SUPPORTING INFORMATION

UNSATURATED ZONE ARSENIC DISTRIBUTION AND IMPLICATIONS FOR GROUNDWATER CONTAMINATION

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The following is the list of supporting materials for the article

10 figures
9 pages

Section A1. Drilling Methods

Boreholes were drilled with a direct push core rig (Model 6620DT, Geoprobe Inc., Salina KS; 22 boreholes) without any drilling fluid, with a commercial drilling rig (CME75, auger; Midway 1500, air rotary; 2 boreholes), and with a casing advance method that returned cuttings to the land surface using compressed air (3 boreholes, USGS NAWQA program)[1] to determine the distribution of arsenic in the unsaturated zone (Fig. 1).

Section A2. Chemical Analyses Methods

Anions

All anion concentrations were determined with an ion chromatograph (Dionex ICS 2000). Standards used for Cl and NO_3 analyses ranged from 0.5 to 100 mg/L (7 point calibration), whereas standards for PO_4 ranged from 0.05 to 10 mg/L (7 point calibration). Replicates and continuing calibration standards were run every 7th sample. Calibration curves had r^2 values ≥ 0.999. All replicates and continuing calibration standards had a relative percent difference ≤ 5%. The method detection limit (MDL) was 0.1 mg/L.

Cations

Arsenic concentrations were initially measured on a graphite furnace Atomic Absorption system (Perkin Elmer AAnalyst 600). Standards used ranged from 1 to 100 μg/L (7 point calibration). Replicates and continuing calibration standards were run every 10th sample. Calibration curves had r^2 values ≥ 0.999. All replicates and continuing calibration standards had a relative percent difference ≤ 5%. The MDL was 0.5 μg/L.

Arsenic and vanadium concentrations were measured with an ICPMS (Agilent 7500 CE). Standards used ranged from 0.1 to 100 μg/L (7 point calibration). Replicates and continuing calibration standards were run every 10th sample. Calibration curves had r^2 values ≥ 0.999. All replicates and continuing calibration standards had a relative percent difference ≤ 5%. The MDL was 0.5 μg/L.

Total Arsenic

Total arsenic was analyzed in 24 soil samples by alternately digesting samples in nitric acid and hydrogen peroxide (EPA Method 3050B) and analyzing arsenic using graphite furnace atomic absorption to assess relationships with water-extractable arsenic concentrations.

Section A3. Statistical Analyses Methods

Depth-weighted mean values were calculated by weighting individual sample depth intervals relative to overall borehole depth to remove bias caused by unequal sample spacing.
Correlations between parameters were determined by simple linear regression using Microsoft Excel software. Ion concentrations were log transformed prior to estimating correlations.

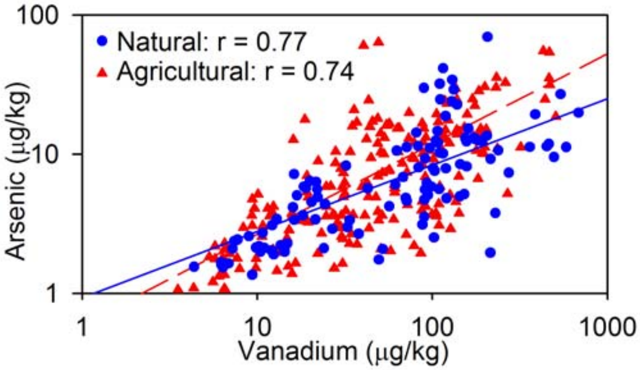

Figure S1. Relationship between water-extractable arsenic and vanadium per kg of dry soil for soil samples in profiles beneath natural grassland/shrubland settings and beneath agricultural settings. Lines represent linear regressions fit to log-transformed concentrations.

