

Unsaturated Zone Arsenic Distribution and Implications for Groundwater Contamination

ROBERT C. REEDY,*
BRIDGET R. SCANLON,
JEAN-PHILIPPE NICOT, AND
J. ANDREW TACHOVSKY

*John A. and Katherine G. Jackson School of Geosciences,
Bureau of Economic Geology, The University of Texas,
University Station, Box X, Austin, Texas 78713-8924*

Arsenic compounds have been applied at the land surface as pesticides in agricultural areas globally. The purpose of this study was to evaluate the fate of anthropogenic arsenic applications related to agriculture, using arsenic applications on cotton in the southern High Plains (SHP), Texas, as a case study and examining possible linkages with contamination of the underlying Ogallala aquifer in this region, where 36% of wells exceed the new EPA 10 $\mu\text{g/L}$ standard. Unsaturated zone soil samples were collected from boreholes beneath natural ecosystems (grassland/shrubland) to provide a control (no arsenic application) (5 profiles) and cotton cropland (20 profiles) for analyses of water-extractable arsenic, vanadium, phosphate, chloride, and nitrate. Natural ecosystem profiles have high arsenic concentrations at depth (maximum of 7.2–69.6 $\mu\text{g As/kg}$ dry soil at 5.9–21.4 m depth) that are attributed to a geologic source. Most profiles beneath cotton cropland have high arsenic concentrations within the upper meter (profile means 1.7 to 31.6 $\mu\text{g/kg}$) that correlate with phosphate ($r = 0.70$, $p < 0.01$) and are attributed to anthropogenic arsenic application associated with phosphate fertilizer application. High arsenic concentrations at >1 m depth (profile means $\leq 36.3 \mu\text{g/kg}$) found in cropland profiles are attributed to a geologic source because of similarity with profiles beneath natural ecosystems, lack of correlation with phosphate, and pore-water ages that predate anthropogenic arsenic application in many profiles. GIS analyses showed poor correlations between groundwater arsenic and percent cultivated land ($r = -0.15$, $p < 0.01$), groundwater nitrate ($r = 0.30$, $p < 0.01$), and water table depth ($r = -0.31$, $p < 0.01$), further supporting the idea that anthropogenic-derived arsenic in the shallow subsurface is not linked to groundwater arsenic contamination in this region.

Introduction

Reduction of the arsenic maximum contaminant level (MCL) from 50 to 10 $\mu\text{g/L}$ by the U.S. EPA in 2002 has resulted in a marked increase in the number of groundwater public and domestic supply systems that exceed the new MCL. Understanding sources of arsenic and mobilization mechanisms

has become critical as water supply systems try to comply with the new regulations. Elevated arsenic levels are also an issue in surface soils because of potential mobilization into surface water and for zoning of residences and kindergartens because of potential exposure pathways through soil ingestion (1). Health risks of chronic exposure to inorganic arsenic in humans include cancers (skin, lung, bladder, and liver) and vascular disease (2).

Most of the literature on groundwater arsenic contamination has focused on geologic sources and mobilization mechanisms (3, 4). Anthropogenic sources of arsenic include agricultural products (pesticides, defoliants, feed additives), wood preservatives (chromated copper arsenate), and industrial wastes (glass production, semiconductors) (5). Agricultural uses were the main source of arsenic until about 1990, when wood preservatives became dominant. Acid lead arsenate (PbHAsO_4) was widely used as the primary insecticide in fruit orchards (recommended annual application rates of $\leq 80 \text{ kg As/ha}$) (6) prior to the introduction of dichloro diphenyl trichloroethane (DDT) in 1947 (7). Lead arsenate has been reported beneath orchards globally (8) and has resulted in soil contamination with lead and arsenic ($\leq 360 \text{ mg total As/kg dry soil}$), mostly in the upper meter (6, 9). Laboratory experiments showed that phosphate fertilizers enhance downward mobility of arsenic through competition for adsorption sites (8). Organoarsenicals (roxsarson) are widely used as a feed additive for poultry to control intestinal parasites and promote growth. Widespread application of poultry litter as a fertilizer results in elevated arsenic concentrations and trace elements (phosphorus, copper, and zinc) in soils (10). Arsenic products have been extensively used in cotton production. Calcium arsenate [$\text{Ca}_3(\text{AsO}_4)_2$] was specifically used to fight a cotton pest, the boll weevil, from the early 1900s until 1947, when DDT was introduced. Arsenic acid [H_3AsO_4] was extensively used as a defoliant for cotton in the 1960s after it became commercially available in 1956 (11) and until it was banned by U.S. EPA in 1992. Organo-arsenical compounds, primarily monosodium methyl arsenate (MSMA), have been used since 1977 as herbicides and are still in use today. Use of these organoarsenicals in the southern U.S. has elevated arsenic concentrations in surface water (12).

