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Mobility of arsenic in soil from the Rocky Mountain Arsenal area

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Abstract

From 1942 to the early 1980s, Rocky Mountain Arsenal (RMA), a superfund site northeast of Denver in central Colorado, served as a facility for the development, manufacture, and disposal of toxic organic and inorganic chemicals including US Army surety agents (including nerve gas and blistering agents), munitions, propellants, and pesticides. Arsenic (As) in the form of Lewisite (blistering agent), arsenic trioxide (herbicide), trisodium arsenate, and arsenic trichloride (process intermediate) was present in extremely large quantities at RMA's South Plants Processing Area. Even though current cleanup efforts are likely to remove the vast majority of As presently polluting the soil and groundwater, there is still a future potential threat for the movement of residual levels of As into groundwater supplies. The distribution and movement of As were monitored over a 2.5-year period to evaluate the threat to groundwater by low levels of As. Because of access restrictions to RMA, an off-site meso-scale (0.6 m diameter by 1.83 m in height) weighing lysimeter study was conducted using excavated soil (i.e., Ascalon sandy clay loam) associated with As contamination at RMA's South Plants Processing Area. The long-term study revealed the persistence of As under aerobic soil conditions, and a limited, but perceptible, mobility of As (0.87% of the total applied As drained beyond 1.5 m) resulting from interacting physical, chemical, and biological factors. Results suggest that even though the movement of As is significantly retarded due to adsorptive processes, preferential flow and chemical factors (i.e., pH and redox potential) can mobilize As at point locations above permissible levels, if precautionary measures are not taken. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic mobility; Arsenic adsorption; Preferential flow; Contaminant transport; Groundwater vulnerability

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1. Introduction

The Rocky Mountain Arsenal (RMA) is a well-known superfund site located on prairie land 16 km northeast of metropolitan Denver in central Colorado (see Fig. 1). The > 78 km^2 facility is owned and operated by the United States Army. Since its inception in 1942, RMA has served as the primary government facility in the western United States for the development, manufacture, storage, demilitarization, and disposal of US Army surety agents (including nerve gas and blistering agents), munitions, and propellants. From the late 1940s to the early 1980s, private companies leased portions of RMA for the production of pesticides.

The most common contaminants present in the soils, lake sediments, and groundwater of RMA are pesticides such as dieldrin, aldrin, chlordane, DDT, DDE, and endrin, and heavy metals including arsenic (As), chromium (Cr), mercury (Hg), and lead (Pb). During the production years at RMA, a variety of methods were used for treating and disposing of wastes generated by manufacturing and munitions-production activities including chemical neutralization, incineration, the use of evaporative basins for the disposal of hazardous liquid/slurry wastes, and on-site burial. Contaminants were disposed of using widely accepted practices of the time. Contamination also resulted from leaks in chemical sewer lines, wind dispersion, accidental spills, and the performance of day-to-day processing and manufacturing tasks.

Soil and groundwater contamination from a wide variety of organic and inorganic chemicals have been documented at RMA (Stollar et al., 1982; Wiley and Rhodes, 1987). The presence of metalloids, particularly As, in soil and groundwater is primarily the consequence of years of production of war chemicals. Arsenic was introduced onto RMA in the form of Lewisite (2-chlorovinyldichloroarsine, a blistering agent), arsenic trichloride (process intermediate for Lewisite), trisodium arsenate (demilitarization byproduct), and arsenic trioxide (process intermediate for insecticides and herbicides). Arsenic was present in extremely large quantities at RMA's South Plants Processing Area.

Since the early 1980s, RMA has been involved in litigation activities that have led to the commencement of short-term and long-term cleanup activities. Even though cleanup efforts are likely to remove the vast majority of As presently polluting soil and groundwater, low levels of residual As still pose a potential threat to groundwater supplies; therefore, a knowledge of the movement and distribution of As over long time periods is useful to determine the potential vulnerability of the groundwater lying beneath RMA.

Arsenic chemistry in soils has been well studied with numerous publications in the literature concerning the high sorptive capacity of soils for As (Jacobs et al., 1970; Elkhatib et al., 1984; Sakata, 1987; Masscheleyn et al., 1991). Arsenic retention in soils is primarily related to the content of Fe and Al oxides, redox potential, pH, the type and content of clay in the soil, and to a lesser extent upon exchangeable Ca and oxyanion competition. The capacity of a soil to retain As is dependent predominantly on adsorption to amorphous and cryptocrystalline hydrous oxides of Fe and Al (Jacobs et al., 1970; Pierce and Moore, 1980; Livesey and Huang, 1981; Pierce and Moore, 1982; Elkhatib et al., 1984; Sakata, 1987; Fuller et al., 1993; Wilkie and Hering, 1996).
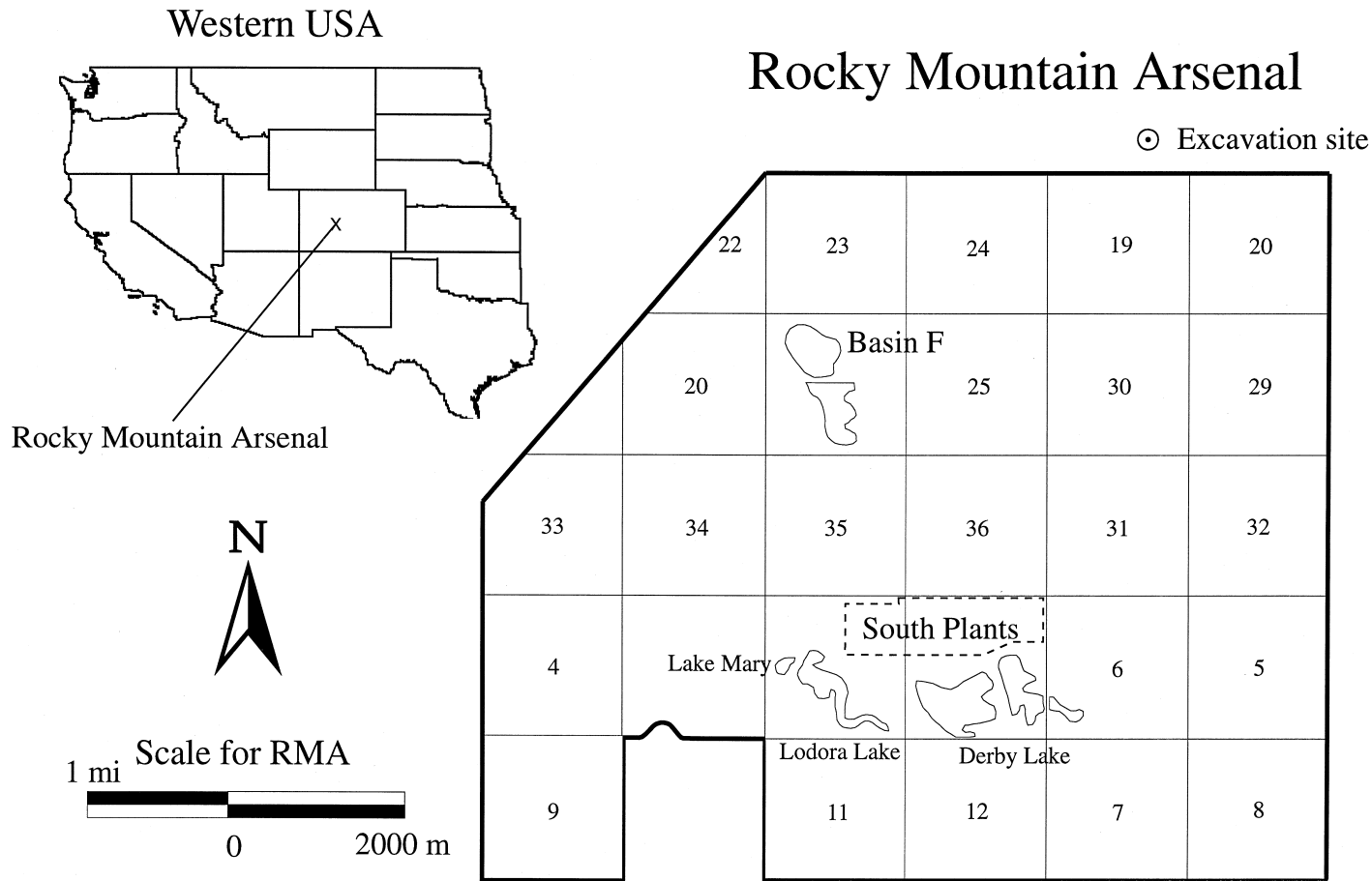
Fig. 1. Map showing the location of the Rocky Mountain Arsenal in the western USA, and the boundary and section lines for the Rocky Mountain Arsenal. * Indicates the location of the off-site soil excavation location.