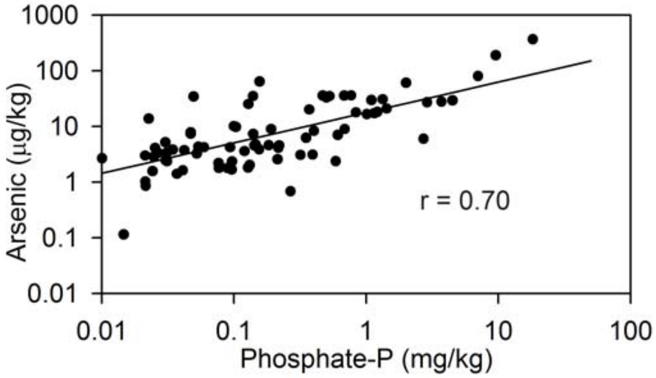

Figure S2. Relationship between water-extractable arsenic and phosphate-P per kg of dry soil for soil samples in the top 1 m in agricultural soil profiles

Section A4. Arsenic Distribution Related to Cotton Gin Waste

Results from a borehole drilled ~ 150 m from a cotton gin in the Texas Gulf Coast provide evidence of the subsurface distribution of arsenic related to surface application of cotton-gin waste. The peak arsenic concentration (943 μg As/kg dry soil) was found at a depth of 1.3 m and arsenic concentrations decreased sharply at 2.2 m depth to an average value of 13 μg/kg (Fig. S3, Table 1). Cotton-gin waste was disposed on this pasture over about 45 yr (1920s to 1960s). The zone of high arsenic concentrations has low chloride concentrations (6 to 33 mg/kg dry soil) that increase below this zone to 533 mg/kg dry soil at the base. The time required to accumulate chloride ranges from 54 yr in the upper 2.2 m to 1252 yr at the base of the profile (4.7 m). Therefore, restriction of arsenic to the shallow subsurface underlain by high chloride and associated large accumulation times indicate that the shallow arsenic from the cotton-gin waste is not connected to the underlying aquifer and is unlikely to be the source of groundwater contamination. Phosphate concentrations are also high, with a peak value of 41 mg/kg (0.7 m depth) and are highly correlated with arsenic concentrations ($r = 0.82$, $p < 0.01$). Correlation between arsenic and phosphate is attributed to co-application of both to cotton. Therefore, even in this area, where cotton-gin waste was disposed directly, high arsenic concentrations are restricted to the upper 2.2 m and are unlikely to reach the water table because the chloride data indicate very low rates of water movement.

This cotton-gin site in the Gulf Coast represents a conservative estimate of downward transport of arsenic relative to sites in the SHP because mean annual precipitation at this site (640 mm/yr) is much higher than mean annual precipitation in the SHP (~ 450 mm/yr). Arsenic loading at this site is much higher than typical arsenic pesticide applications at most of the SHP sites. Soil textures in both regions are similar (sandy clay loam, based on SSURGO data and on core texture analyses).

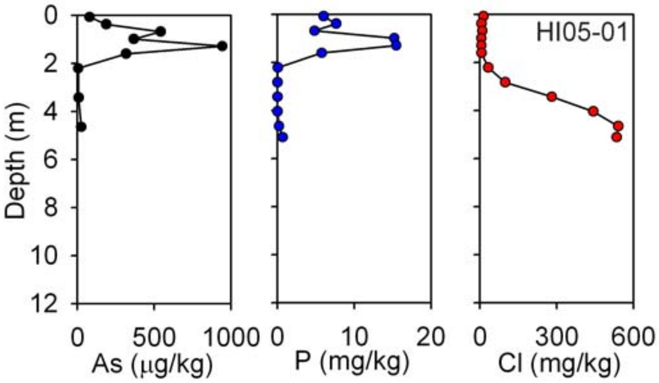

Figure S3. Concentration profiles of water-extractable arsenic, phosphate-P, and chloride per kg of dry soil from a site adjacent to a cotton gin in the Gulf Coast.

