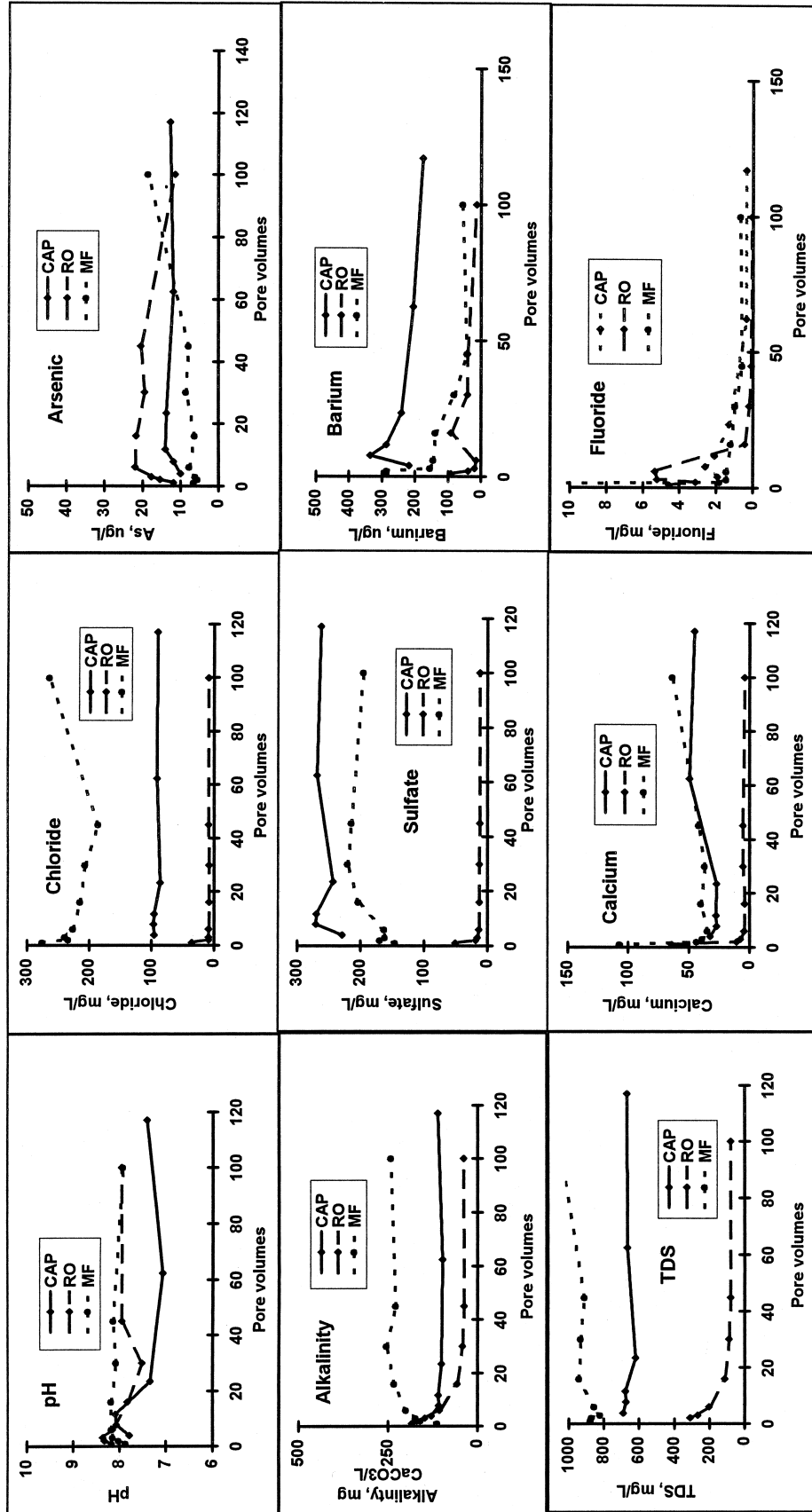


Fig. 4. Temporal trends for As, Ba, F, pH, alkalinity, Ca²⁺, Cl⁻, SO₄²⁻ and TDS for the column experiment. Plotted lines show average concentrations for the six soil columns receiving each type of water.

