



Desorption of Metals from Aquifer Soils During Infiltration of Low Ionic Strength Water by pH Effect†

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Primary and trace metals from S400 samples are higher than that from S700 because the size of S400 is smaller than one of S700. The effects of solution chemistry, *i.e.*, ionic strength and pH, on metal immobilization were evaluated *via* batch desorption equilibrium experiments for aquifer soils during infiltration of low ionic strength water. For S400 and S700, cumulative desorption amount of Ca is, respectively 2050 and 1900 mg/kg-soil with 12 times extraction at 58 mg/L of TDS water at pH = 4. It was found that desorption of Ca, Mg and Ba decreases with increasing pH. For S400 and S700, cumulative desorption amount of As is 0.9 mg/kg-soil with 15 times extraction at 58 mg/L of TDS water at pH = 9. On the contrary, desorption of As was found to increase slightly with increasing solution pH, although the effect of pH is not as great as that for the other metals. This effect was offset by the less dissolution of CaCO₃ at higher pH, which reduced release of carbonate associated arsenic.

Keywords: Desorption of metals, Aquifer soils, Infiltration of low ionic strength water, pH effect.

INTRODUCTION

Artificial recharge using source waters of impaired quality can potentially introduce microbial, inorganic and organic contaminants into groundwater. Meanwhile, biochemical and geochemical reactions between the recharge water and the aquifer materials may lead to mobilization of inorganic species that are part of the mineral framework of the aquifer.

Metals, unlike hazardous organics, cannot be degraded. In addition to the primary metals, a number of heavy metals are naturally present in soil, such as Cu, As, Cr, Pb, Ni and Co. Many soils in arid areas contain naturally occurring, easily leachable contaminants of relevance to drinking water quality, notably F, B, As, Cr, Pb and Ba¹. Interactions between metals and soil mainly involve precipitation/dissolution and sorption/desorption. The effects of solution chemistry, *i.e.*, ionic strength and pH, on metal immobilization were evaluated *via* batch desorption equilibrium experiments in this study. The research objective is to evaluate the potential for release of metals of public concern from surface infiltration operations when reclaimed water of low TDS is used for recharge.

EXPERIMENTAL

Recharge water and soil samples: Reclaimed water with municipal wastewater treated to drinking water quality using microfiltration and reverse osmosis (referred to as RO water) was used as the model low ionic strength recharge water. The reverse osmosis water is one of the two recharge waters currently used for vadose zone injection at the Water Campus Project (WCP) in the City of Scottsdale, AZ, USA.

At the WCP site, both the top layer, from the surface to approximately 200 ft and the aquifer, approximately 550 ft below the ground surface, are sand dominated with silt and gravel, with silt dominated soils in between. Well #140 was drilled using a reverse circulation rotary drilling method near the WCP recharge site. Drill cuttings at the depth of 180', 400', 550' and 700' (designated S180, S400, S550 and S700, respectively) were collected in polyethylene freezer bags and kept in new 1-gallon paint cans by the hydrogeologist for the Water Resource Department, City of Scottsdale, AZ, USA.

Water sample analysis and soil characterization: Table-1 lists some water quality parameters relevant to this study.

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TABLE-1
RELEVANT WATER QUALITY DATA FOR RO
WATERS AT WATER CAMPUS PROJECT

Water quality	RO	
	Mean	SD
pH	6	0.11
Total alkalinity (mg/L as CaCO ₃)	19	0.24
TOC (mg/L)	0.4	0.13
TDS (mg/L)	25.6	3.2
Conductivity (μs)	50.6	0.25

All water and soil samples were analyzed in duplicate. Blank extraction tests were performed in parallel with samples for each extraction method following exactly the same procedure for soil samples.

Major soil characteristics important to sorption/desorption of heavy metals include mineralogical composition, hygroscopic moisture, soil pH, particle size distribution, specific surface area, pore size distribution, organic matter, cation exchange capacity and total metal load. All soil characterization tests were conducted using soil fractions smaller than 2 mm in diameter, which were thoroughly mixed before use. Analytical methods used for soil characterization are summarized in Table-2.