Section A5. Water-Extractable Arsenic and Total Arsenic

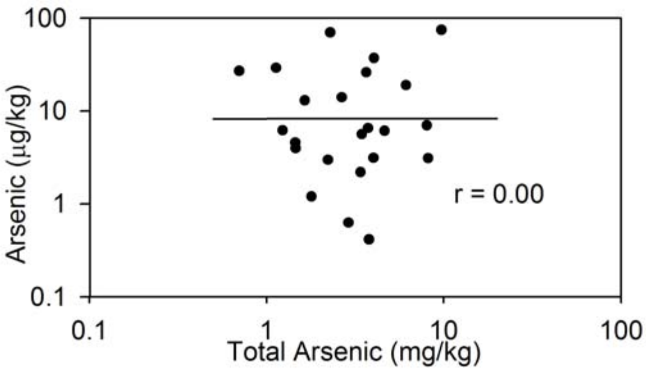

Figure S4. Relationship between water-extractable arsenic and total arsenic for 24 selected samples. Line represents linear regression. Lack of correlation between water-extractable and total arsenic (r = 0.00, p= 0.99) in this study is consistent with findings from a previous study in the SHP (r = 0.10; 44 soil samples)[2] and with what is generally reported in the literature[3] and indicates that arsenic solubility is not the controlling process in arsenic mobility.

Section A6. Relationship of Groundwater Arsenic Concentrations to Indicators of Anthropogenic Arsenic

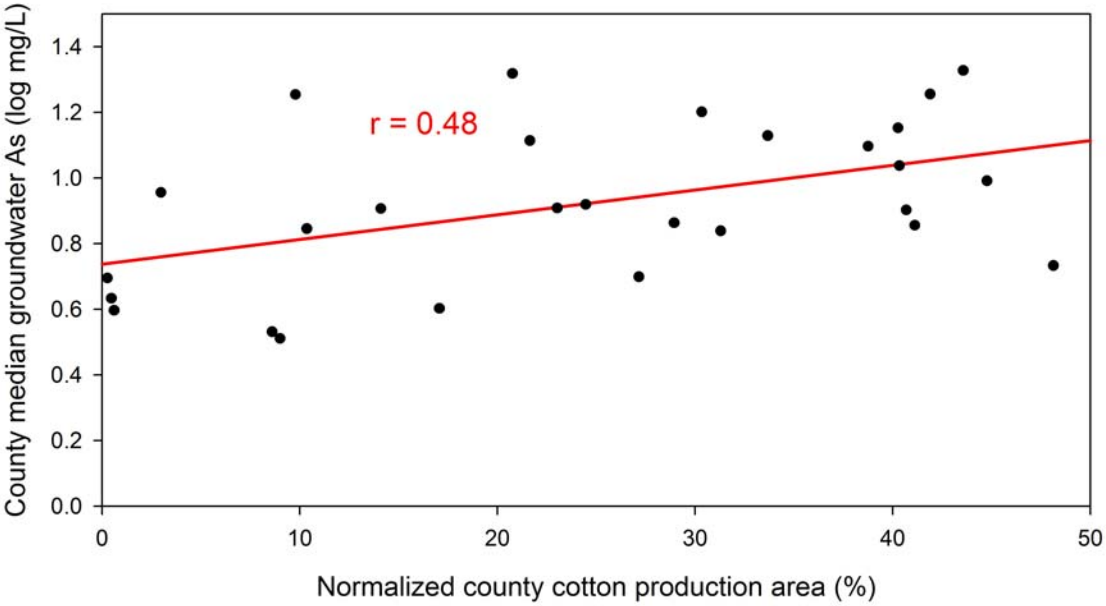

Figure S5. Relationship between median groundwater arsenic concentration and cotton production area at the county level. Points represent the median groundwater arsenic concentration for all SHP aquifer wells in each of 28 county areas versus the percentage of cotton farmland within each county based on data from 1968 to 1992 and normalized by the SHP aquifer outcrop area within the county. The line represents linear regression (r = 0.48; p = 0.01).