The biological availability, and physiological and toxicological effects of As depend upon its chemical form as determined by redox potential (Webb, 1966; Penrose, 1974). Arsenate [As(V)] and arsenite [As(III)] are the primary As forms in soils. The distribution between dissolved As(III) and As(V) is dependent on redox potential. Under oxidizing conditions, the predominant species is As(V), which exists as deprotonated oxyanions of As acid (i.e., $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}), in strongly reduced environments elemental As and AsH_3 exist, under mildly reduced conditions (i.e., $< +100$ mV), As(III) is thermodynamically stable and exists as arsenious acid, i.e., $H_3AsO_3^0$, $H_2AsO_3^-$, and $HAsO_3^{2-}$ (Deuel and Swoboda, 1972; Hess and Blanchar, 1976). Arsenite is 25 to 60 times more toxic than arsenate and has been reported to be more mobile in the environment.

The influence of pH upon sorption depends upon the sorbent material and chemical form of As with maxima exhibited in the pH range of 3 to 9 followed by declining sorption with increasing pH. On the same sorbent material, As(V) generally reaches a sorption maximum at a lower pH than As(III). The retention of As on clay is dependent on the quantity and type of clay. In general, soils with a higher clay content retain more As than soils with a lower clay content (Tammes and de Lint, 1969; Woolson and Kearney, 1973; Elkhatib et al., 1984). The order for the sorption of As on clay type is kaolinite > vermiculite > montmorillonite (Dickens and Hiltbold, 1967). Arsenate, phosphate, and molybdate are oxyanions that can compete for retention sites on the mineral surfaces of soils (Barrow, 1974; Murali and Aylmore, 1983; Roy et al., 1986; Manning and Goldberg, 1996).

Sorption and redox reactions strongly influence the toxicity, bioavailability, solubility, and potential mobility of As in soils (Deuel and Swoboda, 1972; Gulens et al., 1979; Brannon and Patrick, 1987; Masscheleyn et al., 1991; McGeehan and Naylor, 1994; Mariner et al., 1996; Onken and Adriano, 1997). The effect of the sorption of As onto soils is the retardation of the movement of As; consequently, the mobility of As in soil is a result of the physical and chemical properties of soil that influence its sorption. The greater the sorption of As onto soil, the less that is available for transport through soil pores. The mobility of As in soil depends upon the factors of redox potential, pH, clay mineralogy, the presence of competing oxyanions for retention sites, and the presence of iron and aluminum oxides.

Even though considerable work has been done to understand the chemical reactivity of As in soil, very little work has been done on the mobility of As in soil systems, and even less has been done on determining the mobility of As through the root zone. The predominantly unsaturated root zone provides an increased complexity over strictly saturated soil because of the wide range of water contents resulting from plant water uptake, which significantly complicate the flow of water and transport of As, and the wider range of chemical conditions. An early study by Gulens et al. (1979) used sand columns to study the mobility of As. Sadler et al. (1994) found As could be leached by distilled water from contaminated soil. Jones et al. (1997) used column transport experiments to determine the extent of As mobilization in low pH mine tailings after liming. Peryea and Kammereck (1997) used a laboratory column to examine the potential fate of phosphate-released As. Melamed et al. (1995) studied the effect of adsorbed phosphate on the mobility of arsenate through an Oxisol, but under saturated

conditions. Davis et al. (1994) and Mariner et al. (1996) studied the transport of As in groundwater.

The objective of this weighing lysimeter study was to assess the mobility of As through the root zone of a Rocky Mountain Arsenal soil. To evaluate the potential threat to groundwater, the distribution and movement of As were monitored over a 2.5-year period. Knowledge of the fate of As in this soil is particularly valuable for risk assessment and for the affirmation of selected remediation actions agreed upon in the Record of Decision for the cleanup of the Rocky Mountain Arsenal signed in June of 1996.

2. Methods and materials

Because of access restrictions to RMA, it was not possible to conduct an on-site field study. Rather, a meso-scale (0.6 m in diameter and 1.83 m in height) weighing lysimeter experiment was conducted at the US Salinity Laboratory in Riverside, CA. The soil used to fill the weighing lysimeter was excavated adjacent to RMA from the same soil series associated with previously known locations of As processing and disposal, specifically RMA's South Plants Processing Area.

2.1. Soil selection and pretreatment

Fig. 1 shows a map of RMA, its location in the western United States, and the location of the South Plants complex on RMA where Lewisite was manufactured during the 1940s, and later demilitarized and disposed. The South Plant complex was also the location of the production of pesticides using arsenic trioxide as a chemical intermediate. The South Plant complex is situated over the Ascalon sandy clay loam soil series (fine-loamy, mixed, mesic Aridic Argiustoll), which is the soil series most commonly found in areas of high As contamination on RMA. The actual site selected for the excavation of the Ascalon soil used in the weighing lysimeter column was obtained from outside the confines of the RMA facility adjacent to its northeast corner (see Fig. 1). Soil was obtained from outside of the RMA facility because soil sampling within RMA was not permitted by the US Army, and obtaining soil from outside the RMA perimeter assured a noncontaminated soil, which eliminated the need for an interstate permit to transport hazardous material.

A disturbed soil sample of approximately 1.6 metric tons of soil was manually excavated from the top 1.5 m of a site lying within the Ascalon soil series map unit. The collection of an undisturbed soil sample was not permitted due to manpower limitations and to heavy-equipment restrictions dictated by the property owner of the excavation site. The soil was sieved through a 0.635-cm screen to remove any large organic debris, stones and gravel, mixed in a concrete mixer to make it as homogeneous as possible, and placed in the weighing lysimeter column.

2.2. Weighing lysimeter column

The design and construction of the weighing lysimeter column used in the As-transport study were previously described in detail by Corwin and LeMert (1994). Fig. 2