The purpose of this study was to evaluate the fate of anthropogenic arsenic applications related to agriculture using arsenic applications on cotton in the southern High Plains (SHP), Texas, as a case study. Previous studies suggested that arsenic pesticide applications were the source of groundwater arsenic contamination in the SHP because of collocation of high-arsenic contamination in areas of shallow water tables and correlations between groundwater arsenic and nitrate levels from fertilizer (13, 14).

Unique aspects of this study include detailed soil profiling (27 profiles) to much greater depths (4–46 m) than evaluated in many previous studies ($\sim 1\text{--}2$ m) related to fate of anthropogenic arsenic compounds (6, 10), detailed conceptual model of flow and transport provided by chloride environmental tracer data (15), and regional analysis of anthropogenic indicators of arsenic contamination (percent cropland, soil texture, groundwater nitrate levels, and groundwater table depth) and groundwater arsenic levels using geographic information systems (GIS) analysis. Different pathways for arsenic transport (areally distributed recharge beneath cropland versus runoff from cropland into ephemeral lakes [playas] and focused recharge beneath playas) and impacts of irrigation on arsenic transport were evaluated to a limited extent. This study should provide a

* Corresponding author address: 10100 Burnet Rd., Bldg. 130, Austin, Texas, 78758; phone: 512-471-7244; fax: 512-471-0140; e-mail: bob.reedy@beg.utexas.edu.

general analog for assessing the fate and transport of anthropogenic arsenic compounds.

Materials and Methods

This study evaluated the distribution of arsenic in the unsaturated zone relative to anthropogenic arsenic applications and natural geologic sources and implications for groundwater arsenic contamination. The focus of the study is in the SHP (75 000 km²) in Texas, which is underlain by the Ogallala or High Plains aquifer, the largest aquifer in the U.S.

Inorganic arsenic compounds have been used on cotton in the SHP since the early 1900s. Originally calcium arsenate [Ca₃(AsO₄)₂] was used against boll weevil in cotton from the early 1900s to 1947, when DDT became available. Reported application rates ranged from ~3.8 to 6.2 kg/ha for elemental As (16). The annual number of calcium arsenate applications ranged from 0 to 10, depending on pest pressure, with resulting annual application rates up to 62 kg/ha (17). Arsenic acid [H₃AsO₄] was used to defoliate cotton from the early 1960s (11) until it was banned by the EPA in 1992. Arsenic acid was generally sprayed from a ground-based vehicle or from an airplane. Reported application rates of arsenic acid ranged from 1.7 to 2.6 kg/ha elemental As (16). In addition, cotton gin waste, with residual total arsenic concentrations of ≤240 mg/kg (16), was returned to fields adjacent to cotton gins to provide an organic mulch because burning of waste was banned by the Texas Air Control Board in 1972 (16). Cotton is generally planted in May and harvested in October/November in the SHP. Defoliants were applied in late summer/fall to aid harvesting. Short cotton varieties, usually grown in the dry plains of Texas and Oklahoma, were machine-stripped and treated with desiccants (previously, inorganic arsenic acid; currently, organic desiccants, e.g., paraquat). Profiles beneath natural ecosystems provided end-member information related to natural sources (atmospheric, geologic, or both) because arsenic was never applied in these areas.

Study Area Characteristics. The SHP consists of 52% cropland and fallow and 46% grassland/shrubland (Figure 1) (18). Cotton production represents an average of 41% of all cropland and an average of 17% of total U.S. cotton production from 1968 to 2005 (19). Approximately 11% of the SHP (21% of cropland) is irrigated, and irrigation accounts for 98% of groundwater use (20). Cotton crops represent 54% of all irrigated areas. Approximately 50% of cotton fields are irrigated, resulting in an average of 68% of total regional cotton production.

Groundwater arsenic concentration data in the SHP were obtained for 1026 wells in the study area from the Texas Water Development Board (www.twdb.state.tx.us; Figure 1). These samples were filtered and acidified in the field. Reported arsenic concentrations range from 1.7 to 561 µg/L (median As = 7.6 µg/L). Approximately 36% of wells throughout the SHP exceed the new EPA arsenic MCL of 10 µg/L. The spatial distribution of groundwater arsenic can generally be separated into southern and northern regions based on total dissolved solids (TDS). Arsenic contamination occurs primarily in the southern region, where TDS is generally >500 mg/L (median 850 mg/L) and 55% of wells exceed the As MCL (median 11.0 µg/L), whereas only 8% of wells exceed the As MCL in the northern region (median 4.5 µg/L), where TDS is <500 mg/L (median 390 mg/L).