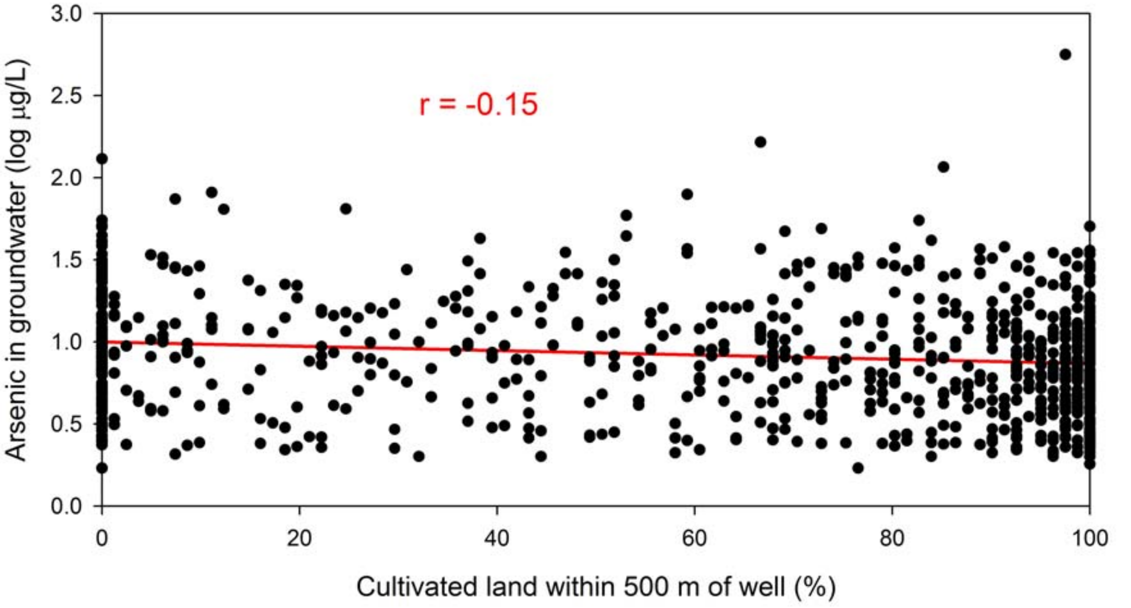

Figure S6. Relationship between groundwater arsenic concentration and cultivated land within 500 m of the well location. The line represents linear regression (r=-0.15; p < 0.01).

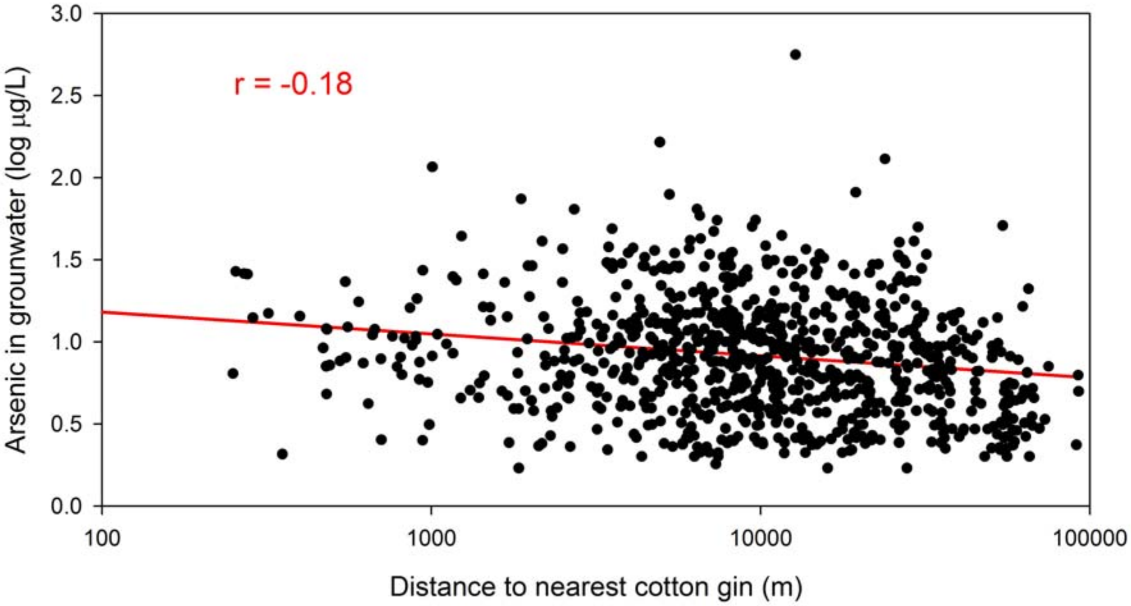

Figure S7. Relationship between groundwater arsenic concentration and distance to the nearest cotton gin facility. The line represents linear regression (r=-0.18; p < 0.02).

