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Elevated naturally occurring arsenic in a semiarid oxidizing system, Southern High Plains aquifer, Texas, USA

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ABSTRACT

High groundwater As concentrations in oxidizing systems are generally associated with As adsorption onto hydrous metal (Al, Fe or Mn) oxides and mobilization with increased pH. The objective of this study was to evaluate the distribution, sources and mobilization mechanisms of As in the Southern High Plains (SHP) aquifer, Texas, relative to those in other semiarid, oxidizing systems. Elevated groundwater As levels are widespread in the southern part of the SHP (SHP-S) aquifer, with 47% of wells exceeding the current EPA maximum contaminant level (MCL) of 10 µg/L (range 0.3–164 µg/L), whereas As levels are much lower in the north (SHP-N: 9% ≥ As MCL of 10 µg/L; range 0.2–43 µg/L). The sharp contrast in As levels between the north and south coincides with a change in total dissolved solids (TDS) from 395 mg/L (median north) to 885 mg/L (median south). Arsenic is present as arsenate (As V) in this oxidizing system and is correlated with groundwater TDS (Spearman's $\rho = 0.57$). The most likely current source of As is sorbed As onto hydrous metal oxides based on correlations between As and other oxyanion-forming elements (V, $\rho = 0.88$; Se, $\rho = 0.54$; B, $\rho = 0.51$ and Mo, $\rho = 0.46$). This source is similar to that in other oxidizing systems and constitutes a secondary source; the most likely primary source being volcanic ashes in the SHP aquifer or original source rocks in the Rockies, based on co-occurrence of As and F ($\rho = 0.56$), oxyanion-forming elements and SiO₂ ($\rho = 0.41$), which are found in volcanic ashes. High groundwater As concentrations in some semiarid oxidizing systems are related to high evaporation. Although correlation of As with TDS in the SHP aquifer may suggest evaporative concentration, unenriched stable isotopes ($\delta^2\text{H}$: –65 to –27; $\delta^{18}\text{O}$: –9.1 to –4.2) in the SHP aquifer do not support evaporation. High TDS in the SHP aquifer is most likely related to upward movement of saline water from the underlying Triassic Dockum aquifer. Mobilization of As in other semiarid oxidizing systems is caused by increased pH; however, pH in the SHP aquifer is near neutral (10–90 percentiles, 7.0–7.6). Although many processes, such as competitive desorption with SiO₂, VO₄, or PO₄, could be responsible for local mobilization of As in the SHP aquifer, the most plausible explanation for the regional As distribution and correlation with TDS is the counterion effect caused by a change from Ca- to Na-rich, water as shown by the high correlation between As and Na/(Ca)^{0.5} ratios ($\rho = 0.57$). This change in chemistry is related to mixing with saline water that moves upward from the underlying Dockum aquifer. This counterion effect may mobilize other anions and oxyanion-forming elements that are correlated with As (F, V, Se, B, Mo and SiO₂). Competition among the oxyanions for sorption sites may enhance As mobilization. The SHP case study has similar As sources to those of other semiarid, oxidizing systems (original volcanic ash source followed by sorption onto hydrous metal oxides) but contrasts with these systems by showing lack of evaporative concentration and pH mobilization of As but counterion mobilization of As instead in the SHP-S aquifer.

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1. Introduction

Elevated groundwater As levels are a widespread problem in the US and globally (Nordstrom, 2002; Smedley and Kinniburgh, 2002; Welch and Stollenwerk, 2003; Mukherjee et al., 2008). Occurrence of high levels of groundwater As in areas with near average total As levels in source rocks indicates that As mobiliza-

tion is often a more critical issue than source (Smedley and Kinniburgh, 2002). Important factors for generating high As concentrations in groundwater are (1) a source of As, (2) a mobilization mechanism for releasing As into groundwater, and (3) limited flushing of groundwater. Smedley and Kinniburgh (2002) identified several factors important in defining aquifer vulnerability to elevated As concentrations. Typical environments containing high As groundwater include both (1) low temperature (1a – nonmining; 1b – mining) and (2) high temperature (geothermal) settings. High As concentrations are most widespread in low

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temperature, nonmining areas that are characterized by young aquifers (Quaternary, ≤ 1.8 my), low hydraulic gradients, and low flow rates. Mobilization mechanisms in low temperature, non-mining areas include (1) desorption from and dissolution of Fe oxides under reducing conditions and (2) desorption from Fe oxides and mineral weathering and evaporation under oxidizing conditions (Smedley and Kinniburgh, 2002). The conceptual model for As in oxidizing systems is typified by that in aquifers in Argentina characterized by As influx from dissolution of volcanic glass in volcanic ash, adsorption of As onto hydrous Fe or Al oxides, followed by mobilization related to increased pH (8–9) associated with mineral weathering (Smedley et al., 2005; Bhattacharya et al., 2006).

Elevated groundwater As concentrations were identified previously in the Southern High Plains (SHP) aquifer in Texas by Nativ and Smith (1987), Nativ (1988), and Hudak (2000). This region would be classified as low temperature, non-mining according to Smedley and Kinniburgh (2002). Groundwater is oxidizing based on concentrations of dissolved O_2 (DO), NO_3 and SO_4 . Previous studies attribute high As concentrations to an anthropogenic source related to As application as a defoliant on cotton because of collocation of elevated groundwater As concentrations and cotton production, higher groundwater As concentrations in areas of shallower water tables, and association with other agricultural contaminants (e.g. NO_3) (Nativ, 1988; Hudak, 2000). However, more recent studies, that include detailed unsaturated zone drilling, sampling and analyses, indicate that water-extractable As from pesticide application is restricted to the shallow subsurface (≤ 1 m) and is associated with high PO_4 concentrations from fertilizer application (Reedy et al., 2007). High As concentrations at depths ≥ 1 m beneath natural rangeland and cropland areas were attributed to a geologic source because pesticides were never applied in natural rangeland settings and there was no associated PO_4 at depth beneath natural rangeland and cropland areas.

The objectives of this study were to evaluate the distribution of As in the SHP aquifer, determine potential sources, and assess mobilization mechanisms relative to previous studies in semiarid, oxidizing systems. This study is challenging because of the number of potential sources of As in the SHP aquifer (saline lakes, volcanic ashes, hydrous Al, Fe or Mn oxides, collectively termed hydrous metal oxides) and the near neutral pH values, which eliminate the potential for As mobilization from hydrous metal oxides caused by increased pH found in most previously studied semiarid oxidizing systems (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006). The study provides a unique opportunity to evaluate high groundwater As concentrations because of the existence of large databases on groundwater chemistry from the Texas Water Development Board (TWDB) and other sources, detailed groundwater isotopic analyses (Nativ, 1988), extensive information on geologic setting (including distribution of volcanic ashes), intensive studies of groundwater recharge (Wood and Sanford, 1995a; Scanlon and Goldsmith, 1997), comprehensive evaluation of unsaturated zone flow and chemical characteristics (Scanlon et al., 2007), and previous groundwater models that provide a hydrogeologic framework to understand flow and transport in the system (Blandford et al., 2003, 2009; Ewing et al., 2009).

2. Materials and methods

2.1. Southern High Plains aquifer

The main geologic unit that makes up the SHP aquifer is the Ogallala Formation (Fm.), which is late Tertiary in age (late Miocene–Pliocene, ~ 4 –12 Ma) (Supporting Information, Fig. S1) (Nativ, 1988). The Ogallala Fm. consists of eolian loess and thin sand sheets with numerous paleosols recording periods of pedogenesis

(Gustavson and Holliday, 1999). Grain size generally ranges from fine sand to coarse silt and decreases from west to east. A resistant calcite layer up to several meters thick, locally termed caprock, is present at or near the top of the Ogallala Fm. Buried argillic horizons are common and are characterized by illuvial clay and pedogenic structure. The Ogallala Fm. is overlain by Quaternary-age (Pleistocene–Holocene, ≤ 1.4 Ma) eolian, fluvial and lacustrine sediments of the Blackwater Draw Fm. (Holliday, 1989) and locally underlain by lower Cretaceous sediments. The Ogallala and Blackwater Draw Fms. together compose the High Plains aquifer. The top of the Cretaceous is marked by an erosional surface that represents the end of the Laramide orogeny. The paleotopography on the Cretaceous includes paleovalleys where the Cretaceous sediments were eroded and paleouplands. The Ogallala Fm. was deposited on this topographic surface and consists of eolian sands in paleouplands and coarse fluvial sandstones and conglomerates interspersed with and overlain by eolian sands in intervening paleovalleys (Gustavson and Holliday, 1985). These paleovalleys and paleouplands can generally be seen in variations in the saturated thickness of the aquifer (Supporting Information, Fig. S2). The SHP aquifer is unconfined throughout its extent and groundwater flows from NW to SE, parallel to the topographic gradient (Supporting Information, Fig. S1).

The study area is arbitrarily subdivided into two regions by an interpolated contour line that represents the 500 mg/L TDS concentration in the SHP aquifer. The contour extends across the aquifer in Texas and defines the boundary between the SHP north (SHP-N) and south (SHP-S) regions (Fig. 1). The SHP-N generally corresponds to a paleovalley area where the SHP aquifer is thicker (median predevelopment saturated thickness 45 m), whereas the SHP-S corresponds to a paleoupland area where the SHP aquifer is much thinner (median predevelopment saturated thickness 16 m) and sediments are finer grained. The boundary between the north and south regions of the SHP aquifer generally corresponds to the subcrop limit of Cretaceous sediments (Supporting Information, Fig. S3). The Cretaceous sequence includes two main aquifer units: the Antlers Sandstone (~ 15 m thick) at the base and the Edwards Limestone (~ 30 m thick), with a confining limestone in between and a shale (Kiamichi Shale) on top in some regions. The term Edwards Trinity High Plains (ETHP) aquifer is generally used to describe these units (Ashworth and Hopkins, 1995).