Table 4. Average differences in concentrations of trace elements between controls (source water only) and treatments (water + soil) after 30 days in the batch experiment

Water type	Fluoride (mg/l)	Arsenic ($\mu\text{g/l}$)	Barium ($\mu\text{g/l}$)
RO control	0.2	0	8
Soil + water	1.2	16	214
Difference	1.0	16	206
MF control	0.7	3	64
Soil + water	0.9	16	174
Difference	0.2	13	110
CAP control	0.3	7	100
Soil + water	0.8	14	162
Difference	0.5	7	62
Source water blends: change compared with initial			
1/3 RO + 2/3 MF	0.4	8	169
2/3 RO + 1/3 MF	1.1	7	200
1/3 RO + 2/3 CAP	0.7	8	85
2/3 RO + 1/3 CAP	0.9	10	135

the batch experiment whereas concentrations of chromium, boron and lead remained at or near detection limits (Table 4). As expected, leaching was greatest with the RO water: concentrations of F, As and Ba increased by 88, 100 and 96% during the batch experiment. The blended source waters generally exhibited intermediate behavior.

Fluoride was undersaturated with respect to fluorite in all samples at the end of the batch experiment (Table 3). This may have occurred because there was too little fluorite in the soil initially to bring the water to saturation or because the source of F was not fluorite. The MF and CAP waters were slightly oversaturated with respect to barite at the end of the contact period, although the reason for this was not clear. The RO water was close to equilibrium with barite.

FLOW-THROUGH COLUMNS

Major ions

For many ions, a “washout” phenomenon occurred during the startup period. This was observed in all columns for Ca^{2+} , Mg^{2+} and alkalinity and to varying extents for SO_4^{2-} , Cl^- and TDS. Washout generally occurred in the first two or three sampling periods (Fig. 4). During initial washout, effluent from the columns was often oversaturated with respect to several Ca- and Mg- carbonate minerals (Table 5). A reasonable explanation for the apparent oversaturation is that solubilities of several constituents were controlled by amorphous evaporite precipitates rather than the crystalline forms represented in MINTEQA2. These amorphous phases form under conditions of alternating soil moisture and are often more soluble

Table 5. Average saturation indices of selected minerals for each water type before and after passage through the soil columns (n/a = one or both constituents in the constituents was below detection limits)

Mineral	Sample	RO	MF	CAP
Calcite CaCO_3	influent	n/a	0.37	-0.3
	effluent, 2-4 pore vols.	0.17	0.35	-0.11
	effluent, ~100 pore vols.	-1.21	0.55	-0.4
Dolomite $\text{CaMg}(\text{CO}_3)_2$	influent	n/a	0.66	-0.43
	effluent, 2-4 pore vols.	0.34	0.99	0.14
Barite BaSO_4	effluent, ~100 pore vols.	-2.38	1.05	-0.67
	influent	-1.7	0.36	1
	effluent, 2-4 pore vols.	-0.49	1	1.07
Fluorite CaF_2	effluent, ~100 pore vols.	-1.42	0.34	1.04
	influent	n/a	-1.23	-1.91
	effluent, 2-4 pore vols.	-0.48	-0.52	-0.6
Aragonite CaCO_3	effluent, ~100 pore vols.	-4.35	-1.22	-1.9
	influent	n/a	0.235	-0.44
	effluent, 2-4 pore vols.	0.04	0.21	-0.24
Ferrihydrate $\text{Fe}(\text{OH})_3$	effluent, ~100 pore vols.	-1.35	0.42	-0.54
	influent	1.47	2.47	2.46
	effluent, 2-4 pore vols.	2.39	2.44	2.71
Magnesite MgCO_3	effluent, ~100 pore vols.	n/a	2.6	2.55
	influent	n/a	-0.21	-0.03
	effluent, 2-4 pore vols.	-0.33	0.14	-0.25
Halite NaCl	effluent, ~100 pore vols.	-1.66	0	-0.77
	influent			
	effluent, 2-4 pore vols.	-7.9	-6.0	-6.6
	effluent, ~100 pore vols.	-8.9	-5.9	-6.7

Table 6. Peak concentrations of trace elements compared with mean concentrations late in the experiment (>40 pore volumes; last two sampling points). The peak:late mean ratio is the peak concentration divided by the late-experiment mean. Values shown are averages for all six soil columns

Water	Fluoride (mg/l)			Barium ($\mu\text{g/l}$)			Arsenic ($\mu\text{g/l}$)		
	peak (day)	mean	ratio	peak (day)	mean	ratio	peak (day)	mean	ratio
RO	6.4 (3)	0.1	91	100 (18)	36	3.2	23.8 (20)	15.5	1.5
MF	21.6 (1)	0.4	143	313 (2)	46	6.9	18.8 (75)	13.1	1.4
CAP	2.6 (2)	0.3	7.5	344 (2)	191.2	1.8	16 (8)	12.3	1.4

than their stable crystalline counterparts (Harmsen, 1977).