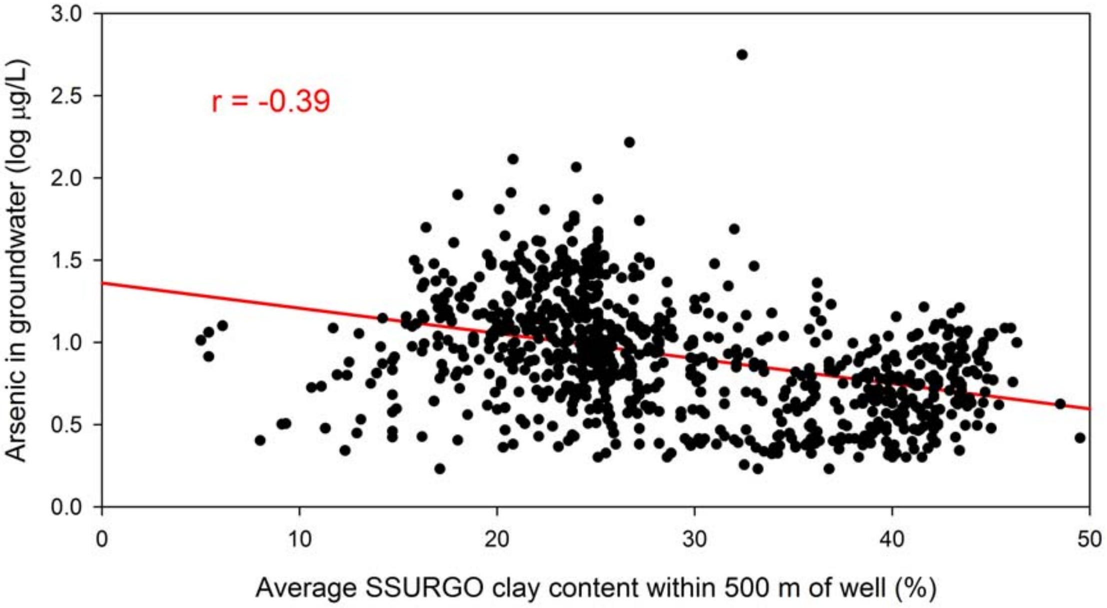

Figure S8. Relationship between groundwater arsenic concentration and depth-weighted spatial average surface soil (1.8 to 2.0 m depth) clay content based on SSURGO data. The line represents linear regression (r = -0.39; p < 0.01).