Lysimeter Construction Schematic
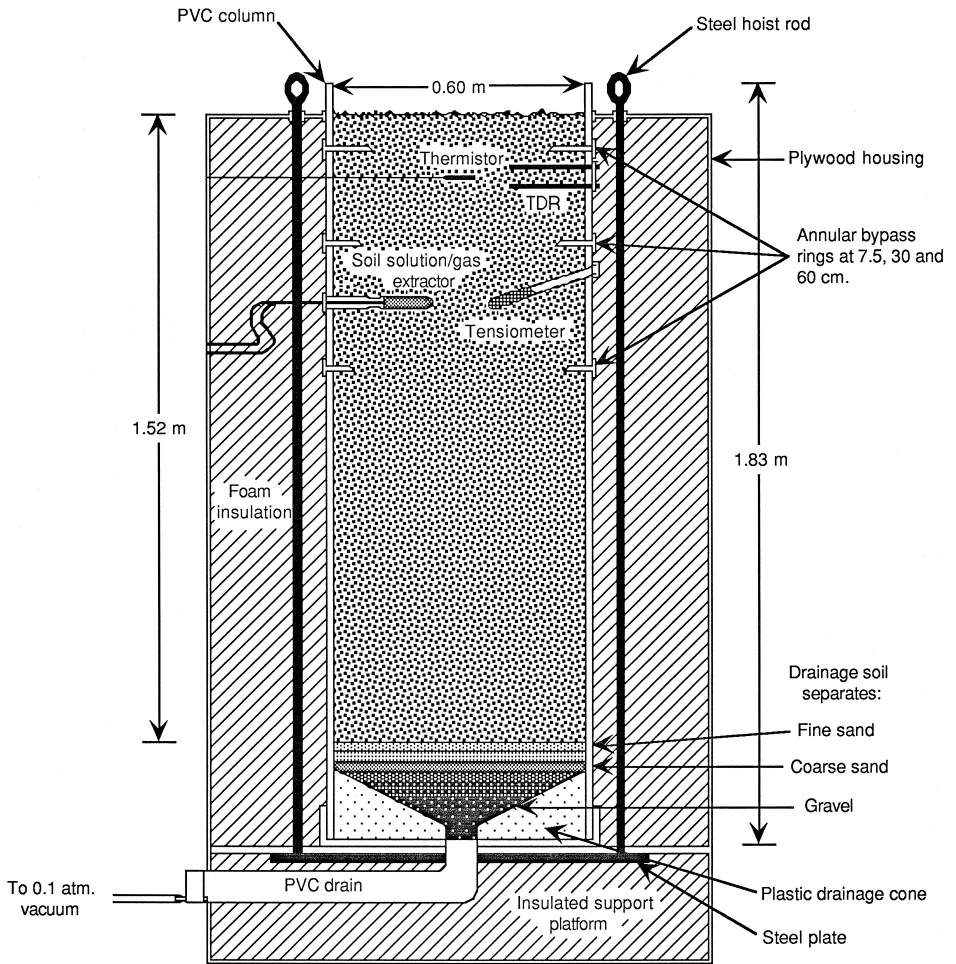
Instrumentation at depths: 0.15, 0.45, 0.75, 1.05 and 1.35 m.

Fig. 2. Schematic of the weighing lysimeter column used in the arsenic transport study. Instrumentation at depths of 0.15, 0.45, 0.75, 1.05 and 1.35 m.

shows a schematic of the weighing lysimeter. The excavated soil was packed into the 1.52-m long space above the drainage soil separates in the weighing lysimeter (see Fig. 2). The column of soil was packed with a series of 0.5–1 cm increments of soil that were individually wetted to compact the added soil layer. After approximately 0.3 m of soil was added, the soil was irrigated four or five times to further compress the soil, then the whole process was resumed again until the entire 1.52-m long space above the drainage system was filled.

Prior to the commencement of the As-transport study, the soil in the column was subjected to a series of wetting-drying cycles (8 irrigations) over a 6-month period without a crop present to further consolidate the soil. A drought-tolerant tall fescue (*Festuca elatior* L.) was then planted and allowed to grow for 12 months. The developed root system helped to rebuild the soil structure that had been destroyed during the soil's homogenization. Even though it is highly unlikely that the newly developed soil structure would duplicate the natural structure existing at RMA, it was important for the soil to develop its own structure to create natural flowpaths resulting from cracks and macropores due to structure or the presence of plant roots. The As-transport study began after the 12 months of root system development.

The soil column was instrumented with thermistors, soil solution–gas extractors, tensiometers, and time-domain reflectometry (TDR) probes (for a detailed discussion of the instrumentation see Corwin and LeMert, 1994). The instruments were placed in duplicate at five depths of 0.15, 0.45, 0.75, 1.05, and 1.35 m, except for TDR probes that were installed at depths of 0.15, 0.30, 0.45, 0.60, 0.75, 0.90. 1.05, 1.20, and 1.35 m. The duplicates were located on opposite sides (i.e., north and south sides) of the soil column. The duplicated instrumentation served as both a backup and a measure of the local variability.

2.3. Soil characterization

The physical and chemical properties of the homogenized RMA soil were measured prior to packing the weighing lysimeter column. Six subsamples of soil were taken for soil chemical analysis. The soil chemical properties of cation exchange capacity (CEC), percent organic and inorganic carbon, $\%CaSO_4 \cdot H_2O$, $\%CaCO_3$, $\%Fe_2O_3$, and $\%Al_2O_3$ were determined (Table 1). Cation exchange capacity was determined with the method by Polemio and Rhoades (1977) for calcareous and gypsiferous soils. A carbon analyzer was used to determine percent organic and inorganic carbon. The method outlined in US Salinity Laboratory Handbook 60 (US Salinity Laboratory Staff, 1954) was used to determine $\%CaSO_4 \cdot H_2O$. The method of Rhoades and Clark (1978) was followed in the determination of $\%CaCO_3$. Iron and aluminum oxides were determined by the method of Coffin (1963).

The saturation extract of each subsample was analyzed for electrical conductivity (EC_e), pH_e, arsenite [As(III)], arsenate [As(V)], soluble arsenic [soluble As = As(III) + As (V)], anions (CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^-), and cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}). Arsenite and arsenate were analyzed using atomic absorption spectrometry. Na^+, K^+, Ca^{2+}, Mg^+, and SO_2^{2-} were analyzed with inductively coupled plasma, CO_3^{2-} and HCO_3^- were measured potentiometrically, and NO_3^- was measured with UV spectrometry.

Five subsamples of soil were taken to determine saturation percentage and particle size distribution (Table 1). Saturation percentage was measured gravimetrically from the saturation paste and from pressure plate measurements, and converted to a volumetric measurement based on the bulk density. Bulk densities were determined from the extracted soil cores where the soil solution extractors were installed (duplicate samples taken at depths of 0.15, 0.45, 0.75, 1.05, and 1.35 m) and again after the experiment had been terminated. Particle size distribution was measured using the hydrometer method.

Table 1
Chemical and physical analysis of homogenized Rocky Mountain Arsenal soil

EC_e (dS m^{-1})	pH_e	As(III) (μg l^{-1})	As(V) (μg l^{-1})	Total As (μg l^{-1})	Anions (meq l^{-1})					Cations (meq l^{-1})				CEC (meq/100 g)	% Carbon		% $CaSO_4 \cdot H_2O$	% $CaCO_3$
					CO_3^-	HCO_3^-	Cl^-	SO_4^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}		Organic	Inorganic		
0.89	7.84	0.305	0.561	0.866	b	2.95	1.32	4.15	0.83	4.29	0.14	2.66	2.08	9.56	0.177	0.29	b	2.48
(0.10)	(0.22)	(0)	(0.422)	(0.422)		(0.59)	(0.30)	(0.71)	(0.37)	(0.51)	(0.02)	(0.43)	(0.28)	(2.18)	(0.015)	(0.03)		(0.12)

% $Fe_2O_3^a$	% $Al_2O_3^a$	Saturation percentage (volumetric)		Particle size distribution			Texture	Bulk density (g cm^{-3})
		Paste	Pressure plate	Sand (2 mm–50 μm)	Silt (50–2 μm)	Clay (<2 μm)		
1.330	0.104	33.2	35.6	55.5	23.7	20.8	Sandy clay loam	1.50
(0.055)	(0.004)	(1.6)	(3.8)	(0.8)	(1.3)	(0.7)		(0.07)

[a] Values represent an average of three subsamples.
[b] Undetectable.
Values represent averages of six subsamples for the chemical analysis and five for the physical analysis. Standard deviations are shown in parentheses.

2.4. Arsenic adsorption experiment

Arsenic adsorption experiments were carried out in batch systems to determine adsorption isotherms (amount of anion adsorbed as a function of equilibrium solution anion concentration). Two hundred grams of soil were added to low profile saturation cups and equilibrated with sufficient solution to attain the saturation percentage of 33.2% ± 1.0. Equilibration at saturation was selected to more closely simulate moisture conditions that would occur during the transport experiment at the time of irrigation. The equilibration solution contained 0, 5, 10, 15, 20, 30, 40 or 50 mg l^{-1} of As prepared from a source material of $Na_2HAsO_4 \cdot 7H_2O$. Samples were mixed with a spatula, sealed with a lid to prevent moisture loss, and equilibrated for 1, 7 and 14 days in a 25 ± 0.1°C laboratory, for 7 days in a 8 ± 0.1°C cold room, and for 7 days in a 40 ± 0.1°C oven. After the appropriate reaction time, saturation extracts were obtained as described by Rhoades (1982), and analyzed for pH and As concentration. Arsenic concentration was determined using atomic absorption spectrometry with hydride generation and the method of Glaubig and Goldberg (1988).