RO. The effluent from the soil columns receiving RO water exhibited the largest changes in major ion composition (Fig. 3). The average FWAC for TDS of the RO water increased from 40 to 240 mg/l during passage through the soil columns (Table 2). Over the entire duration of the experiment, a significant gain in HCO_3^- (0.8 meq/l) was balanced by increases in Ca^{2+} , Na^+ and Mg^{2+} ($\Sigma = 0.9$ meq/l), indicating dissolution of carbonate minerals. Buffering provided by the dissolution of carbonates caused the pH to increase from 6.5 in the source water to ~7.5–8.0 in the column effluent. Concentrations of SO_4^{2-} , Cl^- and K^+ changed little as water passed through the columns.

The SAR in the effluent was ~2.5 during the first 3 days, due to leaching of Na^+ , but then declined to <2. On day 2, effluent from the RO columns was apparently close to saturation with several carbonate minerals, but by day 100, the effluent was highly undersaturated with respect to calcite, dolomite, aragonite and magnesite. Undersaturation late in the experiment was likely caused by a gradual depletion of source minerals.

MF. Changes in the composition of MF water during passage through the soil columns were modest. A net gain in Mg^{2+} (FWAC = 1.5 meq/l; an increase of 74%) was approximately balanced by small gains in SO_4^{2-} (FWAC = 0.68 meq/l, an 18% increase) and HCO_3^- (FWAC = 0.25 meq/l, a 5% increase) and a small loss of Ca^{2+} (FWAC = -0.38 meq/l). Na^+ , Cl^- , K^+ and NO_3^- were nearly conservative. Equilibrium modeling shows that the MF source water was oversaturated with respect to calcite, dolomite and aragonite, indicating the potential for precipitation of these minerals in the columns. Column effluents also had SI values >0, indicating that either precipitation was incomplete or that other reactions (e.g. ion exchange) were occurring. The MF source water was undersaturated with respect to magnesite whereas the MF column effluents were close to equilibrium with magnesite. This is consistent with the observation that Mg^{2+} concentrations were higher in the effluent than in the inflow. It is likely that ion exchange reactions and/or dissolution of other minerals (not included in MINTEQA2) may have been taking place in the MF columns. Overall, the change in composition of MF water passing

through the columns was modest, resulting in a 5% increase in TDS (based on FWAC).

CAP. Changes in the composition of CAP water during passage through the columns also were modest. TDS increased by only 10 mg/l, a gain of 1.6% and there was no appreciable change in the SAR (~1.8), except during the first day, when it increased to 2.5. At these TDS and SAR levels, salinity-induced infiltration loss should not be a problem. The only ions whose concentrations changed by >10% during passage through the columns were Mg^{2+} (+23%) and K^+ (+33%). Because the increase in the equivalent concentrations of these ions (+0.7 meq/l) was <4% of the overall sum of charges (18.6 meq/l), changes in the charge balance cannot be used to infer mechanism. Solubility calculations indicate that both the CAP source water and the CAP column effluent at day 2 were near equilibrium with several carbonate minerals. By the end of the experiment (day 30), effluent from the CAP columns was distinctly undersaturated with respect to modeled carbonate minerals.

Trace elements

As in the batch studies, only three trace elements, As, F and Ba, were found in the effluent from the columns at concentrations above detection limits. During the first few days of operation, concentrations of F and Ba in the effluent from the columns were far higher than concentrations in the source waters, representing the same type of washout phenomenon observed for several major ions (Fig. 4). For F, the average peak concentrations in the column effluents ranged from 2.6 to 21 mg/l and occurred during the first few days of column operation (Table 6). The average ratios of the peak [F]:average [F] in the column effluents during the last two sample periods were 91, 143 and 7.5 for the RO, MF and CAP columns, respectively, indicating that the flushing of F is a transient phenomenon. By late in the experiment, F levels in the column effluents were always <1.0 mg/l (Fig. 4). Even during the initial F peak, the column effluents were undersaturated with respect to fluorite; by late in the experiment, the degree of undersaturation increased (Table 5). By late in the experiment, F concentrations in the column effluents were nearly identical to concentrations in the source waters.