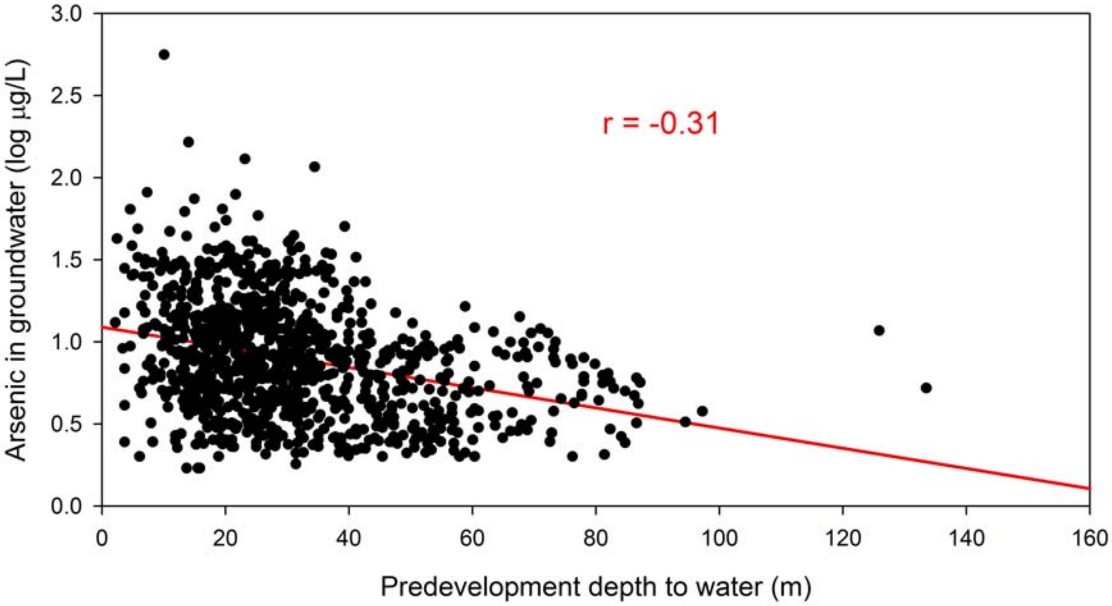

Figure S9. Relationship between groundwater arsenic concentration and aquifer predevelopment depth to water. The line represents linear regression (r = -0.31; p < 0.01).

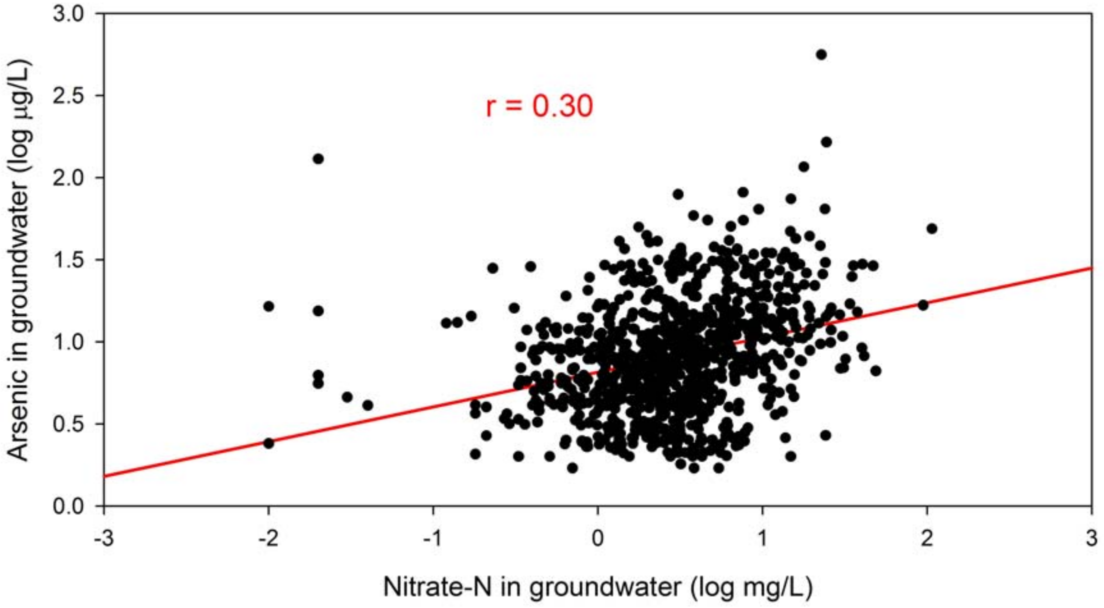

Figure S10. Relationship between groundwater arsenic concentration and groundwater nitrate-N concentration. The line represents linear regression ($r = 0.3$; $p < 0.01$).

References

(1) McMahon, P. B.; Dennehy, K. F.; Bruce, B. W.; Bohlke, J. K.; Michel, R. L.; Gurdak, J. J.; Hurlbut, D. B. Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States, *Water Resour. Res.* **2006**, *42*, doi:10.1029/2005WR004417.

(2) Aurelius, L. Investigation of arsenic contamination of groundwater occurring near Knott Texas, *Texas Department of Agriculture, Austin, TX, 53 p.* **1988**.