The As adsorption isotherms were described using the Langmuir adsorption isotherm equation:

$$x = \frac{bKc}{1 + Kc} - x_0 \tag{1}$$

where x is the amount adsorbed per unit mass of soil, c is the As equilibrium solution concentration, x_0 is the initial As adsorption, and b and K are empirical parameters. Langmuir adsorption isotherms were fit to the As adsorption data using the nonlinear least squares optimization program ISOTHERM (Kinniburgh, 1985). The Langmuir adsorption isotherm model was used rather than the Freundlich isotherm because it provided a slightly better fit to the data for the observed conditions of the weighing lysimeter study. Use of the nonlinear least squares routine avoided the changes in error distribution and biased parameters often resulting from linear transformations of isotherm equations. The parameter x_0 was optimized only for adsorption isotherms containing > 1 mg l^{-1} in the equilibrium solution after reacting with distilled water. Goodness-of-fit of the nonlinear models was evaluated statistically using the coefficient of determination, R^2:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (s_i - \hat{s}_i)^2}{\sum_{i=1}^{n} (s_i - \bar{s})^2} \tag{2}$$

where s_i are the observed values, $\hat{s}_i$ are the fitted values, $\bar{s}$ is the mean value of the set of s_i, and n is the number of observations. Table 2 is a compilation of the Langmuir adsorption coefficients and corresponding R^2 values.

2.5. As-transport experiment

The As-transport study was 900 days in length and consisted of 35 irrigation events (13 irrigations without As, and 22 irrigations with As added at concentrations of about

Table 2
Temperature- and time-dependent Langmuir adsorption isotherm coefficients for Rocky Mountain Arsenal soil

Temperature (°C)	Time (days)	Langmuir coefficients			R^2
		K (1 kg^{-1})	b (mg kg^{-1})	x_0 (mg kg^{-1})	
25	1	1.70	68.7	0	0.989**
25	7	2.92	69.2	0	0.983**
25	14	3.98	66.3	0	0.970**
8	7	1.74	66.7	0	0.987**
40	7	6.13	66.0	0	0.970**

** Indicates significance at the 1% level of confidence.

5 mg l^{-1}). The initial 13 irrigations without As added were used to establish the tall-fescue root system to help develop soil structure and natural flow channels. The irrigation water used in the study was tap water from Riverside, CA, which was spiked with approximately 5 mg l^{-1} of As in the form of As$_2$O$_3$. Table 3 shows the chemical composition of the tap water prior to the addition of As. The irrigation amount and concentration of As for each irrigation is shown graphically in Fig. 3a and b. Sufficient irrigation water was applied to approximate an average leaching fraction (i.e., leaching fraction = drainage amount/irrigation amount) of 0.25. A leaching fraction of 0.25 would simulate a worst-case leaching scenario for the arid conditions found at RMA. Recharge in areas of natural vegetation and precipitation near RMA was estimated to be 10%. The fact that As was applied within the irrigation water, rather than incorporating it into the soil and leaching with As-free irrigation water, also simulates a worst-case scenario. This is because As in the irrigation water is free to preferentially move with the flow of irrigation water down cracks in the soil with less likelihood of removal from sorptive soil surfaces, thereby enhancing its downward transport.

Irrigation water was applied when the water content at 0.15 m was depleted to approximately 0.10 cm^3 cm^{-3}. After each irrigation, TDR measurements of water content were taken every 0.15 m to a depth of 1.35 m, and tensiometer readings were taken at depths of 0.15, 0.45, 0.75, 1.05, and 1.35 m. The time interval between measurements varied from as little as 10 min to several days based on the time since the irrigation had occurred. The primary objective was to be able to follow the wetting front and the redistribution of water as it moved through the soil column, and the subsequent removal of soil water by the process of evapotranspiration. The TDR measurements also provided another means of evaluating the degree of water flow along the wall of the column. The TDR measurements showed that the column was well drained with no depths remaining saturated for more than a few hours.

Daily soil temperatures were taken near noon at the same soil depths as TDR measurements. Soil temperatures were measured using buried thermistors. Duplicate thermistors were located at each depth: a thermistor in the center of the column and a thermistor half the distance from the center to the column wall. The temperatures were taken to determine gross seasonal fluctuations. Even though the column was not sufficiently insulated for the soil to simulate the fluctuation of natural soil temperature conditions over a depth of 1.35 m, the insulation was sufficient to eliminate the rapid

Table 3
Chemical composition of the water used to prepare the As-spiked irrigation water

Sample date (month-day-year)	Arsenic ($\mu g\ l^{-1}$)			Anions (meq l^{-1})					Cations (meq l^{-1})				SAR	EC_e (dS m^{-1})	pH_e	B (mg l^{-1})	Mo (mg l^{-1})
	As (III)	As (V)	Soluble As[a]	CO_3^-	HCO_3^-	Cl^-	SO_4^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}					
4-17-92	0.427	0.181	0.608	c	4.378	1.160	1.471	0.124	1.627	0.038	4.357	1.074	0.987	0.628	7.92	0.063	c
4-20-92	0.427	0.181	0.608	c	4.260	1.226	1.278	0.128	1.609	0.036	4.288	1.066	0.983	0.630	7.65	0.083	c
4-27-93	0.427	0.181	0.608	c	3.960	1.186	1.504	0.135	1.602	0.049	4.021	1.162	0.995	0.611	7.52	0.096	c
5-4-94	0.366	0.275	0.641	c	4.100	1.136	1.470	0.123	1.575	0.062	3.914	1.172	0.988	0.600	7.35	0.107	c
Average	0.412	0.205	0.616	c	4.175	1.177	1.431	0.128	1.603	0.046	4.145	1.119	0.988	0.617	7.61	0.087	c
Std. dev.[b]	0.031	0.047	0.017		0.183	0.039	0.103	0.005	0.022	0.012	0.211	0.056	0.005	0.014	0.24	0.019	

[a] Soluble As = As(III) + AS(V).
[b] Standard deviation.
[c] Undetectable.
Four water samples were analyzed at different times to determine temporal variation in the water composition.
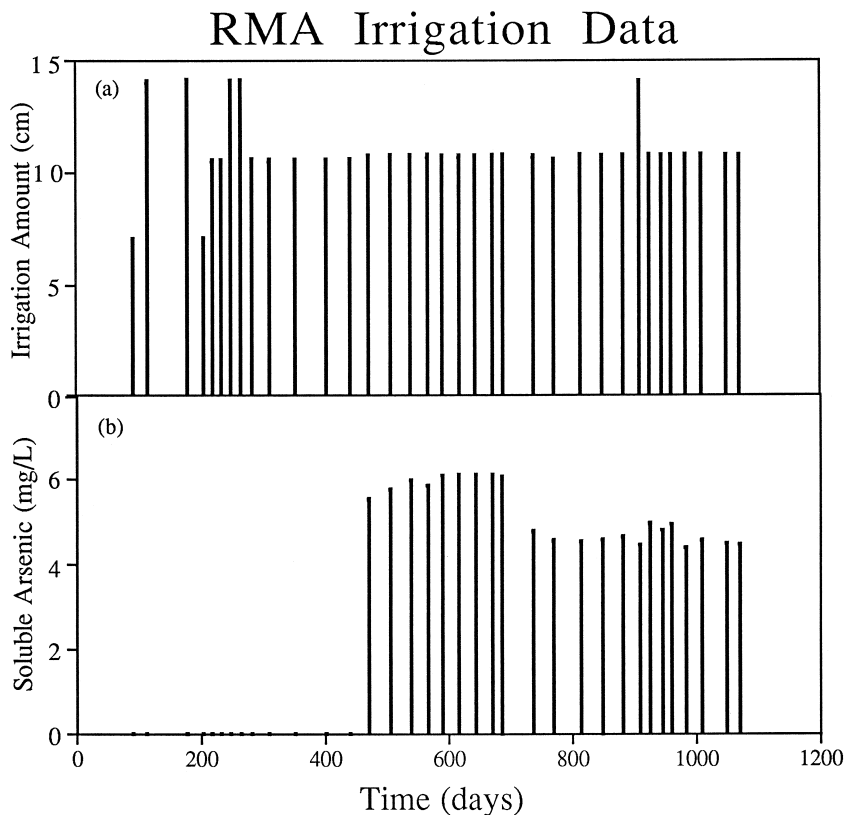
RMA Irrigation Data