Barium exhibited less extreme washout peaks. Average peak concentrations in the column effluents

were 100–344 $\mu\text{g}/\text{l}$ (Table 6) and the ratios of peak: late experiment average concentrations were 1.8–6.9. During the last two sampling periods, concentrations of Ba in the CAP and MF columns were nearly the same as those in the source water. For these two waters, Ba was slightly oversaturated with respect to barite in the source water and in the column effluent (day 2 and day 100; Table 5). At the end of the experiment, Ba concentrations in the effluent from the RO columns were still three times higher than in the source water. This is consistent with solubility calculations, which shows that barite was highly undersaturated in the source water and less undersaturated in the column effluents (Table 5).

Arsenic solubilization occurred consistently throughout the study, with peak: average ratios of 1.4–1.5. For the CAP and MF columns, concentrations declined slowly following peaks, whereas for the RO columns, As concentrations continued to increase throughout the experiment (Fig. 4). Late in the experiment, As levels in the column effluents were 2–10 times higher than in the source waters (Table 6), although concentrations never quite reached the 50 $\mu\text{g}/\text{l}$ MCL. These data indicate that As leaching would continue for some time after the initiation of recharge with RO water. The mechanism by which As is leached in desert soils is not well understood. Natural As contamination is common in this region, but the extent of As leaching is highly variable among soil types (Baker and Bolitho, 1995; Baker *et al.*, 1998). In similar batch tests with soil–water slurries, Baker *et al.* reported As concentrations > 100 $\mu\text{g}/\text{l}$ in soils from the mid-Verde River valley region; As concentrations in some wells in the Phoenix region can approach 100 $\mu\text{g}/\text{l}$ (Wolff, Salt River Project, Phoenix, personal communication).

DISCUSSION

Implications of major ion reactions

Chemical processes that involve major ions are important in the context of groundwater recharge for several reasons. First, exchange of soil-bound divalent ions (Ca^{2+} and Mg^{2+}) with Na^+ from the recharge water can lead to dispersion of clays, which is often responsible for reduced infiltration in irrigated cropland. We observed very little evidence of Na^+ exchange in our study, suggesting that clay dispersion would not be a concern. On the other hand, leaching of mineral salts from certain soils could cause elevated salinity in recharged water. This study showed that leaching of salts was not sufficient to raise the TDS or change the SAR of either CAP water or MF water appreciably, but the TDS of RO water increased to around 200 mg/l .

Precipitation/dissolution reactions could potentially alter infiltration rates. The MF source water was oversaturated with respect to several carbonate

minerals and solubility calculations indicate that precipitation of these minerals occurred in the soil columns. This might be problematic over long periods because precipitation of carbonates would decrease porosity and reduce infiltration rates. Conversely, dissolution of minerals could be problematic from a standpoint of infiltration capacity because the structure of certain types of soils in arid lands depends upon “cements” comprised of clays, fine silts and mineral salts. The dissolution of the cementing material can lead to soil “collapse”, a phenomenon in which the natural cementing material dissolves, allowing particles to settle (Houston *et al.*, 1988). However, laboratory testing and theoretical calculations by Duryea (1996) indicate that the loss of infiltration capacity due to soil collapse is probably small relative to other mechanisms of clogging during infiltration (e.g. biofilms, chemical precipitation).

Implications for regulated contaminants

Among regulated contaminants measured in this experiment, only As, F and Ba appeared in elevated concentrations. Only F appeared at concentrations well above its MCL. Concentrations of F and Ba peaked early in the column experiment and then declined. As leaching was sustained, with little or no decline by the end of the experiment. This suggests that As leaching may not abate quickly. Although XRD analysis of oriented samples did not reveal mineralogical sources of As, Ba or F, these minerals could have been present at low concentrations and therefore not detected by XRD.

We cannot make quantitative predictions regarding concentrations of contaminants in the field-scale recharge project for two reasons. First, the soil columns used in our experiment were only 20 cm long, whereas water would infiltrate through many hundreds of meters of soil during vadose zone injection. Second, our columns were screened to remove coarse material, so that the reactivity of our soil matrix would be higher than that of a comparably sized column filled with unaltered soil.