The Ogallala Fm. is directly underlain by the Triassic Dockum Group in the SHP-N region and in the extreme south region, whereas the Cretaceous ETHP is found in the south central

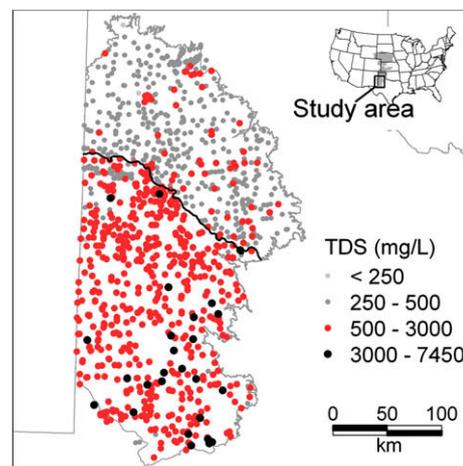


Fig. 1. Distribution of total dissolved solids (TDS) concentrations in the Southern High Plains aquifer ($n = 1220$). Dark line represents the 500 mg/L TDS contour that defines the regional north/south water quality boundary.

region of the SHP. The Dockum Group is exposed along the margins of the study area (~150 m thick) (Dutton and Simpkins, 1986). The sediments of the upper Dockum consist of red mudstones (termed red beds) that generally form an aquitard, except on the eastern edge of the High Plains where they are absent and where the lower Dockum subcrops. Some of the units of the lower Dockum (e.g. Santa Rosa Sandstone) are aquifers. The sediments of the Dockum were deposited in a continental fluvio-lacustrine environment that included streams, deltas, lakes, and mud flats (McGowen et al., 1977) under alternating arid and humid climatic conditions.

Climate in the study area is semiarid, with mean annual precipitation ranging from 376 mm in the south (Midland, 1931–2005) to 501 mm in the north (Amarillo, 1947–2005). Recharge occurs primarily through ephemeral lakes or playas with little or no recharge in interplaya settings beneath natural ecosystems (Wood and Sanford, 1995a). Cultivation increased recharge from 0 beneath native grasslands and shrublands to a median value of 24 mm/a beneath rain-fed cropland (Scanlon et al., 2005). Irrigated agriculture has resulted in large-scale depletion of groundwater resources, particularly in the SHP-N region, with groundwater tables decreasing by a mean of 30 m over an 11,000 km² area in a paleovalley region where the predevelopment saturated thickness is high (1950–2003). Saline lakes (35) are mostly restricted to the southern portion of the study area and represent groundwater discharge areas where the Ogallala Fm. has been eroded locally and Cretaceous sediments crop out (Supporting Information, Figs. S1 and S3) (Wood and Jones, 1990; Wood and Sanford, 1995b).

2.2. Data sources and analysis

Groundwater sample analyses for 1522 wells were used in this study, including wells completed in the SHP (1220 wells), Cretaceous (88 wells), and Dockum (214 wells) aquifers. The primary source of these data (SHP, 1020 wells; Cretaceous, 81 wells; Dockum, 185 wells) is the Texas Water Development Board (TWDB) groundwater database (www.twdb.state.tx.us). Additional data include analyses from a recent study on groundwater perchlorate concentrations in the Southern High Plains (Rajagopalan et al., 2006) (SHP, 171 wells; Cretaceous, 7 wells; Dockum, 29 wells). Another study conducted by the USGS involved drilling and sampling 29 wells in the SHP ~1.5 m below the water table with ~3 m screened sections (Stanton and Fahlquist, 2006). Analyses from all sources include major ion, trace element and DO concentrations and pH, with varying degrees of completeness for individual samples (Table 1). Information on well depth and groundwater levels is also available from these databases. Because there were very few analyses of U, information on U was obtained from the National Uranium Resource Evaluation (NURE) database and included 665 analyses of groundwater samples collected between 1976 and 1979 (<http://pubs.usgs.gov/of/1997/ofr-97-0492/>). The data are restricted to the eastern part of the SHP aquifer. Information on As concentrations in multilevel wells in Bailey, Gaines and Martin counties was obtained from water samples collected for this study to evaluate stratification of groundwater As concentrations.

Table 1

Median values for physical and chemical parameters for wells sampled from 1996 through 2008 in the SHP region.

Parameter	Units	SHP		Dockum		SHP-N		Dockum-N		SHP-S		Cretaceous		Dockum-S	
		#	Med.	#	Med.	#	Med.	#	Med.	#	Med.	#	Med.	#	Med.
Well depth	m	982	67	202	244	489	93	112	129	493	50	24	33	90	460
pH		1158	7.3	176	7.9	506	7.4	106	8.0	652	7.2	72	7.6	70	7.8
DO	mg/L	277	6.1	28	4.9	98	5.7	8	0.14	179	6.4	44	7.1	20	5.8
TDS	mg/L	1220	543	206	1050	569	395	113	620	651	885	79	1280	93	3010
SiO ₂	mg/L	1049	53	181	12	493	49	102	14	556	56	63	46	79	12
Ca	mg/L	1220	57	211	37	569	43	119	18	651	87	82	94	92	69
Mg	mg/L	1220	40	211	15	569	33	119	11	651	68	87	93	92	26
Na	mg/L	1220	56	206	296	569	37	115	199	651	97	78	283	91	1080
K	mg/L	1220	7.8	154	6.0	569	6.8	92	4.3	651	11	33	7.5	62	8.3
HCO ₃	mg/L	1142	294	209	361	506	303	117	345	636	285	79	320	92	375
Cl	mg/L	1220	61	213	163	569	21	119	42	651	167	88	293	94	615
SO ₄	mg/L	1220	77	213	224	569	34	119	93	651	205	88	424	94	987
F	mg/L	1220	2.6	186	2.0	569	2.3	110	2.0	651	3.0	73	4.1	76	2.1
NO ₃	mg/L	1220	9.5	175	0.4	569	6.2	101	1.8	651	16	73	7.4	74	0.1
As	µg/L	1220	6.3	73	2.8	569	4.1	52	2.3	651	9.4	16	6.6	21	3.6
V	µg/L	995	30	70	4.0	438	21	49	9.2	557	44	16	38	21	<20
Mo	µg/L	995	4.2	72	9.1	438	3.6	49	6.7	557	4.8	16	6.1	23	32
Se	µg/L	995	9.6	76	3.0	438	5.3	52	2.0	557	18	16	11	24	13
B	µg/L	995	259	82	769	438	201	56	340	557	332	21	632	26	1200
Fe	µg/L	995	<50	113	49	438	<50	69	38	557	<50	59	25	44	240
Mn	µg/L	995	<1	102	5.2	438	<1	69	3.9	557	<1	50	3.8	33	24
NO ₂	µg/L	341	20	47	13	97	16	15	23	244	23	59	33	32	13
PO ₄	µg/L	106	<1	14	31	65	<1	6	31	41	17	15	184	8	<31
U ^a	µg/L	665	9.6		398	8.0				267	14				
Na/Ca	M/M	1220	1.7	204	40	569	1.5	114	22	651	1.9	78	6.5	90	59
Na/(Ca) ^{0.5}	M/M	1220	2.0	204	32	569	1.6	114	14	651	3.0	78	9.6	90	72
Calcite	SI	1050	-0.11		465	-0.10				585	-0.10				
Dolomite	SI	1050	-0.07		465	-0.07				585	-0.07				
Gypsum	SI	1050	-1.83		465	-2.30				585	-1.42				
Am. silica	SI	898	-0.29		395	-0.35				503	-0.27				

Median values are shown for the entire Southern High Plains aquifer (SHP) and for the northern and southern regions delineated by the 500 mg/L TDS line (SHP-N and SHP-S). SI: saturation index. The Cretaceous aquifers are only found in the southern region (SHP-S). Parameters for the Triassic Dockum aquifer are also shown for the corresponding SHP regions.

^a Uranium data obtained from the National Uranium Resource Evaluation (NURE) database (<http://pubs.usgs.gov/of/1997/ofr-97-0492/>). Am. silica represents amorphous silica.

Data for the SHP aquifer from the TWDB database were screened for this study to include only the most recent groundwater sample collected for a given well from 1996 through 2008 and for which there was an As analysis. Samples from the SHP aquifer contained 48 As concentrations (<5%) below detection limits ranging from 1 to 2 $\mu\text{g/L}$, with 40 of those nondetects in the SHP-N region. Data for F, NO_3 , NO_2 , PO_4 , and trace elements (V, Mo, Se, B, Fe, and Mn) include varying numbers of nondetect values. Different laboratories were used for analysis at different times, although analytical methods were generally consistent among laboratories. Arsenic and trace metals were determined at all laboratories using inductively coupled plasma mass spectrometry (ICPMS) following EPA method 200.7. Most (77%) major cation analyses were performed by ICPMS following EPA method 200.8, with the remaining following EPA method 200.7. All major anions were determined using ion chromatography (IC) following EPA method 300.

Correlations between different ions were used to assess sources and mobilization of As in the SHP aquifer. Preliminary analysis indicated that concentrations of many of the ions are not normally or log-normally distributed. Therefore, Pearson's correlation coefficient (r) could not be applied because it requires the data to be normally distributed (i.e. it is parametric). Spearman's rank correlation coefficient (ρ) was used instead because it does not require any assumptions regarding distributions (i.e. it is nonparametric) (Helsel and Hirsch, 1992). Because ρ can be properly applied only to data with a single detection limit level, nondetects in data sets containing multiple nondetect levels were first adjusted to equal the highest nondetect level. Where present, nondetects generally account for <5% of data, with the exceptions of Se, Fe and Mn (Table 1). For further comparison, Kendall's τ_b , another nonparametric correlation coefficient capable of incorporating multiple nondetect levels, was also calculated using the (unadjusted) data (Helsel, 2005). Median values for constituent distributions that contain nondetects were calculated using the Kaplan–Meier method (Helsel, 2005). The significance of ρ was determined using a two-tailed Student's t -test with $n - 2$ degrees of freedom. The significance of τ_b was determined using the Z test statistic (Helsel, 2005).