TABLE-2
ANALYTICAL METHODS FOR SOIL CHARACTERIZATION

Soil characteristics	Analytical methods
Mineralogical composition	XRD to identify major mineral phases
Major element analysis	SEM-EDS
Hygroscopic moisture	Analysis of weigh loss after oven dried at 105 °C
Particle size distribution	Sieve analysis using ASTM standard sieves
Bet surface area	N ₂ adsorption/desorption
Pore size distribution	N ₂ adsorption/desorption
Organic content	Analysis of weight loss after heating at 400 °C for 4 h ^{2,3}
Metal concentration	Wet extraction followed by ICP or ICP-MS analysis
Cation exchange capacity	The Palmio and Rhoades ⁴

Total metal analysis was performed using the EPA 3050B method⁵. This method determines total metal concentrations in soil that are “environmentally available”.

Desorption equilibrium experiments: For all experiments, 1 g of soil was mixed with 15 mL desorption solution in a 20 mL polypropylene tube. The suspension was equilibrated for 20 h on a rotary shaker (Vibrax*VXR, VWR) at 30 rpm with 9,610 G, followed by 10 min of centrifugation. The

clear supernatant was decanted, filtered through a membrane syringe filter and then collected in a 10 mL polypropylene plastic centrifuge tube for analysis of target metal concentrations.

RESULTS AND DISCUSSION

Soil properties: Table-3 summarizes some general properties of the soil samples. The total concentrations of some metals of soil samples are summarized in Table-4. The particle size distributions of soil samples collected from the Water Campus Project (WCP) site are shown in Fig. 1.

TABLE-3
GENERAL CHARACTERISTICS OF SOIL SAMPLES AT WCP

Sampling ID	S180	S400	S550	S700
pH	8.8	8.2	8.8	8.9
Hygroscopic moisture (%)	1.2	2.8	1.2	1.0
Organic matter (g/kg)	18.1	13.4	9.7	8.3
CEC (meq/100 g-soil)	3.3	12.6	2.5	2.3
BET surface area (m ² /g)	7.63	18.87	5.4	2.25

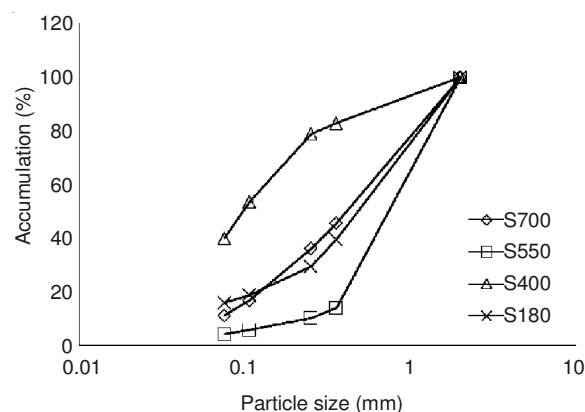


Fig. 1. Particle size distribution of soil samples from the WCP site

Fig. 2 presents the total metal concentrations in the soil samples. Only data for S400 and S700 are presented. Primary and trace metals from S400 samples are higher than that from S700 because the size of S400 is smaller than one of S700 (Fig. 1).

Metal desorption equilibrium

Effect of pH: It was found that desorption of Ca, Mg and Ba decreases with increasing pH. Fig. 3 presents the amount of Ca desorbed from S400 and S700 as a function of cumulative desorption solution volume. For S400 and S700 samples, cumulative desorption amount of Ca is, respectively 2050 and