Fig. 3. Graphs of weighing lysimeter column data including (a) irrigation water applied vs. time and (b) soluble arsenic concentration of irrigation water vs. time. Soluble As refers to As(III) + As(V).

fluctuations found in daily changes; consequently, the column showed seasonal fluctuations over all depths with very little lag time from one depth to the next, but rapid daily fluctuations were minimized. Seasonal soil temperatures showed the customary sinusoidal curve ranging from a minimum of 9°C to a maximum of 33°C.

Just prior to and again immediately after an irrigation, the weight of the soil column was measured with a load cell to determine the total evapotranspiration that had occurred between two successive irrigations. Total drainage water samples were taken prior to each irrigation. Drainage amount and As concentration of the drainage water were determined. Both arsenite [As(III)] and arsenate [As(V)] concentration were determined and the soluble As concentration was calculated as their sum.

Soil solution extracts were taken between 2–4 days after an irrigation when the soil at a particular depth had reached field capacity based on TDR measurements of water content taken over time. The field capacities at the depths of 0.15, 0.30, 0.45, 0.60, 0.75, 0.90, 1.05, and 1.35 m were approximately 0.20, 0.22, 0.26, 0.27, 0.28, 0.29, 0.30, and 0.33 cm^3 cm^{-3}, respectively. Continuous care was taken to assure that no soil solution samples were exposed to air in an effort to minimize any change in pH resulting from

exposure to CO_2 in the atmosphere: (1) soil solution extractors were used that minimized the exposure of the extracted soil solution to air (Suarez, 1986), (2) the soil solution samples were stored in containers with no air space present in the container, and (3) pH was measured with a micro-sample pH meter as soon as each solution sample was placed in a collection container and then measured again just prior to the sample's analysis.

2.6. Chemical analysis of soil solution extracts

The duplicate soil solution extracts at each instrumented depth (i.e., 0.15, 0.45, 0.75, 1.05, and 1.35 m) were analyzed for pH, EC, Cl^-, arsenite [As(III)], and arsenate [As(V)] for the entire duration of the study. For several irrigations prior to the addition of any As to the irrigation water, soil solution extracts were analyzed for pH, EC, anions (i.e., CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}), cations (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}), arsenite [As(III)], and arsenate [As(V)]. Soluble As was calculated as As(III) + As(V). These initial chemical analyses determined a baseline of significant soil chemical constituents.

Redox potential was measured, but only for soil core samples taken immediately after the termination of the As-transport experiment. The potentiometric method outlined by Hesse (1971) was used. Soil cores were taken at 0.3-m increments to a depth of 1.5 m. Fig. 4 shows the vertical Eh distribution, and associated As speciation and vertical pH distribution.
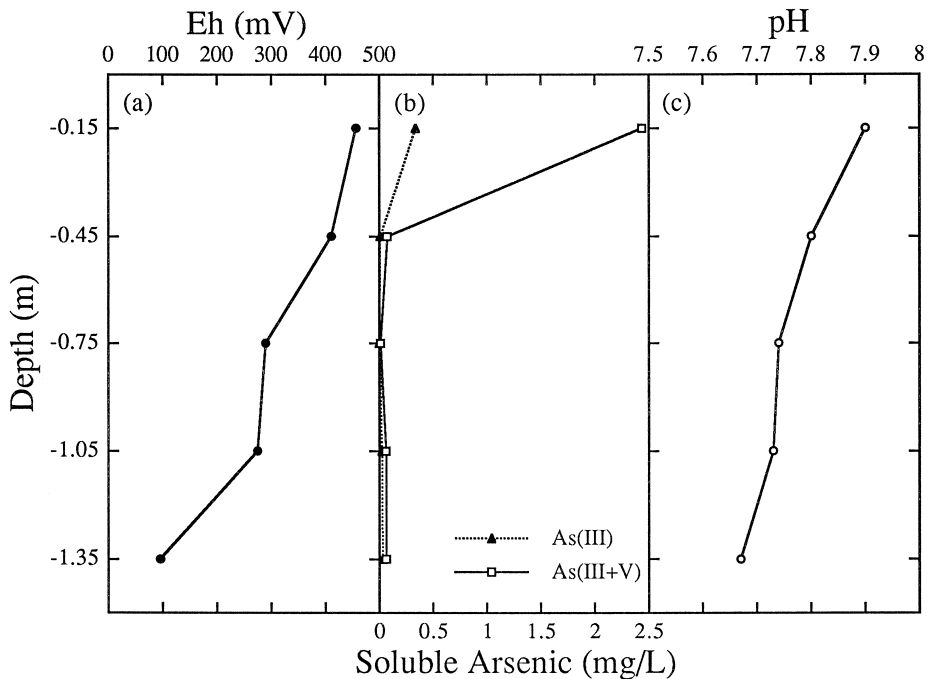

Fig. 4. (a) Vertical distribution of Eh, and associated (b) soluble As species, and 8 pH of soil samples taken after the termination of the As-transport experiment.

2.7. Chloride tracer and As mass-balance calculations

After the As-transport experiment had been completed, a chloride-tracer experiment was conducted to evaluate the effectiveness of the weighing lysimeter's design to minimize sidewall flow with annular rings (for details of this tracer experiment see Corwin and LeMert, 1999). A plug of chloride was applied to the soil surface of the weighing lysimeter to evaluate the preferential-flow dynamics. The drainage from the weighing lysimeter was monitored until an increase in chloride concentration was detected, indicating that the leading edge of the chloride-tracer plug had broken through the soil column. Further irrigation was immediately stopped and the soil in the weighing lysimeter was sampled to get a snapshot of the distribution of chloride through the lysimeter. Two sets of soil samples were taken at 0.15 m depth increments of soil for the entire 1.5 m length of the soil column (i.e., 10 depth increments of 0.15 m each). One set of samples consisted of a continuous 2.5-cm thick band of soil peripherally located at the soil–sidewall interface, subsequently referred to as the 'external soil samples.' A second set of samples consisted of composite soil cores taken in a concentric circle from within the center area of the weighing lysimeter, subsequently referred to as the 'internal soil samples.' When combined, these two sets of soil samples comprised nearly 20% of the total volume of soil in the column. These soil samples were analyzed for chloride concentration. A comparison of the chloride concentrations at each 0.15-cm depth increment for the set of internal and external samples showed that the internal and external chloride distributions corresponded well, suggesting that preferential sidewall flow was not significant.

The same internal and external soil samples were also analyzed for soil solution As. These measured soil solution As values were used with the Langmuir adsorption isotherm coefficients to estimate the partitioning of As in the soil and solution phases through the soil column. Knowing the measured As in the drainage, the measured As applied, and the estimated As in the soil column, a simple mass-balance calculation was used to determine unaccounted-for As.