2.3. Methods

Groundwater samples from three multilevel wells, one each in Bailey, Gaines and Martin counties, were analyzed for As and trace metals using ICPMS (Agilent 7500 CE) (Supporting Information, Table S1, Fig. S4). A total of 20 samples were collected from the SHP

aquifer for As(III/IV) redox speciation (Table S2). Initially, 10 groundwater samples (8 mL) were collected, filtered, preserved with sufficient EDTA to achieve $\text{pH} < 2$ and stored in opaque bottles according to methods described in McCleskey et al. (2004). Because of possible impacts of the sample preservation technique on the analyses, another 10 samples were collected using a similar protocol, with three replicates using either no preservative, HCl or EDTA. The latter samples included three wells that were sampled during the initial round of sampling. The speciation analyses were conducted at the USGS Boulder Laboratory in Denver (Colorado) using the technique described in McCleskey et al. (2004). Samples were analyzed using Hydride-Generation Atomic-Absorption Spectrometry. These samples were also analyzed for PO_4 at the USGS.

Water samples collected from eight saline lakes were analyzed for cations using ICPMS and anions using IC (Dionex ICS 2000) (Supporting Information, Table S3). A total of 123 geophysical well logs, including gamma ray logs, mostly from the SHP-S region (17 counties) were examined to determine the presence of elevated gamma ray values that would indicate volcanic ashes (Supporting Information).

3. Results and discussion

3.1. Spatial distribution of groundwater arsenic concentrations

Groundwater As detections range from 0.2 to 164 $\mu\text{g/L}$ (median 6.3 $\mu\text{g/L}$) in the SHP aquifer (1220 wells) (Table 1, Fig. 2). Arsenic is highest in the southern part of the SHP aquifer (SHP-S; median 9.4 $\mu\text{g/L}$; range 0.3–164 $\mu\text{g/L}$), which corresponds to a zone of high TDS (median 885 mg/L; range 273–7447 mg/L); As generally is much lower in the northern part (SHP-N, median 4.1 $\mu\text{g/L}$; range 0.2–43 $\mu\text{g/L}$), where TDS also is lower (median 395 mg/L; range 166–4218 mg/L) (Table 1, Figs. 1 and 2). The sharp line that separates the areas of higher and lower TDS and As closely follows the northern extent of the underlying Cretaceous aquifer (Fig. S3). The correlation between As and TDS is high ($\rho = 0.57$; Fig. 2b, Table 2) and significant at $P < 0.001$ (Supporting Information, Table S4). The number of wells that exceed the As MCL is much greater in the SHP-S (47%) than in the SHP-N (9%). Reduction in the MCL from 50 to 10 $\mu\text{g/L}$ increased the number of wells that exceeded the MCL in the SHP-S from 2% to 47%.

It is difficult to accurately evaluate the vertical distribution of As within the aquifer because the general well construction prac-

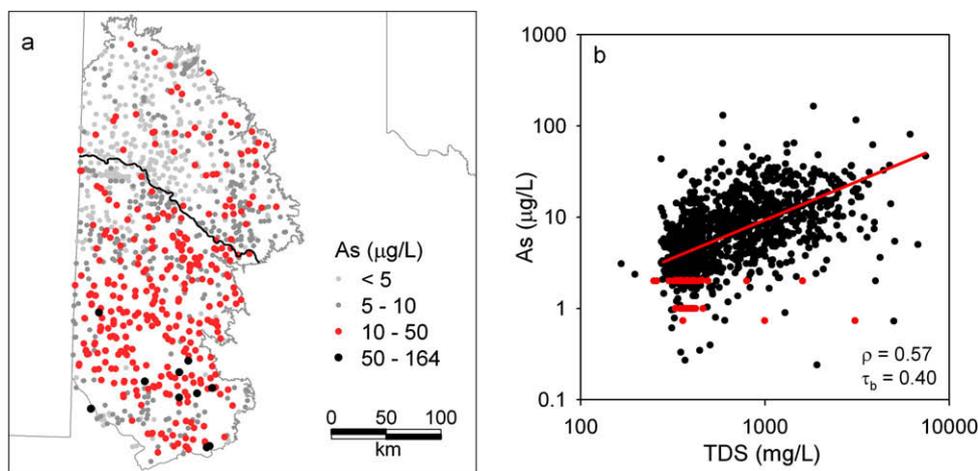


Fig. 2. Distribution of (a) As and (b) relationship between As and total dissolved solids (TDS) concentrations in the Southern High Plains aquifer ($n = 1220$). Dark line in (a) represents the 500 mg/L TDS contour that defines the regional north/south water quality boundary. Red points in (b) represent detection limits for As nondetect values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Nonparametric correlation coefficients between various parameters and As in the Southern High Plains aquifer. Values of Spearman's $\rho > 0.5$ and associated values of Kendall's τ_b are shown in bold. Population sizes are given in Table 1. Correlations are significant at $P < 0.001$, unless otherwise noted.

Parameter	SHP		SHP-N		SHP-S	
	ρ	τ_b	ρ	τ_b	ρ	τ_b
Well depth	-0.45	-0.26	-0.04 ³	0.03 ³	-0.32	-0.21
pH	-0.11	-0.07	0.09 ²	0.08 ²	0.07 ³	0.05 ²
DO	-0.03 ³	-0.02 ³	-0.06 ³	-0.05 ³	-0.06 ³	-0.04 ³
Na/Ca	0.45	0.31	0.30	0.21	0.51	0.36
Na/(Ca) ^{0.5}	0.57	0.40	0.31	0.21	0.53	0.37
Ca/TDS	-0.49	-0.34	-0.42	-0.28	-0.54	-0.38
Mg/TDS	-0.01 ³	-0.01 ³	0.01 ³	0.00 ³	0.21	0.14
SO ₄ /TDS	0.45	0.31	0.00 ³	0.00 ³	0.25	0.17
TDS	0.57	0.40	0.24	0.16	0.39	0.27
SiO ₂	0.41	0.28	0.35	0.23	0.31	0.21
Ca	0.27	0.17	-0.21	-0.14	0.01 ³	0.00 ³
Mg	0.53	0.37	0.13 ¹	0.09 ¹	0.45	0.32
Na	0.58	0.41	0.27	0.18	0.47	0.33
K	0.52	0.36	0.36	0.24	0.40	0.28
HCO ₃	0.06 ²	0.04 ²	0.25	0.17	0.10 ²	0.06 ²
Cl	0.52	0.36	0.06 ³	0.06 ²	0.33	0.25
SO ₄	0.53	0.37	0.10 ²	0.07 ²	0.37	0.25
F	0.56	0.40	0.44	0.31	0.63	0.44
NO ₃ -NO ₃	0.23	0.16	-0.24	-0.17	0.23	0.16
V	0.88	0.72	0.83	0.66	0.86	0.70
Mo	0.46	0.32	0.50	0.35	0.42	0.30
Se	0.54	0.40	0.27	0.24	0.34	0.24
B	0.51	0.36	0.37	0.25	0.40	0.28
Fe	-0.04 ³	0.08 ²	-0.07 ³	0.00 ³	-0.02 ³	0.05 ³
Mn	-0.03 ³	0.03 ³	-0.06 ³	-0.03 ³	-0.11 ²	-0.05 ³
NO ₂ -NO ₂	0.23 ¹	0.17 ¹	0.13 ³	0.10 ³	0.29 ¹	0.21 ¹
PO ₄	0.62	0.46	-0.02 ³	0.09 ³	0.05 ³	0.15 ³
U [*]	0.32	0.23	0.22	0.16	0.09 ³	0.06 ³

Spearman's ρ calculated assuming one detection limit value (all nondetects set equal to the highest nondetect value). Kendall's τ_b calculated using all reported nondetect values.

More detailed information on P values is provided in Supporting Information (Table S4).

* Uranium and corresponding arsenic data obtained from the National Uranium Resource Evaluation (NURE) database (<http://pubs.usgs.gov/of/1997/ofr-97-0492/>).

¹ (0.001 < P < 0.01).

² (0.01 < P < 0.05).

³ (P > 0.05).

tice is to drill and screen through the entire aquifer. The regional variation in groundwater As concentrations from north to south generally corresponds with variations in well depth with deeper wells in the north (median 93 m), where the predevelopment saturated thickness of the aquifer is greater (median 45 m), relative to the south (median well depth, 50 m; predevelopment saturated thickness 16 m). Concentrations of As in 29 wells with short screens (3 m) within 1.5 m of the water table range from 1.7 to 21.3 $\mu\text{g/L}$ (Stanton and Fahlquist, 2006), which is within the range of values found throughout the SHP aquifer (0.2–164 $\mu\text{g/L}$). Concentrations of As are fairly uniform (23–27 $\mu\text{g/L}$) with depth in a well cluster (3) in Martin County with 3–6 m long screens in the SHP-S aquifer (mean mid-screen depths: 37, 44, and 47 m; Supporting Information, Table S1). Multilevel wells in Gaines County have lower As concentrations in the SHP aquifer (mean mid-screen depth: 11 m; 6.1 $\mu\text{g/L}$) than in the underlying Cretaceous (34 m; 21 $\mu\text{g/L}$) or Dockum (63 m, 18 $\mu\text{g/L}$) aquifers. In contrast, multilevel wells in Bailey County have higher As levels across the SHP-Cretaceous aquifers (23 m depth; 13 $\mu\text{g/L}$) than in the underlying Cretaceous aquifer (51 m depth; 2.6 $\mu\text{g/L}$). Variations in As concentrations with depth in these multilevel wells are highly correlated with the oxyanion-forming element V based on data from all three sets of multilevel wells ($\rho = 0.90$). Arsenic concentrations in multilevel wells in Hale and Castro counties, in the SHP-N aquifer, are generally low in the SHP aquifer (2.5–7.4 $\mu\text{g/L}$) and slightly higher

in the underlying Triassic Dockum aquifer (12 $\mu\text{g/L}$) (Supporting Information, Table S1) (McMahon et al., 2004).