Evaluation of the fate of anthropogenic arsenic applications requires an understanding of regional flow pathways and controls on such pathways. Potential pathways from the land surface to groundwater include areally distributed recharge throughout the SHP or runoff to ephemeral lakes or playas and focused recharge beneath playas. Previous studies showed that groundwater recharge is focused beneath

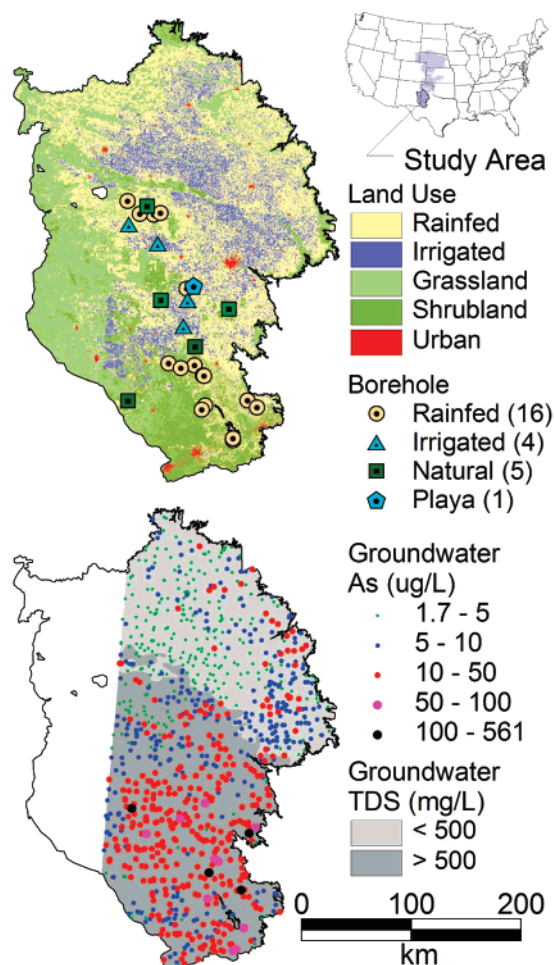


FIGURE 1. Generalized land use and borehole locations in the southern High Plains (above) and groundwater arsenic concentrations in the Texas portion (below). The SHP consists of 52% cropland and fallow and 46% grassland/shrubland. Grassland/shrubland areas may be overestimated by ≤10% because cropland areas converted to grassland/shrubland areas through the Conservation Reserve Program cannot be distinguished from long-term natural grassland/shrubland areas using satellite data.

playas based on low chloride concentrations beneath playas (21, 22). Chloride from precipitation and dry fallout moves into the subsurface with infiltrating water, and concentrations remain low in areas of high downward water fluxes because of flushing. In contrast, there is little or no recharge beneath natural ecosystems in interplaya settings, as evidenced by high chloride concentrations (≤4,171 mg Cl/L pore water, 469 mg Cl/kg dry soil) and upward matric potential gradients (22). Chloride accumulation in interplaya settings results from plants excluding chloride during water uptake for transpiration. The age of soil pore water can be estimated by dividing the total mass of chloride from the land surface to the depth of interest by the chloride input (precipitation times chloride concentration in precipitation). Chloride accumulation ages in interplaya settings range from 5500 to 10 000 years in the central High Plains (22) and 4200, 10 500, and 17 000 years at three sites in the SHP (15, 23). More recent studies showed that rainfed croplands have increased recharge up to ~5% of precipitation (mean 24 mm/year) in the SHP, based on low chloride concentrations in the chloride flushed zone (zone between land surface and depth at which soil pore water chloride concentrations increase sharply) and downward matric potential gradients indicating downward water movement (24). Solutes that accumulated over millennia in the unsaturated zone have been mobilized to the underlying

aquifer by increased recharge related to cultivation and irrigation as shown by increased total dissolved solids and nitrate in groundwater (23, 24). Elevated levels of perchlorate in the SHP aquifer have also been attributed to an atmospheric source and downward transport through the unsaturated zone (25).

Regional Evaluation of Linkage between Agricultural Arsenic Applications and Groundwater Arsenic. Boreholes (27) were drilled without any drilling fluid to determine the distribution of arsenic in the unsaturated zone (Figure 1; Supporting Information). Boreholes were located in natural ecosystems (grassland/shrubland) (5), rainfed cotton cropland (16), irrigated cotton cropland (4), in a playa surrounded by irrigated cotton fields (1) in the SHP, and adjacent to a cotton gin (1) in the Gulf Coast.

Chemical parameters, including arsenic, vanadium, and anion (chloride, nitrate + nitrite, and phosphate) concentrations were analyzed in pore water in 463 soil samples from 27 profiles. Sample depth intervals range from 0.15 to 1.0 m. Arsenic pesticides, including calcium arsenate and arsenic acid, are ultimately derived from geologic sources such as ores and therefore may not have any distinctive chemical signature from an in situ geologic source. Samples of arsenic acid could not be obtained for analysis because it was banned by EPA in 1992. Vanadium was analyzed to assess relationships with arsenic because previous studies have shown positive correlations between arsenic and vanadium related to geologic sources (26).