3. Results and discussion

The high retention of As by the Ascalon sandy clay loam soil is reflected by the high values for the Langmuir affinity coefficient, K, and the adsorption maximum, b, in Table 2. Although the percentages of iron and aluminum oxides (see Table 1) are low within the range commonly found for soils of the USA (Robinson, 1914; Bear, 1953), sufficient iron and aluminum oxides are present to readily adsorb the level of As introduced into the column of soil. Fig. 5 substantiates the high affinity of Ascalon sandy clay loam soil for As. Nearly all the soil solution As is isolated at the surface of the column of soil. Little As is found in the soil solution at depths of 0.45 m and beyond, (Fig. 5b–e). Nevertheless, there is a detectable amount of As that moved through the entire column and into the drainage water (Figs. 5b–e and 6). The first irrigation with spiked As irrigation water occurred on day 470. Arsenic was detected at
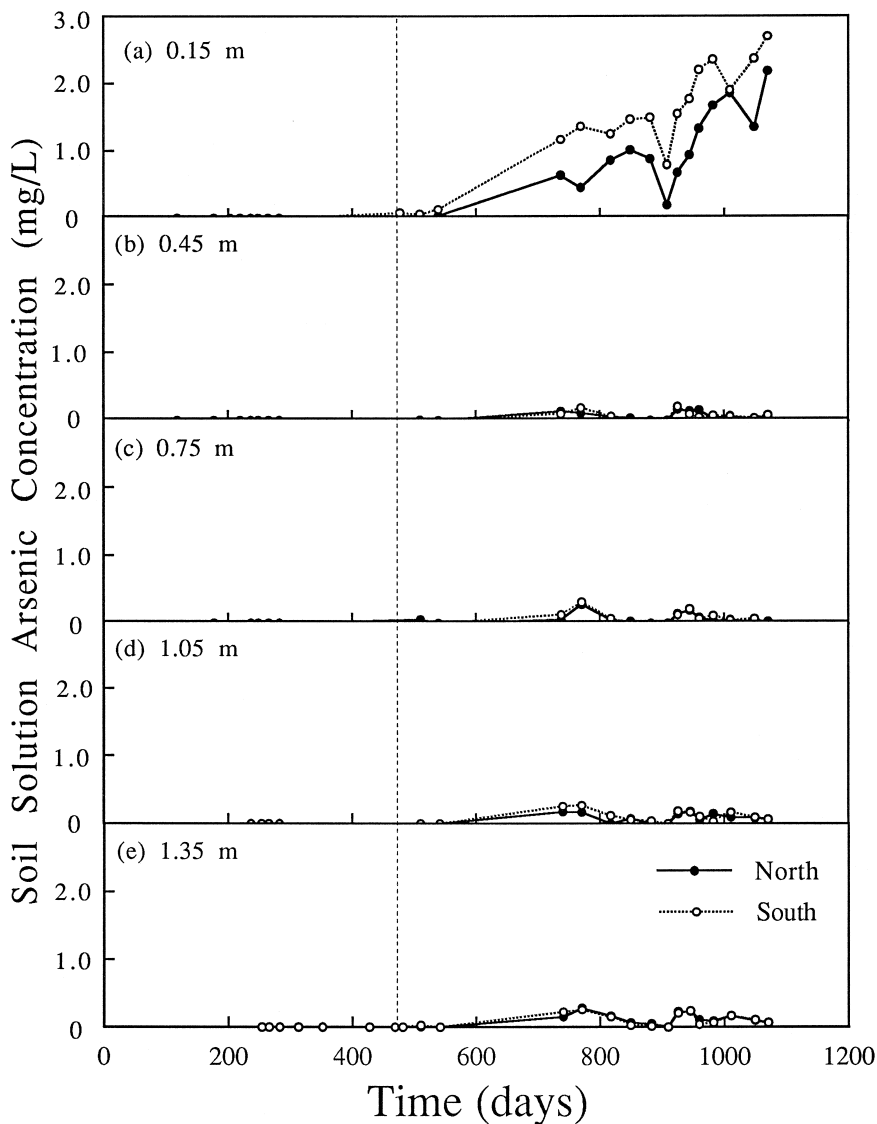
Fig. 5. Soil solution arsenic concentration at depths of (a) 0.15, (b) 0.45, (c) 0.75, (d) 1.05, and (e) 1.35 m over the duration of the experiment. Solid circle symbol represents soil solution samples extracted from the column's northern side, and the empty circle symbol represents soil solution samples extracted from the column's southern side. Soil solution As refers to As(III) + As(V). Vertical dashed line marks the time (day 470.4) when the first irrigation with spiked As occurred.

depths below 0.15 m on day 737. Unfortunately, soil solution extract samples were not obtained for irrigations made on days 616, 642, 670 and 687 due to vandalism that occurred on two separate occasions during this time period. Fortunately, drainage
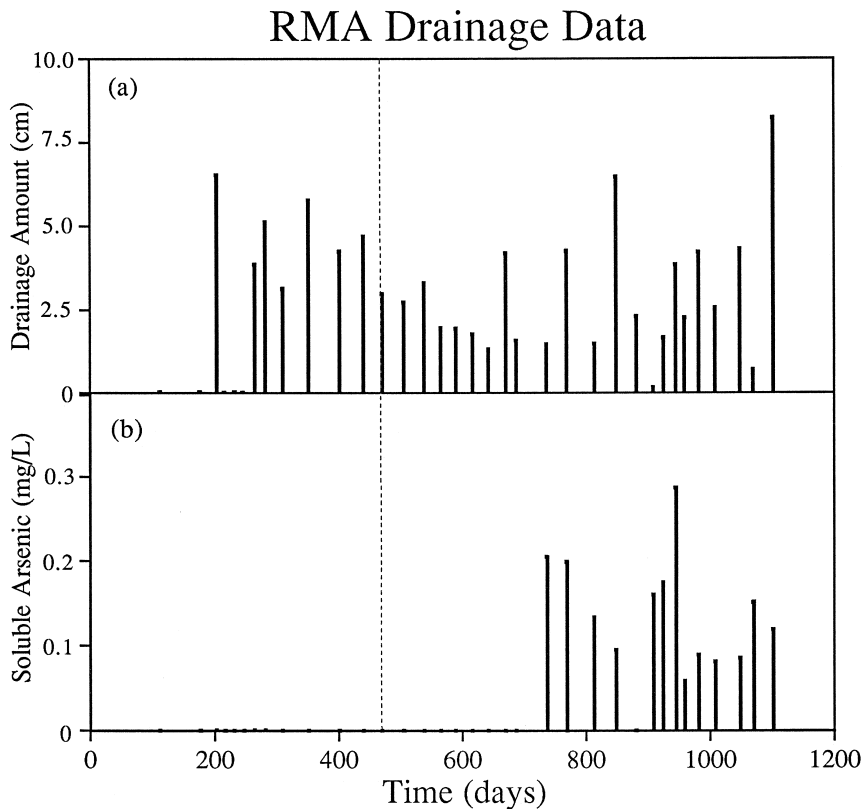
Fig. 6. Graphs of drainage data including (a) amount drained vs. time and (b) soluble arsenic concentration of drainage water vs. time. Soluble As refers to As(III) + As(V). Vertical dashed line marks the time (day 470.4) when the first irrigation with spiked As occurred.

samples associated with irrigations for those times were available. The first detection of the presence of As in the drainage water occurred on day 737, which confirmed that a small amount of As had moved through the entire soil column from day 470 to day 737.

In general, the high sorptive capacity of soil for As as cited in the literature (Jacobs et al., 1970; Elkhatib et al., 1984; Sakata, 1987; Masscheleyn et al., 1991) should retain As near the soil surface. In the specific case of Ascalon sandy clay loam, this should also hold true due to the high Langmuir adsorption coefficients. However, the unexpected presence of low levels of As in the lower portions of the soil profile and in the drainage water 267 days after the introduction of As into the soil column suggests otherwise. The 267-day travel time indicates that the movement of As had been retarded, but As is still capable of moving through the column of soil even though calculations with the Langmuir adsorption parameters suggest that all the As should have been retained in the upper 0.30 m of soil.