3.2. Relationship between arsenic and other water quality parameters

Groundwater in the SHP aquifer is generally oxidizing based on DO levels (median 6.1 mg/L), NO₃ (9.5 mg/L NO₃-NO₃), SO₄ (77 mg/L), and generally low concentrations of Fe (<50 $\mu\text{g/L}$), Mn (<1.0 $\mu\text{g/L}$), and NO₂-NO₂ (20 $\mu\text{g/L}$) (Table 1). Arsenic occurs as arsenate, As(V), based on speciation analyses (Supporting Information, Table S2). Results of As speciation based on different preservation techniques are similar (Table S2).

Arsenic concentrations are positively correlated with various anions and oxyanion-forming elements in the SHP aquifer, with ρ values of 0.56 for F, 0.88 for V, 0.54 for Se, 0.53 for SO₄, 0.52 for Cl, 0.51 for B, 0.46 for Mo, 0.41 for SiO₂ and 0.32 for U (Table 2; Supporting Information, Figs. S5–S13). These correlations are statistically significant at $P < 0.001$ (Supporting Information, Table S4). The co-occurrence of elevated As concentrations, along with F and other oxyanion-forming elements, is quite common in semiarid oxidizing systems (Robertson, 1989; Smedley et al., 2002). Correlation between As and NO₃ ($\rho = 0.23$, $P < 0.001$) is much lower than correlations between As and F and oxyanion-forming elements, suggesting a geologic rather than a surface anthropogenic source for As, which is confirmed in previous studies that show that As is not readily flushed through the unsaturated zone to groundwater (Reedy et al., 2007). Correlations between As and HCO₃, Fe and Mn are low and not statistically significant at $P = < 0.01$ (Table 2). The low range in pH (10–90 percentile, 7.0–7.6) and low negative correlation with As ($\rho = -0.11$) (Table 2, Supporting Information, Table S4, Fig. S14) differ from most semiarid, oxidizing systems where increased pH (8.0–9.0) generally mobilizes As (Robertson, 1989; Smedley et al., 2002; Bhattacharya et al., 2006). Correlations between As and various cations are generally high (Na, $\rho = 0.58$; Mg, $\rho = 0.53$; K, $\rho = 0.52$ and Ca, $\rho = 0.27$) and significant at $P < 0.001$ (Table 2). Most groundwater samples are undersaturated with respect to calcite (median SI: -0.11), dolomite (median SI: -0.07), gypsum (median SI: -1.83) and amorphous silica (median SI: -0.29) (Table 1).

3.3. Relationship between arsenic and hydrogeologic parameters

Variations in As and TDS across the SHP aquifer spatially correspond to differences in aquifer saturated thickness and water table depth that reflect the underlying geology. The higher As and TDS water occurs in a paleo-upland region in the south where the SHP current saturated thickness is low (median 15 m), whereas the lower As and TDS water to the north generally occurs in a paleovalley where the current saturated thickness is greater (median 21 m) (Supporting Information, Fig. S2). The aquifer saturated thickness represents the ability of the aquifer to dilute a contaminant from above or below the aquifer, or the assimilative capacity of the aquifer. The regional As distribution also corresponds to the regional water table depth, with high As concentrations in the south where the median water table depth is 25 m and low As concentrations in the north where the median water table depth is 63 m (Supporting Information, Fig. S15). The general relationship between As concentration and water table depth suggests a surficial source of As because shallower water tables have higher As concentrations; however, these relationships are not necessarily causal. Previous analyses of unsaturated zone As levels indicate that As is not readily flushed through the unsaturated zone to the aquifer because of sorption, precluding a surficial source of As (Reedy et al., 2007).

3.4. Potential geologic sources of arsenic

Although 47% of wells exceed the As MCL in the SHP-S aquifer, groundwater As concentrations are generally low compared with As concentrations in semiarid, oxidizing systems in Argentina (range: 7.0–15,000 $\mu\text{g/L}$; median, 54 $\mu\text{g/L}$; Bhattacharya et al., 2006; range: <5–5300 $\mu\text{g/L}$; median 150 $\mu\text{g/L}$; Smedley et al., 2002). There are several potential sources of As in the SHP aquifer. The association between As and TDS suggests a possible common source for both. The source of As should be consistent with the sharp contrast in As concentrations between the north and south areas of the SHP aquifer. Studies in other semiarid oxidizing systems have suggested that high As concentrations are related to evaporation, based on correlations of As with TDS and Cl and enriched $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Fujii and Swain, 1995; Welch and Lico, 1998; Smedley et al., 2002). Although correlations of As with TDS ($\rho = 0.57$) and Cl ($\rho = 0.52$) in the SHP aquifer are moderately high (Table 2), $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in groundwater do not support evaporation because they are not enriched ($\delta^2\text{H}$: -65 to -27 ; $\delta^{18}\text{O}$: -9.1 to -4.2) and the slope of the $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ line in groundwater (6.55) is similar to that based on local precipitation (6.43) (Fig. 3) (Nativ, 1988). The unenriched stable isotopes are attributed to recharge occurring primarily beneath playas with little opportunity for evaporation (Nativ and Smith, 1987; Wood and Sanford, 1995a). Recharge in interplay areas beneath natural ecosystems is negligible, because shown by upward hydraulic gradients, large Cl buildups in the unsaturated zone, and modeling analyses that support drying of soil profiles since Pleistocene times (10–15 ka) (Scanlon et al., 2003). Some flushing of these salts through the unsaturated zone has occurred beneath rain-fed cropland areas, particularly in the southeastern part of the SHP (Scanlon et al., 2007). Direct evapotranspiration of groundwater is also improbable as the current water table is too deep (SHP-S: median 25 m) and the water table is unlikely to have been much shallower during the average residence time of groundwater in the aquifer (~ 1 ka; Dutton, 1995). Saline lakes could also act as a source of high TDS groundwater based on their general restriction to the SHP-S region (Fig. S3) where TDS is much higher. However, saline lakes are groundwater discharge points where evaporation occurs, as shown by enriched stable isotopes ($\delta^2\text{H}$: -15.5 to 30 ; median 3.50; $\delta^{18}\text{O}$: -0.85 to 10.7 ; median 0.98; Fig. 3) (Wood and Jones, 1990). In addition, As concentrations in saline lake water are not sufficiently high (5–205 $\mu\text{g/L}$; median 78 $\mu\text{g/L}$) to explain high As concentrations in the SHP-S aquifer considering that these As values would

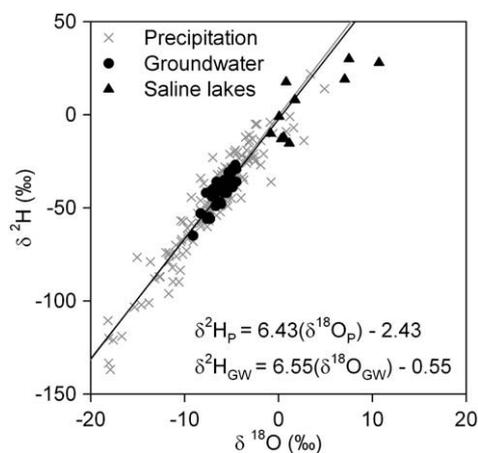


Fig. 3. Relationship between stable isotopes in precipitation and groundwater from Nativ (1988) and saline lakes from Wood and Jones (1990). Linear regression lines and equations are shown for precipitation (P, gray line) and groundwater (G, black line).

have to be reduced by up to a factor of 930 based on comparison of Cl in saline lakes and median Cl in the SHP-S aquifer (167 mg/L) (Supporting Information, Table S3).

The most likely source of high TDS water in the SHP-S aquifer is from saline groundwater in deeper aquifers. Restriction of high TDS groundwater to the SHP-S aquifer (median 885 mg/L) could be explained by low aquifer saturated thickness (median predevelopment saturated thickness 16 m) in this area, which would provide minimal dilution for incoming high salinity groundwater relative to the SHP-N aquifer (median TDS, 395 mg/L; median predevelopment saturated thickness 45 m) (Supporting Information, Fig. S2a). Assessing relationships between the SHP aquifer and deeper aquifers is difficult because many wells are screened across both aquifers and the number of wells classified in the TWDB database as being screened exclusively in subjacent aquifers is limited (88 wells in the Cretaceous ETHP, 214 wells in the Triassic Dockum). The contrast in TDS between the SHP-S and SHP-N regions generally corresponds to the subcrop limit of the underlying Cretaceous aquifer (Supporting Information, Fig. S3). However, the underlying Cretaceous ETHP aquifer is not considered the primary source of high TDS groundwater in the SHP-S aquifer because TDS in the Cretaceous aquifer is only moderately higher (median 1280 mg/L) than that in the SHP-S aquifer (median 885 mg/L) (Table 1) and the two aquifers have similar chemical type, stable isotopes and ^3H levels (Nativ and Gutierrez, 1988). The underlying Triassic Dockum aquifer is the most likely source of high TDS groundwater in the SHP-S aquifer because TDS in the Dockum aquifer is much higher in the south (median 3010 mg/L) than in the north (median 620 mg/L) and is much higher than the overlying Cretaceous ETHP (median 1280) or SHP-S (median 885) aquifers (Table 1).