Soil samples (25 g) were initially air-dried, then leached using about 40 mL of double-deionized (DDI) water (≥ 18.2 M Ω cm), shaken for 4 h, centrifuged at 7000 rpm for 20 min, and filtered to 0.2 μ m. Approximately 20 mL was used for anion analysis using ion chromatography (Dionex ICS 2000), and 10 mL was acidified with nitric acid (ultrapure) to pH < 2 for arsenic analysis using GFAA (Perkin-Elmer Analyst 600). Some samples formed colloids from organic acids after addition of nitric acid; therefore, 10 profiles were reanalyzed using nitric acid digestion including peroxide, and arsenic and vanadium were analyzed using ICPMS (Agilent 7500 CE). Soil samples were then oven dried at 105 °C for 48 h to determine gravimetric water content. The resultant arsenic concentrations represent water-extractable arsenic and are referred to as arsenic throughout this paper. Concentrations of water-extractable elements are represented as micrograms of the element per kilogram of dry soil by multiplying measured concentrations in the supernatant by the ratio of the volume of DDI water to the weight of oven-dried soil (extraction ratio). Total arsenic is referred to as such throughout the paper to distinguish it from water-extractable arsenic. Total arsenic was analyzed in 24 soil samples (EPA Method 3050B) to assess relationships with water-extractable arsenic levels. Additional information related to the chemical analyses is provided in Supporting Information.

GIS analysis was conducted to assess relationships between arsenic concentrations in the aquifer and potential surficial anthropogenic sources of arsenic. If groundwater arsenic contamination is derived from surficial anthropogenic sources, arsenic concentrations should be correlated with (1) percent cropland because arsenic pesticides were only applied to cropland, (2) soil texture because recharge is related to soil texture, (3) water table depth because shallow water tables should be more readily contaminated from surficial sources, and (4) groundwater nitrate levels because nitrogen fertilizers were generally applied on the same fields as arsenic pesticides.

To assess relationships between groundwater arsenic and land cover, percentages of cropland and noncropland (grassland/shrubland) categories were calculated within a 500 m radius of each well from the 1992 National Land Cover Data (NLCD (18)). County-level statistics on cotton produc-

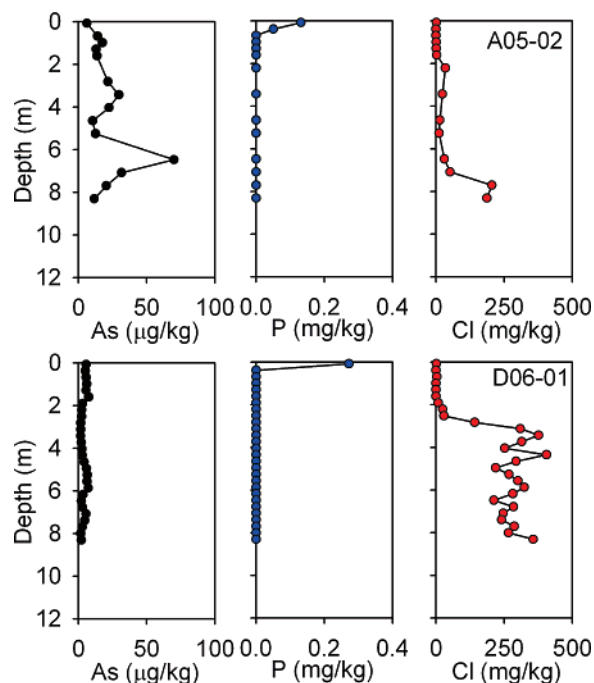


FIGURE 2. Concentration profiles of water-extractable arsenic, phosphate-P, and chloride per kilogram of dry soil in two natural grassland/shrubland settings.

tion were obtained from the National Agricultural Statistics Service (NASS) database. Distribution of cotton gins was obtained from the Texas Commission on Environmental Quality (TCEQ). Depth-weighted mean soil clay percentages were estimated within a 500 m radius of each well using data from Soil Survey Geographic (SSURGO) database (USDA, 1995). Predevelopment (earliest data prior to 1980) aquifer water table depth, aquifer-saturated thickness, and the most recent groundwater nitrate levels (December 2006) were obtained from the TWDB database.