TABLE-4
SOME METAL CONTENTS OF SOIL SAMPLES AT WATER CAMPUS PROJECT

Metal (mg/kg)	S180		S400		S550		S700	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Ca	14600	410	24125	757	11690	560	6997	400
Mg	2727	33.2	7092	232	2434	45	2326	133
Fe	4583	139	11340	339	5051	86	5516	363
Al	3702	85.6	9694	461	3427	118	3369	249
As	1.3	0.1	3.5	0.1	1.8	0.1	2.1	0.2
Cr	4.2	0.1	8.8	0.2	5.3	0.2	6.1	0.1
Pb	2.5	0.3	0.3	5.6	1.2	2.4	0.1	2.3
Zn	14	1.3	20.3	1.0	11.2	1.6	14	0.1

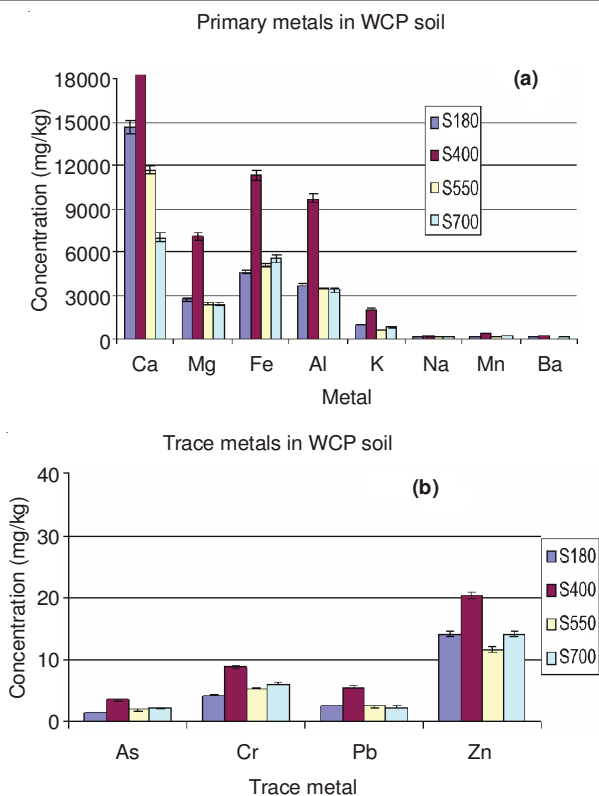


Fig. 2. Primary and trace metal contents of soil samples as (a) and (b)