Increasing TDS in the SHP aquifer is accompanied by a change from Ca– HCO_3 type water to a mixed cation–mixed anion type water dominated by Na and Cl (Table 1). Low TDS Ca– HCO_3 water is found mostly in the SHP-N region, but also in the western portion (toward New Mexico) of the SHP-S region. The source of the high TDS water is upward flow from the underlying Dockum aquifer. Groundwater in the Dockum aquifer varies from Na– HCO_3 to Na-mixed anion type water in the north to NaSO_4 or NaCl type water in the south (Dutton and Simpkins, 1986). A Piper diagram is used to show the relationships between groundwater chemistry in the various aquifers (Fig. 4; Supporting Information, Fig. S16). Groundwater in the SHP-S aquifer may be considered a mixture of groundwater from the Dockum aquifer in the south with Ca– HCO_3 type water, which is currently found in the north and west portions of the SHP aquifer (Fig. 4). The Cretaceous ETHP plots on the Piper diagram in a zone between groundwater in the Dockum and SHP-S aquifers, consistent with upward flow of water from the underlying Dockum aquifer. Nativ (1988) and Nativ and Gutierrez (1988) identified many areas throughout the SHP-S region where upward flow from deeper aquifers may be occurring based on hydraulic head differences. The paleotopography at the base of the SHP aquifer with valleys and uplands is conducive to mixing of groundwater between the Cretaceous ETHP and SHP-S aquifers by lateral and vertical flow (Blandford et al., 2003). Recent numerical modeling to assess water resources of the Triassic Dockum and Cretaceous ETHP aquifers supports both upward and downward water fluxes between these aquifers and the SHP aquifer (Blandford et al., 2009; Ewing et al., 2009).

Although water from subjacent aquifers may account for differences in TDS between the SHP-S and SHP-N regions, As concentrations in wells classified as solely Cretaceous (median As 6.6 $\mu\text{g/L}$) and as Triassic Dockum (median As 2.8 $\mu\text{g/L}$) are relatively low (Table 1), which does not support these aquifers as sources of As. Groundwater As concentrations in the Dockum aquifer from the SHP escarpment to the east are also low (164 wells, median As,

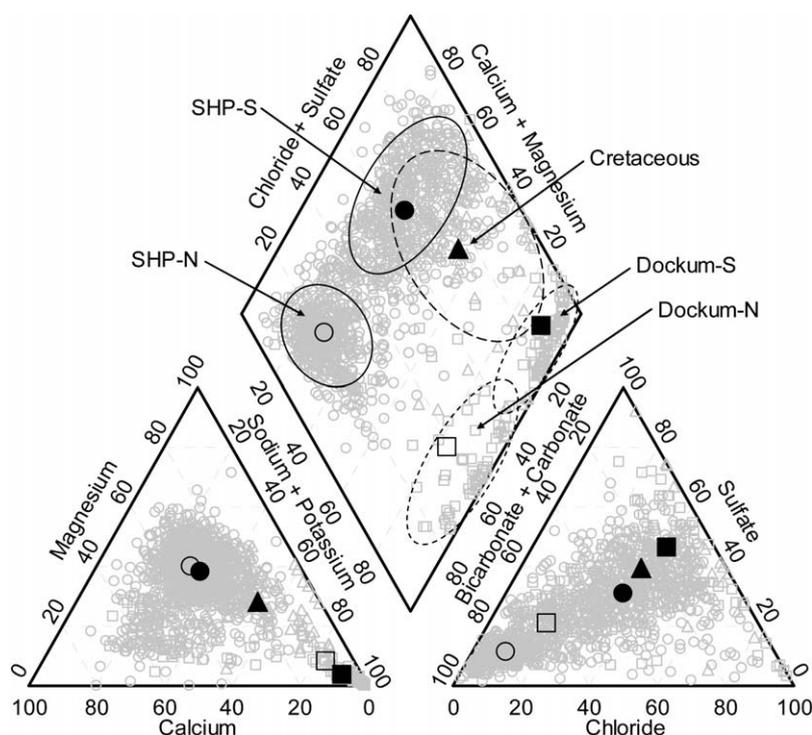


Fig. 4. Piper diagram for groundwater samples (gray symbols, $n = 1421$) throughout the Southern High Plains (1142 points, circles), Cretaceous (78 points, triangles), and Dockum (201 points, squares) aquifers. Black symbols represent median values (SHP-S region: solid symbols, SHP-N region: open symbols). Ellipses indicate general plot areas where most data points are located for the Southern High Plains (solid), Cretaceous (long dash), and Dockum (short dash) aquifers. For clarity, Piper plots for the north and south High Plains are shown separately in Supporting Information (Fig. S16).

2.7 $\mu\text{g/L}$; north, 50 wells, median As 3.4 $\mu\text{g/L}$; south, 114 wells, median As 2.3 $\mu\text{g/L}$). These data from the TWDB database are consistent with some, but not all, results from multilevel wells (Supporting Information, Table S1).

The widespread distribution of As in the SHP-S aquifer and low probability of As input from underlying aquifers suggest that the most likely source of As is within the deposits of the SHP aquifer. The co-occurrence of As and B, F, Mo, Se, SiO_2 , U and V is consistent with a volcanic ash source (Tables 1 and 2) (Smith et al., 1982). Similar relationships among ions are found in aquifers with high As concentrations in Argentina, where volcanic ash is considered the primary source of As (Smedley et al., 2002; Bhattacharya et al., 2006). Rhyolitic volcanic ash layers, collectively termed the Pearlette ash, have been described within the Ogallala Fm. Pliocene and Pleistocene ash falls in the United States originated from three main centers: Wyoming (Yellowstone National Park), California, and New Mexico (Izett, 1981). Some events, such as the Huckleberry Ridge event and the Lava Creek B, blanketed most of the western US, including the Texas Panhandle. Gustavson et al. (1991) indicated that the Huckleberry Ridge (2.2 Ma) and the Lava Creek B (0.62 Ma) volcanic ash layers are present on terraces of the Pecos and Canadian River valleys, north and west of the SHP aquifer, respectively. Cepeda (2001) suggested that there are at least 10 volcanic beds in the Ogallala and Blackwater Draw Fms. originating from the Yellowstone area in the past 12 Ma and varying in thickness from 0.3 to 1.5 m. Volcanic ash probably covered the entire High Plains originally but was eroded from much of the region. The distribution of volcanic ashes in the SHP-S aquifer was characterized using geophysical logs because groundwater As concentrations are highest in this region. However, volcanic rhyolitic ash layers in the Ogallala Fm. are now mostly found in the SW part of the SHP-S aquifer and are not generally collocated with the highest groundwater As concentrations, suggesting leaching is not currently active (Supporting Information, Fig. S17).

The ages of the ashes range from 0.6 to 12 Ma (Supporting Information). Arsenic may also have been derived from volcanic ashes in source rocks for the SHP aquifer in eastern New Mexico and the Rocky Mountains; however, groundwater flow from these western regions was discontinued when the Pecos River became incised in West Texas during Pliocene to Pleistocene time, isolating the High Plains aquifer (Dutton, 1995). Leaching of elements from volcanic ashes generally occurs shortly after deposition (Walton et al., 1981; Smith et al., 1982; Hobday and Galloway, 1999; Stewart et al., 2006). Although volcanic ashes may have provided the primary source of As to the system, they are unlikely to serve as the current source of groundwater As concentrations in the aquifer because of the age of the ashes and the rapid removal of As during the early leaching process (Smith et al., 1982; Stewart et al., 2006). High correlations between As and other oxyanion-forming elements indicate that As may be controlled by sorption/desorption onto hydrous metal oxides. This source probably constitutes a secondary source that currently provides As to the aquifer and is consistent with the current source of As in other semiarid, oxidizing systems in Argentina and Arizona (Robertson, 1989; Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006). Previous studies have shown that these oxides are widely distributed in the SHP aquifer as detrital metal oxides (hematite and magnetite), making up most of the accessory minerals (up to a few percent of the framework minerals), and as authigenic hydrous ferric oxides (hematite, goethite and lepidocrocite) coating quartz grains (Avakian, 1988; McMahan et al., 2004).

3.5. Mobilization mechanisms

The most widely accepted mechanism for mobilizing As in oxidizing systems is increased pH releasing As from hydrous metal oxides (Robertson, 1989; Welch et al., 2000; Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006). Arsenate is generally

highly sorbed onto hydrous metal oxides and clays at low to neutral pH, but much less so at high pH. However, pH in SHP groundwater is near neutral (median: 7.3), and the correlation between As and pH is low and negative ($\rho = -0.11$) (Table 2; Supporting Information, Fig. S14). The range in pH is simply too low (10–90 percentile: 7.0–7.6) because As mobilization generally occurs at $\text{pH} \geq 8.0$ (Smedley and Kinniburgh, 2002).

The most straight forward explanation of As mobilization in the SHP would be if increased TDS mobilized As from hydrous metal oxides because of the high correlation between As and TDS ($\rho = 0.57$). However, previous studies have shown that As(V) adsorption onto Fe and Al amorphous oxides is either not dependent on or increases only slightly with ionic strength over the range 0.01–1.0 M NaCl (Hsia et al., 1994; Goldberg and Johnston, 2001). Similar results were found by Liu et al. (2008) in a study that showed increasing As(V) adsorption onto TiO_2 at NaCl concentrations from 0.001 to 0.01 M. This behavior is attributed to enhanced chemisorption or inner sphere complexation of As(V) onto metal oxides. If outer sphere complexation was found for As(V), as is found for As(III), then adsorption should decrease with increasing ionic strength. Limited recent studies at pH 5 suggest bimodal adsorption of As(V), including inner and outer sphere complexation of As(V) on hematite (Catalano et al., 2008); however, much more research is required at other pH levels and using solid phases to further evaluate this process and assess the significance relative to As(V) mobilization. Groundwater As data from Argentina do not support mobilization by increased ionic strength because there is no positive correlation and even a weak slightly negative correlation between As and indicators of salinity such as Cl (Smedley et al., 2002). The lack of a relationship with salinity is typified by groundwater samples with extremely high Cl concentrations and low As concentrations (e.g. well 970,783, Cl 4580 mg/L, As <4 $\mu\text{g/L}$) (Smedley et al., 2002).