Results and Discussion

Control Provided by Arsenic Distribution beneath Natural Ecosystems. Arsenic concentrations beneath natural ecosystems (grassland/shrubland) are lower near the surface (peak range of 1.6–14.3 μ g As/kg dry soil, ≤ 1 m depth) and are underlain by higher arsenic concentrations (peak range of 7.2–69.6 μ g/kg; 5.9–21.4 m depth) (Figure 2, Table 1). Phosphate-P levels are generally low throughout these profiles. The most likely source of elevated arsenic levels at depth is geologic. High correlation between arsenic and vanadium ($r = 0.77$, $p < 0.01$) also supports a geologic source because previous studies have found such correlations in areas where arsenic is derived from geologic sources (26) (Supporting Information, Figure S1). Low correlation ($r = 0.07$, $p = 0.47$) between arsenic and chloride (which is derived from atmospheric deposition) and the absence of high arsenic levels in some profiles suggest that arsenic is not derived from an atmospheric source. Previous studies have shown large accumulations of chloride in these settings, representing accumulation times of 4200–17 000 years, and upward decreases in matric potential, indicating upward water movement (15).

Arsenic Distribution beneath Cotton Cropland. Arsenic concentrations beneath rainfed cotton cropland (16 profiles) were quite variable (Table 1). High arsenic concentrations were found in the upper meter with depth-weighted mean concentrations up to 31.6 μ g/kg (Figure 3, Table 1). Peak arsenic concentrations occurred at the surface (2 profiles), 0.1 m depth (11 profiles), and 0.4 m depth (3 profiles),

TABLE 1. Concentrations of Arsenic (As), Phosphate-Phosphorus (P), and Nitrate-Nitrogen and Nitrite-Nitrogen (sum of NO₃-N and NO₂-N, N) per Kilogram of Dry Soil^a

borehole	setting	date	total depth (m)	samples	flushed depth (m)	mean ≤ 1 m depth			mean > 1 m depth			maximum ≤ 1 m depth			maximum > 1 m depth		
						As (μg/kg)	P (mg/kg)	N (mg/kg)	As (μg/kg)	P (mg/kg)	N (mg/kg)	As (μg/kg)	depth (m)	age at 1 m (year)	As (μg/kg)	depth (m)	age at As max (year)
A05-02	natural	5/23/05	8.5	14	1.6	9.7	0.04	0.8	23.6	0.02	0.8	14.3	1.0	8	63.7	6.5	1340
D06-01	natural	2/14/06	8.4	28	1.9	5.6	0.05	0.4	3.7	0.00	0.7	6.0	1.0	18	7.2	5.9	10400
MWR	natural	8/5/01	15.2	14	0.8	2.0	0.00	0.6	17.1	0.00	0.4	2.0	0.9	578	41.5	13.1	18600
LY06-01	natural	7/12/06	29.0	34	3.0	2.9	0.13	0.8	14.8	0.01	0.3	4.9	0.1	15	69.6	21.4	26800
T06-03	natural	8/10/06	24.0	24	1.9	1.6	0.00	0.4	7.4	0.00	0.3	1.6	0.4	16	13.5	9.5	1920
HI05-01	gin	6/19/05	5.2	9	1.6	308	9.02	0.1	116.2	0.56	13.7	541.6	0.7	46	943.1	1.3	54
B05-01	rainfed	5/27/05	11.2	22	7.7	1.7	0.07	3.2	9.1	0.06	2.5	4.2	0.1	5	19.4	6.5	46
B05-02	rainfed	5/27/05	6.2	14	2.8	1.7	0.08	4.3	12.3	0.00	1.3	4.5	0.1	13	18.2	4.0	907
B06-01	rainfed	2/16/06	4.7	16	2.5	5.8	0.12	0.9	3.5	0.00	22.5	20.8	0.0	7	6.9	4.6	753
D05-01	rainfed	6/3/05	4.1	10	4.0	20.6	0.28	4.1	9.5	0.01	1.7	35.9	0.1	5	23.0	2.8	17
D06-02	rainfed	2/14/06	9.3	19	9.2	31.6	0.30	0.8	18.2	0.00	4.4	63.8	0.4	4	55.3	9.2	37
D06-03	rainfed	2/15/06	7.9	20	7.9	11.5	0.38	0.7	6.2	0.01	3.5	18.1	0.0	9	12.6	7.9	66
H05-01	rainfed	6/3/05	6.2	14	6.2	13.5	0.09	2.4	36.3	0.05	8.3	39.2	0.1	5	76.8	4.6	32
H05-02	rainfed	6/3/05	8.5	17	1.0	9.9	0.04	38.7	3.2	0.02	10.8	34.8	0.1	22	10.9	1.6	726
G05-01	rainfed	5/31/05	5.0	12	1.6	3.8	0.19	6.1	12.0	0.09	4.6	6.2	0.1	18	17.7	4.0	3300
G05-02	rainfed	5/31/05	10.8	14	8.9	22.7	0.28	0.5	6.7	0.01	6.3	35.5	0.4	4	13.2	5.9	37
L05-01	rainfed	5/26/05	8.6	17	3.4	2.1	0.02	2.1	16.3	0.03	9.1	6.5	0.1	11	37.1	3.4	101
M05-01	rainfed	6/1/05	7.6	16	7.5	7.9	0.08	1.5	17.1	0.01	2.2	32.8	0.1	2	29.6	6.5	22
M05-02	rainfed	6/1/05	9.0	18	2.2	13.3	0.20	4.3	10.4	0.15	6.9	29.6	0.1	8	22.6	8.9	2500
M05-03	rainfed	6/2/05	6.6	14	6.5	21.4	0.60	5.2	8.3	0.01	0.8	35.4	0.1	4	11.0	2.8	9
M05-04	rainfed	6/2/05	4.6	11	3.4	9.9	0.07	4.4	6.1	0.10	5.1	20.1	0.1	9	10.2	4.5	303
T05-01	rainfed	5/24/05	7.2	10	5.9	2.9	0.09	4.9	11.2	0.00	11.5	3.8	0.4	5	22.3	4.6	40
T05-03	irrigated	5/25/05	12.6	15		9.0	0.74	3.6	29.9	0.03	14.5	29.1	0.1		54.5	7.1	
T05-04	irrigated	5/25/05	10.2	12		11.4	0.91	3.2	3.6	0.00	6.0	27.7	0.1		27.7	9.5	
JRW	irrigated	6/26/01	45.7	27		3.4	0.15	3.7	16.1	0.06	0.9	4.1	0.3		29.7	43.0	
MPL	irrigated	7/1/01	42.4	27		1.8	0.00	16.0	8.7	0.00	1.4	1.8	0.8		19.9	36.9	
T05-02	playa	5/24/05	9.3	15		10.3	0.73	7.0	24.7	0.35	0.5	26.9	1.0		66.5	3.4	