We can, however, make qualitative predictions. First, for contaminants that were undersaturated with respect to mineral phases throughout our experiment, peak concentrations during field-scale recharge will probably be higher than we observed, because the recharge water would continue to pick up contaminants as it moved through the vadose zone, until saturation with source minerals is reached. In particular, we would expect this to happen for F, which was always undersaturated with respect to fluorite. Second, the duration of washout will be longer during actual recharge, because the recharged water would have a longer path length than it did in our experiment. Soil contaminants would first be leached from the upper horizons until the mineral source was depleted and then from sequentially deeper horizons, until the entire

soil column was leached. For a deep vadose zone, this process may take months to years.

Comparison of batch and column studies

Batch tests are easier to run than column tests but do not simulate the dynamic aspect of chemical change, such as the washout phenomenon observed in the lab columns. We also used a finer fraction of soils in the batch experiment than in the column experiment. Despite these differences, the same three regulated contaminants (As, F and Ba) appeared in significant concentrations in both the batch and column experiments. In comparing batch and column experiments, each of these chemicals behaved differently. For F, the batch experiments were a good representation of the long-term average concentration in the column experiments but the washout effect was poorly represented. Depending upon the source water, peak concentrations of F in the columns were 3–25 times higher than F concentrations at the end of the batch experiment. In contrast, As concentrations remained fairly steady throughout the column study and were roughly comparable with concentrations in the batch experiment. Peak concentrations of Ba in column effluents were 0.5–2.1 times higher than concentrations in the soil-water slurries in the batch experiment. Effluent Ba concentrations late in the column experiment were consistently lower than concentrations in the batch study.

This study may be used to guide the development of protocols to evaluate potential contamination of recharged water. Batch studies are a fairly good screening test to determine whether certain contaminants are likely to be leached. Contaminants that were leached at measurable concentrations in the column study were also leached in the batch study and visa versa. Batch experiments are less useful than the columns in representing the dynamics of contaminant behavior, such as the potential for washout.

Both batch and column studies are useful as screening studies that can identify potential water quality problems before costly field-scale recharge projects are built. However, neither column nor batch experiments are sufficient to make quantitative predictions of water quality changes that will occur during recharge through the vadose zone. At the present time, it is prudent to operate pilot-scale projects accompanied by monitoring wells to determine the potential for water quality changes before implementing full-scale recharge projects.

Managing recharge projects

Results from this study have several implications regarding artificial recharge. First, recharge waters should not be far out of equilibrium with carbonate minerals in the soil environment. Waters that are highly undersaturated with respect to carbonates (e.g. our RO water) will aggressively dissolve min-

erals, leading to changes in soil structure that may be undesirable (e.g. collapse). Waters that are initially oversaturated may precipitate carbonates during recharge. Controlling the initial carbonate composition of waters is readily achieved through the addition of lime (for undersaturated waters), softening (for oversaturated waters) or blending. Second, some soils leach appreciable concentrations of regulated contaminants. In this study, leaching of As, F and Ba resulted in concentrations that sometimes approached or exceeded MCLs, particularly during the washout period. A pilot-scale study is now underway at the Scottsdale Water Campus to determine whether these contaminants will pose a long-term problem.

Developing improved predictive capability

Column studies are better at representing the chemical dynamics of infiltrating water than are batch studies, but even column studies cannot be used to develop quantitative predictions of water quality in full-scale recharge projects. Developing better predictive capacity will almost certainly require mathematical models that represent both water movement and chemical processes. Our experiments indicate that a predictive model would have to represent the kinetic aspects of mineral processes as well as equilibrium conditions.

CONCLUSIONS

The chemical composition of recharged water may change in important ways during infiltration through the vadose zone. Precipitation/dissolution reactions could lead to reduced infiltration rates by clogging (through precipitation) or physical collapse (through dissolution of soil cements). RO water was by far the most aggressive water used in this experiment whereas the MF water was initially oversaturated with respect to several carbonate minerals. We saw little evidence of Na^+ exchange for any of the soil/water combinations examined, and TDS changes for the CAP and MF waters were small. Among regulated contaminants, F, As and Ba concentrations increased during simulated recharge. For F and Ba, concentrations of these contaminants were highest during the initial washout period and then declined significantly. Leaching of As was more sustained. For some soils in the arid west, leaching of contaminants during recharge could be a serious problem. Laboratory leaching studies (batch studies as a minimum) are a cost-effective tool for identifying potential problems but cannot be used to make quantitative predictions of water quality changes in full-scale recharge projects.

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