Arsenic can also be mobilized from hydrous metal oxides by competitive desorption by PO_4 , SO_4 , HCO_3 , SiO_2 , VO_4 , and other anions/oxyanions. Competitive desorption varies with valency, pH and ion concentration. Strong chemical similarities between As(V), likely to be present mostly as HAsO_4 , and PO_4 result in PO_4 being a strong competitor for As adsorption sites (Peryea and Kammereck, 1997; Su and Puls, 2001). Although PO_4 data are limited (241 analyses) in the SHP-S aquifer, low correlation with HAsO_4 ($\rho = 0.05$), which is not significant at $P = 0.05$, does not support competitive desorption of HAsO_4 by PO_4 (Tables 1 and 2). Smedley et al. (2002) also noted no apparent relationship between HAsO_4 and dissolved PO_4 in groundwater with high As concentrations in La Pampa in Argentina, where PO_4 concentrations are much higher (610–2150 mg/L) than in the SHP-S aquifer (median <20 $\mu\text{g/L}$).

Correlations between As and SO_4 are moderately high throughout the SHP aquifer ($\rho = 0.53$), but lower in the SHP-S aquifer ($\rho = 0.37$) where As concentrations are highest (Table 2, Supporting Information, Fig. S7). However, laboratory experiments show that SO_4 has only a small effect on As sorption onto hydrous Fe oxides (Wilkie and Hering, 1996), onto Fe oxide (Jeong et al., 2007), and onto Fe-coated zeolite (Jeon et al., 2009) and on arsenate removal by ferric chloride (Meng et al., 2000) and by zero valent Fe (Su and Puls, 2001). The correlation between As and SO_4 is most likely a byproduct of the high correlation between As and TDS, as indicated by lower correlations between As and SO_4/TDS ($\rho = 0.00$ –0.45; Table 2).

Other potential competitors for As sorption sites include HCO_3 , SiO_2 and V. The correlation between As and HCO_3 is not statistically significant at $P < 0.01$. Concentrations of HCO_3 are fairly uniform throughout the SHP aquifer and do not vary with TDS ($\rho = 0.03$) (Table 1). Previous studies have indicated that SiO_2 can strongly impact As sorption. A laboratory study by Jeong et al. (2007) indicate

that SiO_2 reduces As sorption onto Fe oxides at pH 6 and at SiO_2 concentrations from 5 to 10 mg/L. Removal of As by zero valent Fe was reduced by 20% at pH 7.7 and SiO_2 concentration of 58 mg/L (Su and Puls, 2001). Silica decreased As removal by ferric chloride from 90% to 45% when SiO_2 concentrations increased from 2 to 20 mg/L using initial As concentrations of 300 mg/L (Meng et al., 2000). Concentrations of SiO_2 are high throughout the SHP aquifer (median: 53 mg/L), and median concentrations are similar in the north (49 mg/L) and south (56 mg/L) regions of the aquifer (Table 1; Supporting Information, Fig. S8). In contrast, SiO_2 concentrations are low in the Triassic Dockum aquifer (median 12 mg/L); therefore, it is unlikely that SiO_2 moved into the SHP aquifer with high TDS groundwater from the Dockum aquifer. If high SiO_2 concentrations competitively desorb As from hydrous metal oxides, and assuming the hydrous metal oxides are distributed throughout the aquifer, one would expect high As concentrations throughout the SHP aquifer, not just in the SHP-S aquifer. Therefore, desorption of As by SiO_2 does not seem to explain the regional As distribution in the SHP aquifer. Oxyanion-forming elements such as V can also compete with As for adsorption sites (Smedley et al., 2005). The correlation between As and V is high in the SHP aquifer ($\rho = 0.88$) (Table 2). Previous studies have shown that V sorbs readily onto hydrous Fe oxides (Naeem et al., 2007). High correlations between V and As have been recorded in other semiarid oxidizing systems and mutual competition for adsorption sites on metal oxides is thought to enhance mobility of both (Smedley et al., 2002; Bhattacharya et al., 2006). Whereas V (median 30 $\mu\text{g/L}$) and As (median 6.3 mg/L) in the SHP aquifer may compete with each other for adsorption sites, the high correlation may simply reflect mobilization of both by a similar mechanism.

The mechanism for mobilizing As should account for the correlation between As and TDS ($\rho = 0.57$; Table 2). The source of the high TDS water is upward flow from the underlying Dockum aquifer (Fig. 4). Although there is no systematic variation in concentrations of As and TDS in the SHP-S because upward flow from the Dockum aquifer is spatially variable, the cumulative effect is generally recorded in highest As and TDS concentrations downgradient toward the SE (Fig. 2a). The change in TDS in the SHP-S aquifer is associated with a change from Ca-rich water to Na-rich water from the underlying Dockum aquifer (Table 1, Fig. 5a). The $\text{Na}/(\text{Ca})^{0.5}$ ratio in Dockum groundwater (median 72) is much higher than that of the overlying SHP-S groundwater (median 3.0). Previous laboratory experiments have shown that As adsorption onto Fe–Al oxides is reduced by up to 100% when CaCl_2 solution is replaced by NaCl solution at a pH range of 6–11 (~30% at pH 7) (Masue et al., 2007). The differences in sorption are attributed to changes in surface charges of hydrous metal oxide solids as a result of divalent Ca versus monovalent Na and stronger sorption with negatively charged arsenate. This process of releasing As with a change from Ca- to Na-rich water is termed the counterion effect. Arsenic correlates with the $\text{Na}/(\text{Ca})^{0.5}$ ratio throughout the SHP aquifer ($\rho = 0.57$, Fig. 5b) and also within the SHP-S aquifer ($\rho = 0.53$) (Table 2), suggesting that the counterion effect may release As from hydrous metal oxides in the system. Additional studies have indicated that Ca increases As sorption, whereas Na decreases As sorption through addition of lime versus Na ash to As residuals (Parks, 2003) and through laboratory experiments (Smith et al., 2002). Some studies indicate that Ca increases As sorption (Smedley and Kinniburgh, 2002), and others have shown that Ca increases As sorption at high pH (Hawke et al., 1989; Jia and Demopoulos, 2005). In the SHP aquifer, As has a weak positive correlation with Ca ($r = 0.27$) but is more strongly negatively correlated with Ca when normalized by TDS (Ca/TDS , $\rho = -0.49$; Table 2), as would be expected because Ca generally enhances As adsorption. Similar relationships between Ca and As have also been found between Ca and PO_4 , which is expected, considering the similarity

in chemistry between HAsO_4 and PO_4 (Rietra et al., 2001). The change from Ca- to Na-rich water may also desorb other oxyanion-forming elements in the SHP-S aquifer (V, Mo, Se), and possibly F and SiO_2 , and may account for their correlation with As (Table 2). Because Ca and Mg are both divalent ions, one might expect a similar relationship between As and Mg; however, this is not the case and a previous study of sorption of PO_4 on goethite in seawater found that Mg does not enhance PO_4 sorption in contrast to Ca which increases PO_4 sorption (Hawke et al., 1989). Although this analysis suggests that increased TDS from the underlying Dockum aquifer is not the source of As, the counterion effect related to the change from Ca- to Na-rich water associated with increased TDS from the Dockum aquifer may mobilize As and other oxyanion-forming elements. The counterion effect provides the most plausible explanation of the regional distribution of higher As associated with increased TDS at near neutral pH values in the SHP-S aquifer. Competitive desorption of As by other ions may play a role in locally mobilizing As but does not explain the regional distribution in the aquifer.

3.6. Future studies

This reconnaissance study of groundwater As sources and mobilization in the SHP aquifer would greatly benefit from additional field sampling, laboratory studies, and numerical modeling analyses. Because of the high correlation between As and TDS and attribution of increased TDS to upward movement of water from underlying aquifers, it is extremely important to further evaluate hydraulic gradients and compare chemical and isotopic analyses of groundwater in underlying aquifers, such as the Cretaceous ETHP and the Triassic Dockum aquifers, with those in the SHP aquifer to constrain this source of high TDS groundwater. Chloride/Br ratios could also be useful in distinguishing the source of the high TDS groundwater in the SHP aquifer. Future studies on inner and outer sphere complexation of As(V) should also be examined to assess impacts of TDS on As mobilization.

Because hydrous metal oxides are regarded as the dominant current source of As in the SHP aquifer, additional thin sections and X-ray diffraction analyses are needed to determine the total Al, Fe and Mn content of the sediment and to assess the distribution of these hydrous oxides (detrital, coatings) beyond the studies conducted by Avakian (1988). Laboratory experiments could be conducted to evaluate hydrous Fe oxides as As sources using acid

ammonium oxalate (Tamm's reagent) and hydrous Mn oxides as sources using hydroxylamine hydrochloride (Loeppert et al., 2003). Batch and column experiments could be conducted using sediments from areas of the aquifer with Ca- HCO_3 type water (e.g. SHP-N) and adding Na water to determine whether this process releases As from the sediments. The effect of Mg on As sorption could also be examined through laboratory experiments. Numerical modeling using PHREEQC could be used to evaluate desorption of As and related anions and oxyanions along a flow line as Na/Ca ratios increase to determine whether the counterion effect on As release could be simulated. These additional studies would further understanding of groundwater As distribution in the study area.