^a Pore-water ages at the indicated depth were calculated using the chloride mass balance method. Mean concentration values are depth-weighted means over the indicated depth intervals. Flushed depth indicates depth of chloride flushing (Cl < 10 Mg/kg). TD indicates flushed zone to total depth. Ages for profiles in irrigated and playa settings could not be determined because of lack of information on chloride input. The first letter in borehole setting refers to the county: A, Andrews; B, Bailey; D, Dawson; G, Gaines; H, Howard; HI, Hidalgo; L, Lamb; LY, Lynn; M, Martin; T, Terry; MWR (Bailey) and JRW & MPL (Cochran) from (23). The second two digits refer to the year of drilling, for example, 05, 2005, and the last two digits refer to the borehole sequence number in that county. Mean values of parameters represent depth-weighted values.

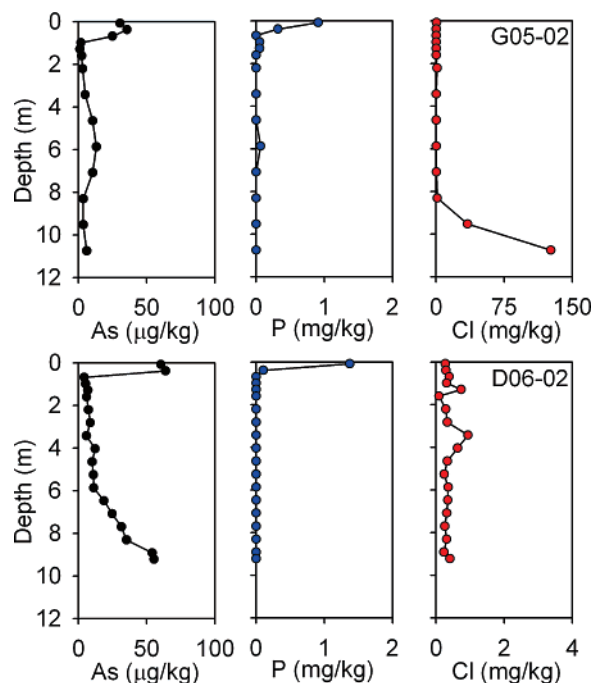


FIGURE 3. Representative concentration profiles of water-extractable arsenic, phosphate-P, and chloride per kilogram of dry soil in rainfed agricultural areas.

supporting a surface anthropogenic source. This near-surface zone of high arsenic strongly correlates with phosphate-P concentrations ($r = 0.70$, $p < 0.01$) (Supporting Information,

Figure S2), which indicates a pesticide source for arsenic because of probable use of both phosphate fertilizer and arsenic pesticide on cropland. Typical phosphate fertilizer application rates in the SHP range from 8 to 32 kg/ha (27). Sampled soil profiles in the SHP range from 1 to 16 km from cotton gins; therefore, most sites are unlikely to have had cotton gin waste applied, which is consistent with land-owner records. The pesticide source for arsenic is also supported by high correlation ($r = 0.82$, $p < 0.01$) between arsenic and phosphate-P in a profile adjacent to a cotton gin in the Gulf Coast (Supporting Information, Figure S3).