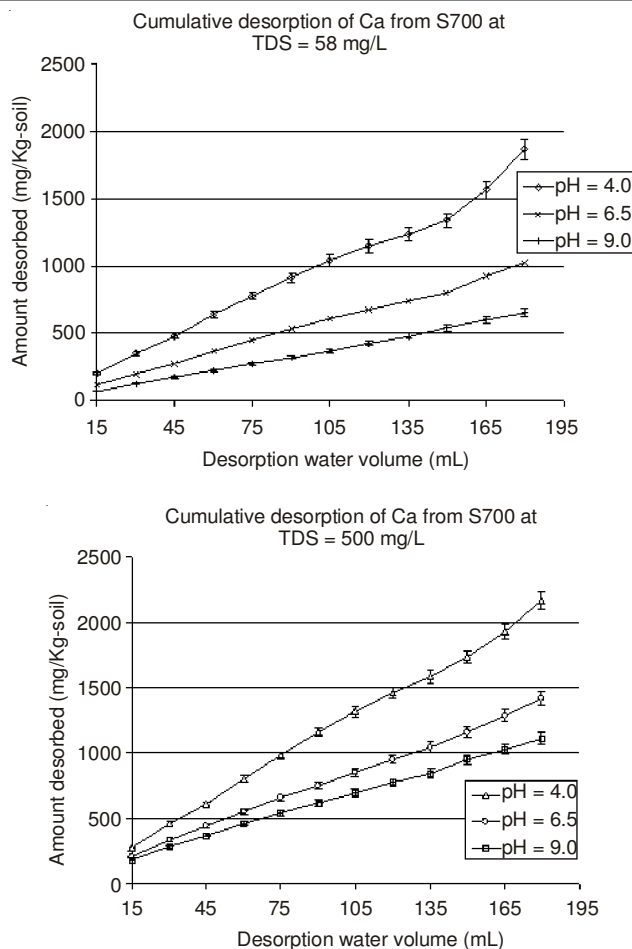
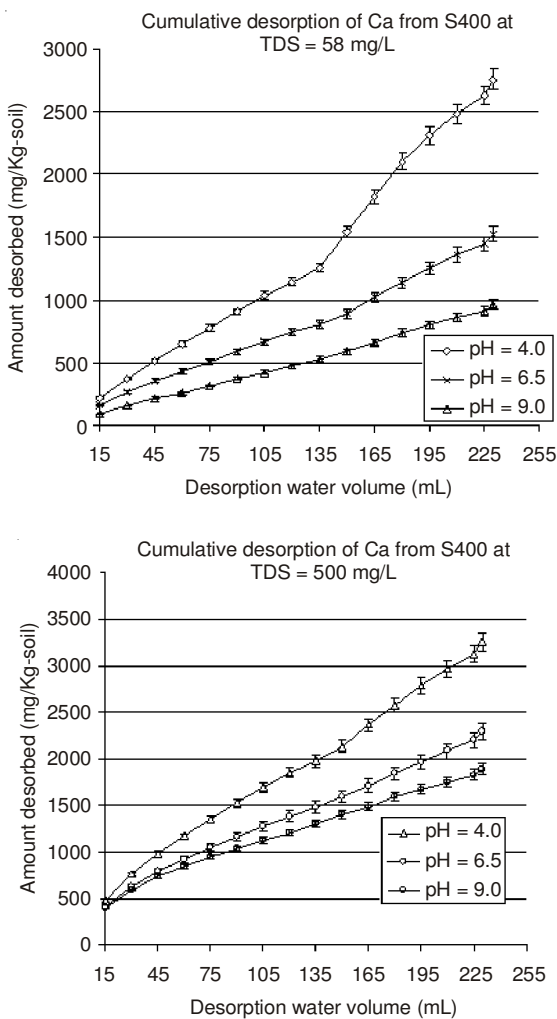


Fig. 3. Effect of pH on cumulative desorption of Ca from S400 and S700

1900 mg/kg-soil with 12 times extraction at 58 mg/L of TDS water at pH = 4. Results for Mg and Ba show the same trend with the amount desorbed one and three orders of magnitude lower, respectively. Desorption of cations from clay and a variety of oxides at low pH has been reported in a number of studies⁶⁻⁸.

For S400 and S700 samples, cumulative desorption amount of arsenic is 0.9 mg/kg with 15 times extraction at 58 mg/L of TDS water at pH = 9. On the contrary, desorption of arsenic was found to increase slightly with increasing solution pH (Fig. 4), although the effect of pH is not as great as that for the other metals. The slightly higher desorption at higher pH is consistent with the lower adsorption of arsenic reported at high pHs. Typically, arsenic exists in soils as either arsenate (AsO_4^{3-}), or arsenite, (AsO_3^{3-}). Because both arsenic acid (H_3AsO_4) and arsenious acid ($As(OH)_3$) are weak acids, their speciation strongly depends on pH. The pKa values of H_3AsO_4 and $As(OH)_3$ are listed in Table-5. Based on the high calcite content of the soil samples and the high amount of Ca released, it is postulated that part of the arsenic desorption is from dissolution of $CaCO_3$ and hence release of arsenic associated with it. The small impact of pH on arsenic desorption may be the result of these two contradicting mechanisms.