4. Conclusions

High groundwater As concentrations are widespread in the SHP aquifer, particularly in the southern part of the SHP aquifer (SHP-S), where 47% of wells exceed the MCL of 10 $\mu\text{g/L}$; however, As concentrations are generally low (median 9.4 $\mu\text{g/L}$; range 0.3–164 $\mu\text{g/L}$). High groundwater As concentrations are correlated with groundwater TDS ($\rho = 0.57$). Groundwater is oxidizing based on the presence of DO, SO_4 and NO_3 . Arsenic is present as As(V) based on speciation analyses.

The correlation between As and TDS suggests a common source for both or mobilization of As related directly or indirectly to TDS. Unenriched stable isotopes ($\delta^2\text{H}$: -65 to -27 ; $\delta^{18}\text{O}$: -9.1 to -4.2) in groundwater and similarity in slope of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ (6.55) in groundwater and in local precipitation (6.43) indicate that evaporation is not responsible for high TDS. The most plausible source of high TDS groundwater is upward movement of high TDS groundwater from subjacent aquifers, particularly the Triassic Dockum aquifer. The TDS is highest in the southern part of the Dockum aquifer, which corresponds to the high TDS zone in the southern region of the SHP aquifer (SHP-S). This high TDS zone corresponds to the subcrop of the Cretaceous Edwards Trinity High Plains aquifer and is restricted to a paleo-land area in the SHP-S region, where the predevelopment saturated thickness of the aquifer is low (median 16 m), resulting in lower dilution of incoming higher salinity groundwater. Although underlying aquifers, particularly the Triassic Dockum aquifer, are the most likely sources of salinity in the SHP-S aquifer, low As concentrations in the Triassic (median As 3.6 $\mu\text{g/L}$) and Cretaceous (median As 6.6 $\mu\text{g/L}$) aquifers relative

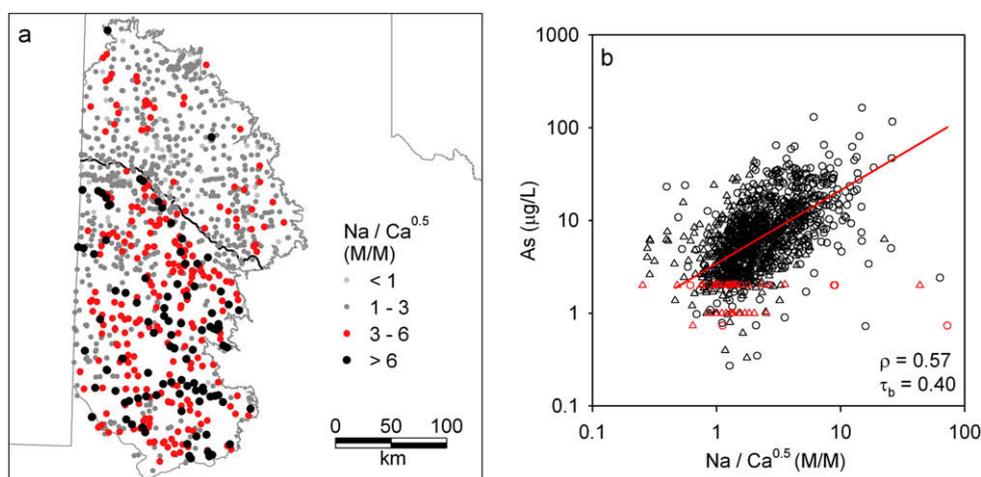


Fig. 5. (a) Distribution of $\text{Na}/\text{Ca}^{0.5}$ ratios ($n = 1220$) and (b) relationship between groundwater As and $\text{Na}/\text{Ca}^{0.5}$ molar ratio in the Southern High Plains aquifer ($n = 1220$, triangles SHP-N; circles, SHP-S). Dark line in (a) represents the 500 mg/L TDS contour that defines the regional north/south water quality boundary. Red points in (b) represent detection limits for As nondetect values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

to the SHP aquifer (median 9.4 $\mu\text{g/L}$) indicate that these underlying aquifers are not likely sources of As in the SHP-S aquifer. Co-occurrence of As with F, V, Se, B, Mo and SiO_2 suggests a common origin in volcanic ashes, which are found within the SHP aquifer and in source rocks to the west in the Rockies. Leaching of these ashes likely occurred early on, followed by adsorption of As onto hydrous metal oxides found dispersed in the SHP aquifer, as indicated by high correlations between As and other anion (F) and oxyanion-forming elements (V, Se, B and Mo).

Although As mobilization in oxidizing systems generally results from high pH, the near neutral pH in the SHP aquifer means that this mechanism is not operating in the SHP aquifer. The most plausible explanation of As mobilization at the regional scale in the SHP aquifer is the counterion effect associated with the change in water chemistry from Ca- to Na-rich water, which is related to upward movement of high Na groundwater along with high TDS from the underlying Dockum aquifer. The counterion effect is supported by the correlation between groundwater As and $\text{Na}/(\text{Ca})^{0.5}$ ratios in the SHP aquifer ($\rho = 0.57$) and may also be responsible for mobilizing other ions and oxyanion-forming elements as indicated by high correlations between As and these elements (F, $\rho = 0.56$; V, $\rho = 0.88$; Se, $\rho = 0.54$; B, $\rho = 0.51$; Mo, $\rho = 0.46$ and SiO_2 , $\rho = 0.41$). The process is supported by laboratory experiments in other studies that show desorption of As from hydrous metal oxides caused by this counter-ion effect. Although competitive desorption by other ions or oxyanions does not explain the regional distribution of As in the SHP-S aquifer, such desorption processes may be important locally within the aquifer.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apgeochem.2009.08.004.