A variety of interacting chemical and physical factors are potentially responsible for the small portion (0.87%) of the total applied As traveling through the soil column,

including pH, redox potential, and preferential flowpaths. The experimental design could not unambiguously ascribe the mechanism of As mobility to any single factor. It is likely that all factors had some degree of influence.

3.1. pH effects and redox potential distribution

Because pH has such a significant influence upon the sorption of As, the pH of the irrigation water, the soil column, and the drainage water were closely monitored to observe any fluctuations in pH that might influence As mobility. Fig. 7 shows the pH of the irrigation and drainage waters. For almost the entire duration of the experiment, the pH of the drainage water fluctuated between 7.5 to 8.0. In contrast, there were several instances when the pH of the irrigation water exceeded 8.0. However, because of the buffering capacity of the soil, the wide ranging fluctuations in the pH of the irrigation water caused modest pH fluctuations in the soil (see Fig. 8). The pH through the soil column tended to be generally uniform with depth, and averaged between 7.5 and 7.6.

Subtle fluctuations in soil solution pH (Fig. 8) following the first addition of As to the irrigation water on day 470, showed no clear correlation with soil solution As
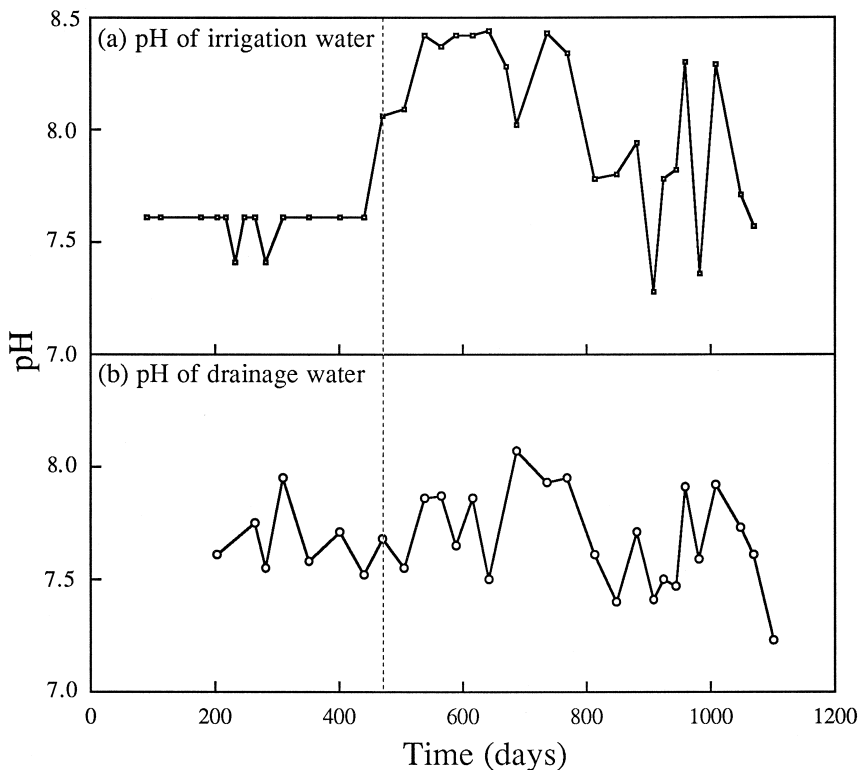

Fig. 7. Graphs of pH data including (a) pH of irrigation water and (b) pH of drainage water. Vertical dashed line marks the time (day 470.4) when the first irrigation with spiked As occurred.
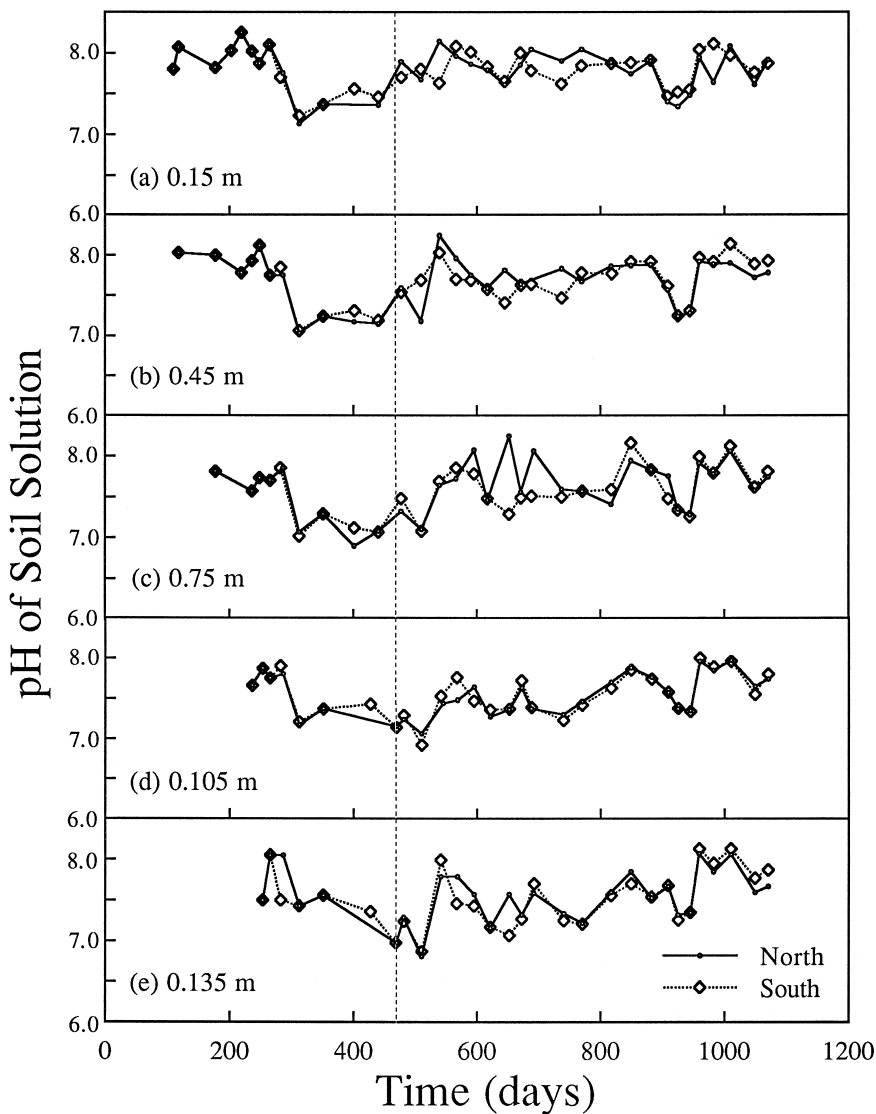
Fig. 8. Soil solution pHs taken at depths of (a) 0.15, (b) 0.45, (c) 0.75, (d) 1.05, and (e) 1.35 m over the duration of the experiment. Vertical dashed line marks the time (day 470.4) when the first irrigation with spiked As occurred.

concentrations (Fig. 5) that would indicate an effect of soil solution pH on As mobility except after day 880. After day 880, a decrease in soil solution pH through the entire soil column to a minimum reached near day 925 followed by an increase in pH corresponded closely to an observed decrease in soil solution As concentration followed by an increase in As concentration. This is particularly apparent for the 0.15-m depth, but is also observable below 0.15 m (see Figs. 5 and 8).

Under natural conditions, Ascalon soil is a well-drained soil. Fig. 4 shows the vertical distribution of Eh and pH, and associated soluble As species. The range of Eh lies between 100 and 450 mV with a decrease in Eh with depth. The Eh values and distribution reflect that the column of Ascalon soil was well drained with the majority of soluble As existing as the less mobile arsenate. Under the pH and redox conditions existing in the soil column, and from the vertical distribution graph of As speciation (Fig. 4), arsenate is the overwhelmingly dominant As species near the soil surface. Arsenite becomes a greater proportion of the soluble As with increased depth. In the top 0.3 m arsenite comprises 14% of the soluble As, which steadily increases until at the bottom of the column arsenite is slightly more than 50% of the soluble As.