Correlations between arsenic and nitrate-N in profiles in the SHP are poor ($r = 0.08$, $p = 0.21$), probably because of dissimilarity in chemical behavior of arsenic and nitrate and possible flushing of nitrate. Arsenic correlates with vanadium ($r = 0.74$, $p < 0.01$), which may reflect the natural geologic origin for arsenic pesticide (Supporting Information, Figure S1). Pore-water ages based on chloride data in the upper meter are young (2–22 years; mean 8 years) (15) and indicate that arsenic derived from pesticide applications is being retained in this zone.

High arsenic concentrations were also found at depths > 1 m in some rainfed profiles with depth-weighted mean concentrations up to 36.3 μg/kg and peak concentrations up to 76.8 μg/kg (Table 1). Elevated arsenic at these depths most likely reflects a geologic source based on similarity in arsenic distributions found in natural ecosystem profiles and a lack of phosphate at these depths. Chloride data indicate pore-water ages at depths of arsenic peaks ranging from 100 to 3300 years in 7 of the 16 rainfed profiles, which predate arsenic pesticide application and further support a geologic source for arsenic in this zone. In addition, high arsenic levels in pore water with ages younger than 100 years in the remaining

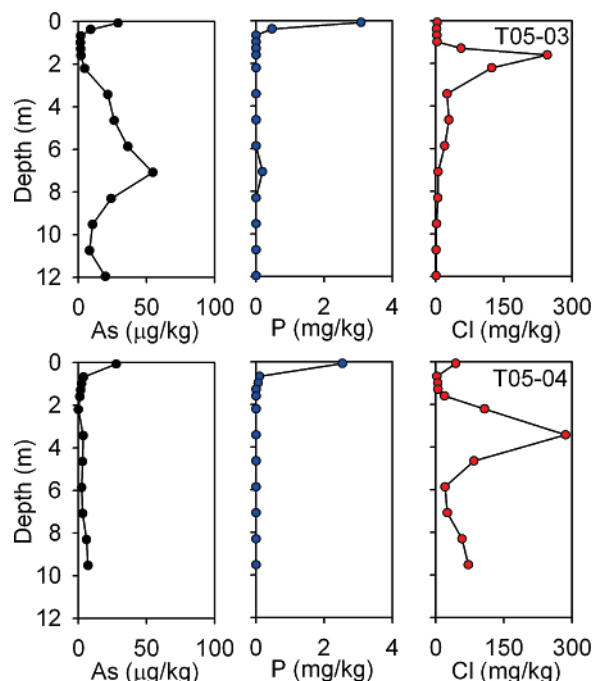


FIGURE 4. Representative concentration profiles of water-extractable arsenic, phosphate-P, and chloride per kilogram of dry soil in irrigated agricultural areas.

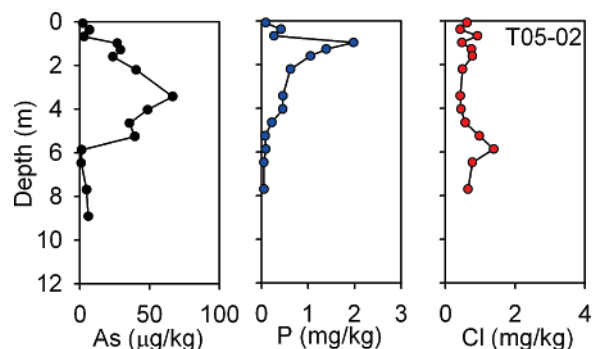


FIGURE 5. Concentration profiles of water-extractable arsenic, phosphate-P, and chloride per kilogram of dry soil beneath a playa surrounded by irrigated agriculture.

9 profiles may also indicate a geologic source because arsenic is generally much less mobile than chloride. Highest arsenic concentrations below 1 m depth were found in the chloride flushed zone in 9 of the 16 profiles (Table 1), indicating that, unlike chloride, arsenic has not been flushed by increased water fluxes beneath rainfed agriculture.

Arsenic concentrations beneath four irrigated agricultural areas were similar to those beneath rainfed agricultural areas; high arsenic concentrations in the upper meter correlated with phosphate and high arsenic concentrations were found at depths of 7.1–43.0 m (Figure 4, Table 1). Elevated arsenic in the near surface is related to pesticide application, whereas the deeper arsenic is geogenic. There is no evidence that soil arsenic is differentially leached by higher downward water fluxes beneath irrigated crops relative to rainfed crops.