References

- Ashworth, J.B., Hopkins, J., 1995. Aquifers of Texas. Texas Water Development Board Report 345.
- Avakian, A.J., 1988. Mineralogy of the Ogallala Formation, Southern High Plains: New Lithologic, Petrographic, and X-ray Diffraction Data from WEST Texas Cores, Univ. Texas at Austin, Bur. Econ. Geol., Unpublished Report.
- Bhattacharya, P., Claesson, M., Bundschuh, J., Sracek, O., Fagerberg, J., Jacks, G., Martin, R.A., Storniolo, A.D., Thir, J.M., 2006. Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province, Argentina. *Sci. Total Environ.* 358, 97–120.
- Blandford, T.N., Blazer, D.J., Calhoun, K.C., Dutton, A.R., Naing, T., Reedy, R.C., Scanlon, B.R., 2003. Groundwater Availability of the Southern Ogallala Aquifer in Texas and New Mexico: Numerical Simulations Through 2050, Texas Water Development Board.
- Blandford, T.N., Kuchanur, M., Standen, A., Ruggiero, R., Calhoun, K.C., Kirby, P., Shah, G., 2009. Groundwater Availability Model for the Edwards-Trinity (High Plains) Aquifer in Texas and New Mexico. Texas Water Development Board Rept.
- Catalano, J.G., Park, C., Fenter, P., Zhang, Z., 2008. Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochim. Cosmochim. Acta* 72, 1986–2004.
- Cepeda, J.C., 2001. A 10 Ma silicic fallout tuff in the Texas Panhandle; comparisons with the Pearlette Ash. *Geol. Soc. Am. Abstr. Prog.* 33, 397.
- Dutton, A.R., 1995. Groundwater isotopic evidence for paleorecharge in U.S. High Plains aquifers. *Quatern. Res.* 43, 221–231.
- Dutton, A.R., Simpkins, W.W., 1986. Hydrogeochemistry and Water Resources of the Triassic Lower Dockum Group in the Texas Panhandle and Eastern New Mexico, Univ. Texas at Austin, Bur. Econ. Geol. Rept. Inv. No. 161.
- Ewing, J.E., Jones, T.L., Yan, T., Fryar, D.G., Pickens, J.F., Gordon, K., Nicot, J.P., Scanlon, B.R., Ashworth, J.B., Beach, J.A., 2009. Groundwater Availability Model for the Dockum Aquifer. Texas Water Development Board Rept.
- Fujii, R., Swain, W.C., 1995. Areal distribution of selected trace elements, salinity, and major ions in shallow ground water, Tulare Basin, Southern San Joaquin Valley, California. U.S. Geol. Surv. Water Resour. Invest. Rep. 95-4048.
- Goldberg, S., Johnston, C.T., 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *J. Colloid Interface Sci.* 234, 204–216.
- Gustavson, T.C., Holliday, V.T., 1985. Depositional Architecture of the Quaternary Blackwater Draw and Tertiary Ogallala Formations, Texas Panhandle and Eastern New Mexico. Univ. Texas at Austin, Bur. Econ. Geol. Open File Rep. West Texas Waste Isolation 1985-23.
- Gustavson, T.C., Holliday, V.T., 1999. Eolian sedimentation and soil development on a semiarid to subhumid grassland, Tertiary Ogallala and Quaternary Blackwater Draw Formations, Texas and New Mexico High Plains. *J. Sed. Res.* 69, 622–634.
- Gustavson, T.C., Baumgardner, R.W.J., Caran, S.C., Holliday, V.T., Mehnert, H.H., O'Neill, J.M., Reeves, C.C.J., 1991. Quaternary geology of the southern Great Plains and an adjacent segment of the Rolling Plains. In: Morrison, R.B. (Ed.), *Quaternary Nonglacial Geology; Conterminous U.S., The Geology of America*, vol. K-2. Geological Society of America, Boulder, CO, pp. 477–501.
- Hawke, D., Carpenter, P.D., Hunter, K.A., 1989. Competitive adsorption of phosphate on goethite in marine electrolytes. *Environ. Sci. Technol.* 23, 187–191.
- Helsel, D.R., 2005. *Nondetects and Data Analysis: Statistics for Censored Environmental Data*. Wiley Interscience.
- Helsel, D.R., Hirsch, R.M., 1992. *Statistical Methods in Water Resources*. Elsevier, Amsterdam.
- Hobday, D.K., Galloway, W.E., 1999. Groundwater processes and sedimentary uranium deposits. *Hydrogeol. J.* 7, 127–138.
- Holliday, V.T., 1989. The Blackwater Draw Formation (Quaternary): a 1.4-plus-m.y. record of eolian sedimentation and soil formation on the Southern High Plains. *Geol. Soc. Am. Bull.* 101, 1598–1607.
- Hsia, T.H., Lo, S.L., Lin, C.F., Lee, D.Y., 1994. Characterization of arsenate adsorption on hydrous iron-oxide using chemical and physical methods. *Colloids Surf., A-Physicochem. Eng. Aspects* 85, 1–7.
- Hudak, P.F., 2000. Distribution and sources of arsenic in the Southern High Plains aquifer, Texas, USA. *J. Environ. Sci. Health Part A - Toxic/Hazard. Subst. Environ. Eng.* 35, 899–913.
- Izett, G.A., 1981. Stratigraphic Succession, Isotopic Ages, Partial Chemical Analyses, and Sources of Certain Silicic Volcanic Ash Beds (4.0–0.1 m.y.) of the Western United States. U.S. Geol. Surv. Open-File Rep. 81-763, 2 Sheets.
- Jeon, C.S., Park, J.K., Oh, K.Y., Lee, S.D., 2009. Adsorption characteristics of As(V) on iron-coated zeolite. *J. Hazard. Mater.* 163, 804–808.
- Jeong, Y.R., Fan, M.H., Van Leeuwen, J., Belczyk, J.F., 2007. Effect of competing solutes on arsenic(V) adsorption using iron and aluminum oxides. *J. Environ. Sci. - China* 19, 910–919.
- Jia, Y.F., Demopoulos, G.P., 2005. Adsorption of arsenate onto ferrihydrite from aqueous solution: influence of media (sulfate vs. nitrate), added gypsum, and pH alteration. *Environ. Sci. Technol.* 39, 9523–9527.
- Liu, G.J., Zhang, X.R., McWilliams, L., Talley, J.W., Neal, C.R., 2008. Influence of ionic strength, electrolyte type, and NOM on As(V) adsorption onto TiO_2 . *J. Environ. Sci. Health Part A - Toxic/Hazard. Subst. Environ. Eng.* 43, 430–436.
- Loeppert, R.H., Jain, A., Abd El-Haleem, M.A., Biswas, B.K., 2003. Quantity and speciation of arsenic in soils by chemical extraction. In: Cai, Y., Braids, O.C. (Eds.), *Biochemistry of Environmentally Important Trace Elements*, Am. Chem. Soc., Oxford Univ. Press, pp. 42–56.
- Masue, Y., Loeppert, R.H., Kramer, T.A., 2007. Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum: iron hydroxides. *Environ. Sci. Technol.* 41, 837–842.
- McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results. *Appl. Geochem.* 19, 995–1009.
- McGowen, J.H., Granata, G.E., Seni, S.J., 1977. Depositional Systems, Uranium Occurrence and Postulated Ground-water History of the Triassic Dockum Group, Texas Panhandle-Eastern New Mexico. Univ. Texas at Austin, Bur. Econ. Geol., Rep. Prepared for the U.S. Geol. Surv. Under Grant Number 14-08-0001-G410.
- McMahon, P.B., Bohlke, J.K., Lehman, T.M., 2004. Vertical Gradients in Water Chemistry and Age in the Southern High Plains Aquifer, Texas, 2002. U.S. Geol. Surv. Sci. Invest. Rep. 2004-5053.
- Meng, X.G., Bang, S., Korfiatis, G.P., 2000. Effects of silicate, sulfate and carbonate on arsenic removal by ferric chloride. *Water Res.* 34, 1255–1261.
- Mukherjee, A., Bhattacharya, P., Savage, K., Foster, A., Bundschuh, J., 2008. Distribution of geogenic arsenic in hydrologic systems: controls and challenges. *J. Contam. Hydrol.* 99, 1–7.
- Naeem, A., Westerhoff, P., Mustafa, S., 2007. Vanadium removal by metal (hydr)oxide adsorbents. *Water Res.* 41, 1596–1602.
- Nativ, R., 1988. Hydrogeology and Hydrochemistry of the Ogallala Aquifer, Southern High Plains, Texas Panhandle and Eastern New Mexico. Univ. Texas at Austin, Bur. Econ. Geol., Rep. Inv. No. 177.

- Nativ, R., Gutierrez, G.N., 1988. Hydrogeology and hydrochemistry of Cretaceous aquifers, Texas Panhandle and Eastern New Mexico. *Univ. Texas at Austin, Bur. Econ. Geol. Circ.* 88–3.
- Nativ, R., Smith, D.A., 1987. Hydrogeology and geochemistry of the Ogallala Aquifer, Southern High-Plains. *J. Hydrol.* 91, 217–253.
- Nordstrom, D.K., 2002. Public health – Worldwide occurrences of arsenic in ground water. *Science* 296, 2143–2145.
- Parks, J.L., 2003. Effect of Ca on As release from ferric and alum residuals. *J. Am. Water Works Assoc.* 95, 108–118.
- Peryea, F.J., Kammereck, R., 1997. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Water Air Soil Pollut.* 93, 243–254.
- Rajagopalan, S., Anderson, T.A., Fahlquist, L., Rainwater, K.A., Ridley, M., Jackson, W.A., 2006. Widespread presence of naturally occurring perchlorate in High Plains of Texas and New Mexico. *Environ. Sci. Technol.* 40, 3156–3162.
- Reedy, R.C., Scanlon, B.R., Nicot, J.P., Tachovsky, T.A., 2007. Unsaturated zone arsenic distribution and implications for groundwater contamination. *Environ. Sci. Technol.* 41, 6914–6919.
- Rietra, R., Hiemstra, T., Van Riemsdijk, W.H., 2001. Interaction between calcium and phosphate adsorption on goethite. *Environ. Sci. Technol.* 35, 3369–3374.
- Robertson, F.N., 1989. Arsenic in ground-water under oxidizing conditions, southwest United States. *Environ. Geochem. Health* 11, 171–185.
- Scanlon, B.R., Goldsmith, R.S., 1997. Field study of spatial variability in unsaturated flow beneath and adjacent to playas. *Water Resour. Res.* 33, 2239–2252.
- Scanlon, B.R., Keese, K., Reedy, R.C., Simunek, J., Andraski, B.J., 2003. Variations in flow and transport in thick desert vadose zones in response to paleoclimatic forcing (0–90 kyr): field measurements, modeling, and uncertainties. *Water Resour. Res.*, 39. Art. No. 1179.
- Scanlon, B.R., Reedy, R.C., Stonestrom, D.A., Prudic, D.E., Dennehy, K.F., 2005. Impact of land use and land cover change on groundwater recharge and quality in the southwestern USA. *Global Change Biol.* 11, 1577–1593.
- Scanlon, B.R., Reedy, R.C., Tachovsky, J.A., 2007. Semiarid unsaturated zone chloride profiles: archives of past land use change impacts on water resources in the southern High Plains, United States. *Water Resour. Res.*, 43. Art. No. W06423.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* 17, 517–568.
- Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. *Appl. Geochem.* 17, 259–284.
- Smedley, P.L., Kinniburgh, D.G., Macdonald, D.M.J., Nicolli, H.B., Barros, A.J., Tullio, J.O., Pearce, J.M., Alonso, M.S., 2005. Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. *Appl. Geochem.* 20, 989–1016.
- Smith, D.B., Zielinski, R.A., Rose, W.I., 1982. Leachability of uranium and other elements from freshly erupted volcanic ash. *J. Volc. Geotherm. Res.* 13, 1–30.
- Smith, E., Naidu, R., Alston, A.M., 2002. Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. *J. Environ. Qual.* 31, 557–563.
- Stanton, J.S., Fahlquist, L., 2006. Ground-water Quality Beneath Irrigated Cropland of the Northern and Southern High Plains Aquifer, Nebraska and Texas, 2003–04. *U.S. Geol. Surv. Sci. Invest. Rep.* 2006–5196.
- Stewart, C., Johnston, D.M., Leonard, G.S., Horwell, C.J., Thordarson, T., Cronin, S.J., 2006. Contamination of water supplies by volcanic ashfall: a literature review and simple impact modelling. *J. Volcanol. Geotherm. Res.* 158, 296–306.
- Su, C.M., Puls, R.W., 2001. Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. *Environ. Sci. Technol.* 35, 4562–4568.
- Walton, A.W., Galloway, W.E., Henry, C.D., 1981. Release of uranium from volcanic glass in sedimentary sequences: an analysis of two systems. *Econ. Geol.* 76, 69–88.
- Welch, A.H., Lico, M.S., 1998. Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada. *Appl. Geochem.* 13, 521–539.
- Welch, A.H., Stollenwerk, K.G. (Eds.), 2003. *Arsenic in Ground Water: Geochemistry and Occurrence*. Kluwer Academic Publishers.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water* 38, 589–604.
- Wilkie, J.A., Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surf. A-Physicochem. Eng. Aspects* 107, 97–110.
- Wood, W.W., Jones, B.F., 1990. Origin of solutes in saline lakes and springs on the southern High Plains of Texas and New Mexico. In: Gustavson, T.C. (Ed.), *Geologic Framework and Regional Hydrology: Upper Cenozoic Blackwater Draw and Ogallala Formations, Great Plains*. Bur. Econ. Geol., Univ. Texas, Austin, pp. 193–208.
- Wood, W.W., Sanford, W.E., 1995a. Chemical and isotopic methods for quantifying ground-water recharge in a regional, semiarid environment. *Ground Water* 33, 458–468.
- Wood, W.W., Sanford, W.E., 1995b. Eolian transport, saline lake basins, and groundwater solutes. *Water Resour. Res.* 31, 3121–3129.