Desorption of all metals from S700 soil sample is lower than that from S400. This is consistent with the higher total metal contents, higher surface area and CEC of S400, as shown in Table-3. The soil has strong buffering capacity because



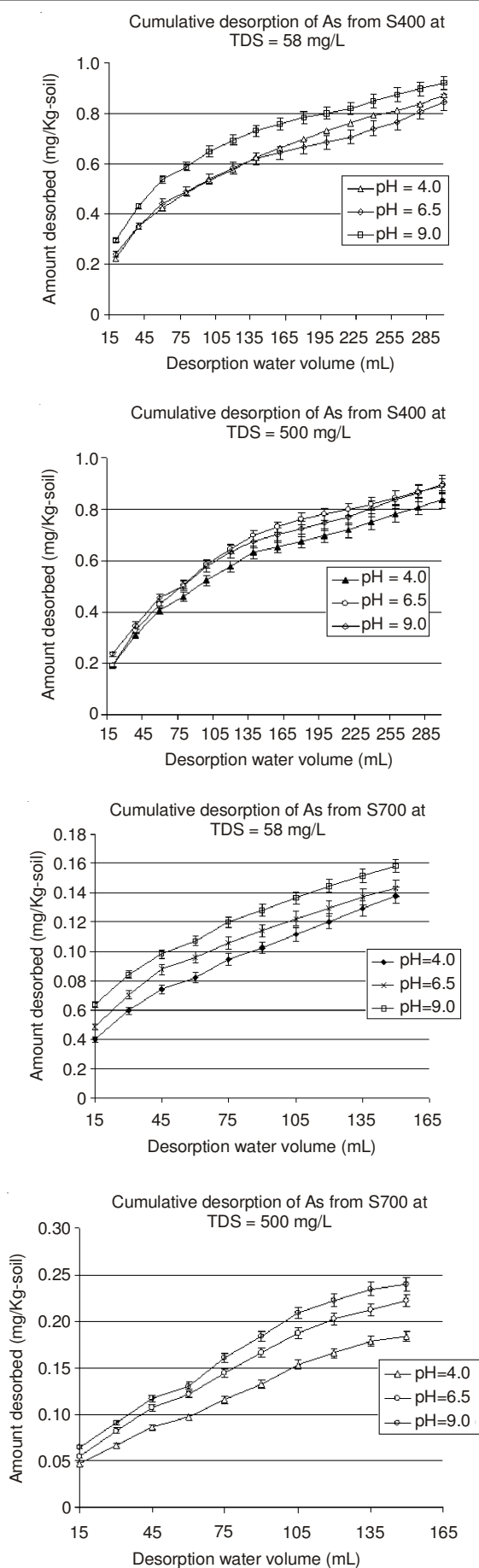


Fig. 4. Effect of pH on cumulative desorption of As from S400 and S700

TABLE-5
ACIDITY CONSTANTS OF ARSENIC COMPOUNDS

As compounds	pK _{a,1}	pK _{a,2}	pK _{a,3}
H ₃ AsO ₄	2.25	6.76	11.60
As(OH) ₃ * ^a	9.23	12.13	13.40

of the abundance of carbonate. Regardless of the initial pH of the desorption solution, the pH of the soil/water mixture after each 20 h contact period stayed within the ranges of 8.3-9.4 and 7.5-9.4 for S400 and S700, respectively.

Conclusion

For S400 and S700 samples, cumulative desorption amount of Ca is, respectively 2050 and 1900 mg/kg-soil with 12 times extraction at 58 mg/L of TDS water at pH = 4. It was found that desorption of Ca, Mg and Ba decreases with increasing pH. For S400 and S700, cumulative desorption amount of As is about 0.9 mg/kg-soil with 15 times extraction at 58 mg/L of TDS water at pH = 9. On the contrary, desorption of As was found to increase slightly with increasing solution pH. Significant desorption of arsenic was observed when a vadose zone soil and an aquifer material collected from the Water Campus Project were contacted with reverse osmosis treated wastewater. The amount of arsenic desorption was a complex function of solution pH, total ionic strength, ionic composition and soil mineral composition. In general, desorption of As increased with increasing solution pH because it desorbs in the form of oxyanion, although this effect was offset by the less dissolution of CaCO₃ at higher pH, which reduced release of carbonate associated arsenic.

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