High arsenic concentrations (maximum 66.5 μg/kg, depth 3.4 m) were also found mostly in the upper 5.3 m beneath a playa that is surrounded by irrigated cotton (Figure 5, Table 1). Arsenic in this profile may result from elevated arsenic in runoff to the playa from irrigated fields and generally higher water fluxes (70–120 mm/year (21, 22)) beneath playas relative to surrounding interplaya areas. Most recharge to the High Plains aquifer in natural ecosystems occurs through

playas (22). High phosphate concentrations are also found beneath the playa; however, the phosphate-P peak (2.0 mg/kg) is shallower (1.0 m depth) than the arsenic peak (3.4 m depth). Deeper penetration of arsenic relative to phosphate may be caused by competitive desorption of arsenic by phosphate, which has been found in orchard sites in Washington state (8). Arsenic and phosphate are highly correlated in this profile when the peaks are superimposed ($r = 0.85$, $p < 0.01$). Evaluation of arsenic beneath playas was restricted to a single profile, and future studies should expand investigations beneath playas.

Total arsenic concentrations measured in this study ranged from 0.7 to 9.7 mg As/kg dry soil (mean 3.5 mg/kg, 24 selected soil samples) (Supporting Information, Figure S4). Total arsenic levels in the upper meter (9 samples) ranged from 0.7 to 8.2 mg/kg (mean 3.5 mg/kg) and are similar to total arsenic levels (≤ 3.9 mg/kg; 7 sites, 44 samples) found in a previous study of arsenic in soils in the SHP where arsenic acid and gin trash were applied (16). These total arsenic levels are similar to average arsenic levels in soils in the U.S. (7 mg/kg) (28). Although the number of analyses is limited, the data suggest that arsenic pesticide applications have not increased total arsenic levels in the soils substantially.

Relationship of Groundwater Arsenic Concentrations to Indicators of Anthropogenic Arsenic. Cotton production is collocated with areas of high groundwater arsenic, as shown by the correlation ($r = 0.48$, $p = 0.01$) between median county-level groundwater arsenic concentrations and median annual county area planted with cotton (1968–1992; Supporting Information, Figure S5). However, groundwater arsenic concentrations are poorly correlated with percent cultivated land within a 500 m radius of each well ($r = -0.15$, $p < 0.01$) (Figure S6). Groundwater arsenic concentrations were negatively correlated with distance from nearest cotton gin ($r = -0.18$, $p < 0.02$, Figure S7). Groundwater arsenic concentrations are negatively correlated with percent clay content ($r = -0.39$, $p < 0.01$) (Figure S8), which may suggest that arsenic is not derived from a surficial source because most recharge is focused beneath playas whose density is positively correlated with clay content in the SHP ($r = 0.75$, $p < 0.01$). Soil texture is finer grained in the north and coarser to the south where arsenic levels are highest. A low negative correlation ($r = -0.31$, $p < 0.01$) between groundwater arsenic concentrations and predevelopment depth to groundwater does not strongly support a surficial arsenic source because although the negative sign supports a linkage, the magnitude of the correlation is low (Figure S9). Correlation between groundwater arsenic and nitrate concentrations is relatively low ($r = 0.30$, $p < 0.01$), which may suggest a nonanthropogenic source of arsenic (Figure S10). Therefore, regional analysis of groundwater arsenic data relative to various indicators of anthropogenic sources does not strongly support a surface anthropogenic source for groundwater arsenic contamination in the SHP.

Implications for Environmental Quality. The results of this study have important implications for environmental quality. Restriction of anthropogenic arsenic to the upper meter of the soil profile in cultivated areas indicates that the probability of groundwater contamination from this source is very low. Arsenic is likely sorbed onto iron oxides and hydroxides that are common and coat abundant quartz grains (28). In addition, detrital iron oxides (magnetite and hematite) make up most of the accessory minerals in the subsurface (28). Distinguishing between anthropogenic and geological sources of arsenic is provided by correlations with phosphate derived from fertilizers, similar to correlations between As and phosphate in a profile adjacent to a cotton gin in the Gulf Coast and by profiles beneath cotton cropland in the SHP. Collocation and high correlation of elevated arsenic and phosphate-P concentrations in the near-surface zone

indicate that phosphate is generally not displacing arsenic in these profiles. Similarity in arsenic profiles beneath rainfed and irrigated land indicates that irrigation is not effective in leaching arsenic to greater depths. Irrigation application rates are generally low (250–900 mm/year) in this region because of limited water supplies (23). The shallow zone (<1 m) of moderate to high arsenic is consistent with the findings of previous studies related to arsenic in poultry litter (10) and beneath orchards (6), where elevated arsenic is generally restricted to the upper meter. Concentration of arsenic near the surface provides a long-term source for potential contamination of surface water and playas and contamination of vegetation related to bioavailability, phytotoxicity, and land zoning issues that should be evaluated in future studies.

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Supporting Information Available

Additional information related to borehole sampling methods, chemical analysis methods and results, arsenic distribution related to a cotton gin in the Gulf Coast, and GIS analysis results relating to anthropogenic arsenic indicators. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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