3.2. Preferential flow

A semi-quantitative argument can be developed that points to preferential flow as a significant factor in the movement of As through the soil column. Using the Langmuir adsorption isotherm coefficients obtained from the batch adsorption experiments (i.e., K = Langmuir affinity coefficient = 2.92 l kg^{-1}, b = Langmuir adsorption maximum = 69.2 mg kg^{-1} at 25°C and equilibrated for 7 days) and the measured soil solution As for internal and external soil samples taken at 0.15-m depth increments, calculations showed that approximately 87% of the total As added to the soil column remained in the top 0.30 m of soil with less than 5% of the total applied As residing deeper than 0.30 m. Presumably, the 5% of the total applied As that resided deeper than 0.30 m was associated with preferential flowpaths. This is corroborated with solute transport model simulations described later. The drainage water was measured as containing 0.87% of the total applied As, leaving 7% of the applied As unaccountable.

The mass-balance calculations showed that the sorbed As between 0.3 and 1.5 m was unevenly and erratically distributed with depth, and that As was not concentrated in the upper portion (i.e., 0.3–0.6 m) of this section of the soil profile. The vertical distribution of As below 0.3 m is noteworthy because it does not follow the smooth, gradually decreasing distribution characteristic of chloride in the tracer study. Rather, the As distribution was erratic with a 'hot spot' occurring at the 0.60 to 0.75 m depth increment. Just under half of the sorbed As (i.e., about 2% of the total applied As) found below 0.3 m was inexplicably located between 0.60 and 0.75 m. This would either suggest that an increased density of preferential flowpaths existed at the 0.60 to 0.75 m depth or that a retardation of the movement of As via preferential flowpaths was occurring due to adsorption.

The trace element transport model TETrans (Corwin et al., 1991) was applied to determine the potential significance of preferential flow. TETrans is a transient-state model of solute through the vadose zone that has been shown to account for preferential flow (Corwin et al., 1991, 1992, 1999) and for plant–soil–water interactions (mass transport, adsorption–desorption, rooting depth, plant water uptake distribution, ET influences on soil solution concentration, etc.). Simulations with TETrans without accounting for any preferential flow showed that 100% of the applied As was isolated in the top 0.75 m. However, when preferential flow was considered and a representative

bypass coefficient (i.e., a preferential-flow parameter in the TETrans model) of 0.5 was used (Corwin et al., 1991), then 0.59% of the applied As moved beyond 1.5 m, which compares favorably with the 0.87% measured in this study. The TETrans simulations accounted for preferential-flow considerations, but did not account for redox potential effects and no pH-affected adsorption data was available. Presumably, the discrepancy between simulated and measured As draining from the soil column (i.e., 0.28% of the total applied As) could be attributed to chemical factors (pH and redox effects) influencing As mobility. The model was unable to closely simulate the erratic distribution of As below 0.3 m as determined from the mass-balance calculations, specifically the increased As measured at 0.60–0.75 m, which was an anomaly.

The missing soil solution data for As from days 616 to 687 makes it difficult to determine the rate of movement of As through the soil column. In addition, there is a problem with using the data presented in Fig. 5 to provide additional insight into the preferential-flow dynamics. Even though there were two soil solution extractors at each depth, there is no way of knowing whether any preferential flowpaths crossed the sphere of extraction of any of the soil solution extractors. The presence of As in the drainage water, when adsorption studies indicate that As should have remained near the soil surface under the pH and redox conditions present, is the most convincing argument for the occurrence of preferential flow. The fact that it took 267 days for the As to appear in drain water suggests that adsorption was retarding the movement of As while preferential flow was occurring. Perhaps adsorption was occurring continuously along the preferential-flow channel walls and/or the preferential flowpaths may have been discontinuous.

Discontinuous preferential flowpaths would retard the movement of As because it would take time to fill As retention sites on the soil interrupting the preferential flowpath, whereas continuous preferential flowpaths would probably show a more rapid, possibly even immediate, movement of small amounts of As from the soil surface to the bottom of the soil column due to the uninterrupted flow of water and transport of solute. Pinpointing where a discontinuity in preferential flow may have occurred is inconclusive. The mass-balance calculations would suggest 0.60–0.75 m as a likely location. Coincidentally, the layer of soil from 0 to 0.75 m corresponds roughly to the depth increment over which root activity was the greatest, although some minor root activity could be seen to occasionally occur at depths up to 1.35 m.

In a prepared soil column of homogenous soil, preferential flow is most likely due to cracks and fissures resulting from shrinkage, and to root channels. Based on the observed data, possible scenarios are that preferential flow occurred in cracks and along root channels with either a discontinuity in the preferential flowpaths or an increase in the density of preferential flowpaths at 0.60–0.75 m. Though speculative, these scenarios would help to explain the As 'hot spot' and the retarded movement of As.

A factor not fully considered in this study was that of the direct and indirect influences of the plant on As mobility. Except for evapotranspiration, plant water uptake distribution, biomass, and rooting depth, no other measurement of the plant was made. The fact that 7% of the applied As could not be accounted reflects on either the inaccuracy of using the batch adsorption study data in the mass-balance calculation and/or the phytoaccumulation of As. Aside from phytoaccumulation, possible effects of

the plant include evapotranspiration effects on soil solution As concentration (this was accounted for in the TETrans simulation), effects on As speciation through influences on soil pH and redox potential, and as previously mentioned the creation of preferential flowpaths.

4. Summary and conclusions

The primary objective of this study was to determine the mobility of As in a soil similar to the predominant soil associated with As contamination on the Rocky Mountain Arsenal to assess the potential vulnerability of groundwater to As contamination. Once As was found to appear in the drainage water of the weighing lysimeter, it became of interest to try to understand how very small (parts per billion), but detectable, concentrations of As were able to move beyond the root zone based on the collected physical, chemical, and biological data.

In all likelihood the chemical influences of pH and redox potential, the physical influences of preferential flow, and the direct and indirect influences of the plant root system contributed to the observed mobility of As through the Ascalon sandy clay loam soil. However, the appearance of As in the drainage water, when adsorption studies would suggest that no As should leave the upper portion of the soil profile under the existing pH and redox conditions, is an anomaly. This anomalous behavior points to preferential flowpaths as the predominant cause, which is supported by model simulations with TETrans. These preferential flowpaths may exist as cracks and/or channels created from root activity. The As found at depths below 0.3 m was presumably soil solution As present in preferential-flow channels and sorbed As present on soil associated with the preferential-flow channels. Based on the mass-balance calculations, the distribution of soil solution As over time and depth, and the TETrans simulations, the 0.87% of the total applied As that was measured in the drainage water moved through the soil profile via preferential flowpaths with chemical influences on mobility due to pH and redox potential effects.

Even though the lack of plant data (i.e., phytoaccumulation and plant influences on the pH and redox potential of the rhizosphere) did not compromise the primary objective, a full understanding of the mechanism of As mobility requires a detailed study of the direct and indirect influences of the plant. Simulations with TETrans did account for plant–water–soil interactions, but no data had been collected to measure phytoaccumulation or subtle chemical changes in the rhizosphere due to plant-root activity. For these reasons, a full understanding of the influence of the plant on the fate and movement of As was not possible.

This As-mobility study was based on a number of experimental design assumptions that were imposed to render a slightly liberal estimate of the mobility of As, thereby favoring health and safety concerns. The limited, but perceptible, mobility of As through the root zone reaffirms the proposed remediation efforts at Rocky Mountain Arsenal specifying the precautionary construction of a 4-ft cap with a biota barrier as fill for the excavation of the top 5 ft of soil underlying the South Plants Processing Area. The cap

should act as a barrier to minimize water flow that might transport residual levels of As into the groundwater via preferential channels.

Acknowledgements

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