

Hydrogeochemical controls and health risk assessment of co-occurring nitrate and arsenic in private wells of the western Kansas High Plains Aquifer USA

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Abstract

Private domestic wells in western Kansas, USA, supply drinking water to a rural population outside routine monitoring under the Safe Drinking Water Act, while the underlying High Plains Aquifer is exposed to anthropogenic nitrate loading and geogenic arsenic mobilization. Fifty-one wells and springs across Ellis, Norton, Russell, and Decatur counties were analyzed for major ions and trace elements by inductively coupled plasma–mass spectrometry and ion chromatography. Non-parametric statistics, principal component analysis, Hazard Quotient (HQ), Incremental Lifetime Cancer Risk (ILCR), and a composite Health Risk Water Quality Index (HQ-WQI) were applied. Nitrate ranged from 0.0 to 25.2 mg L⁻¹ (mean 5.41 mg L⁻¹; 9.8% above the U.S. Environmental Protection Agency Maximum Contaminant Level), and arsenic from below detection to 19.0 µg L⁻¹ (mean 3.88 µg L⁻¹; 2.0% above the Maximum Contaminant Level). Kruskal-Wallis tests detected no significant inter-county differences (As H = 3.19, p = 0.20; nitrate H = 2.17, p = 0.34), indicating contamination is structured at the well scale. Arsenic correlated with iron (r = + 0.41, p < 0.01), pH, and fluoride, consistent with reductive dissolution of iron oxyhydroxides; nitrate correlated with chloride, calcium, and total dissolved solids, consistent with diffuse agricultural loading. The HQ-WQI classified 84.3% of wells as moderate-to-very-high pediatric risk despite 90.2% regulatory compliance, and 25.5% of wells exceeded the unacceptable adult ILCR threshold (1×10^{-4}). Prospective 5 mg L⁻¹ nitrate and 5 µg L⁻¹ arsenic thresholds reclassified 52.9% of wells as non-compliant, supporting risk-informed private well governance.

1 Introduction

In western Kansas (United States of America), rural households depend predominantly on private domestic wells as the primary, and frequently sole, source of drinking water (DeSimone et al. 2015), and two chemically distinct contaminants converge in the same aquifer: nitrate, derived from decades of intensive nitrogen fertilization, and arsenic, mobilized through geogenic mineral weathering. Both contaminants threaten the same population through different and potentially compounding pathways. The High Plains Aquifer, and specifically its Ogallala Formation, underlies this agricultural landscape as a largely unconfined, highly permeable system composed of unconsolidated Miocene–Pliocene alluvial sands, gravels, silts, and clays that offer limited natural attenuation capacity against surficial nitrogen inputs and localized geochemical arsenic release (Gutentag et al. 1984; Scanlon et al. 2012; Whittemore et al. 2018). The structural vulnerability of this aquifer system, compounded by the explicit exclusion of private domestic wells from routine monitoring requirements under the Safe Drinking Water Act (DeSimone et al. 2015), places a substantial rural population at chronic contaminant exposure risk that existing regulatory compliance frameworks are not designed to detect.

Nitrate contamination in the High Plains Aquifer has historically been evaluated through the lens of infantile methemoglobinemia, the condition that formed the original scientific basis for the United States Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 10 mg L⁻¹ for nitrate-N (USEPA 2011). However, the epidemiological literature has expanded fundamentally beyond this acute toxicological framework. Large-scale prospective cohort studies now document statistically significant

associations between chronic nitrate ingestion at concentrations as low as 3–5 mg L⁻¹ and elevated risks of colorectal cancer, thyroid dysfunction, neural tube defects, and preterm birth (Schullehner et al. 2018; Ward et al. 2018; Temkin et al. 2019). Schullehner et al. (2018), analyzing a Danish cohort of 1.7 million individuals, identified a significant dose–response relationship between colorectal cancer hazard and drinking-water nitrate concentrations beginning at 3.87 mg L⁻¹, well below the current federal MCL. Ward et al. (2018) and Temkin et al. (2019) further document associations with adverse reproductive outcomes and estimate that nitrate in United States municipal drinking water may account for between 2,300 and 12,594 annual cancer cases attributable to sub-MCL exposures. These associations implicate the endogenous formation of N-nitroso compounds, carcinogenic and endocrine-disrupting intermediates, as the probable mechanistic pathway (Fowler et al. 2013; Ward et al. 2018).

Arsenic contamination introduces a parallel and geochemically distinct public health burden. Classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC 2012), inorganic arsenic carries no demonstrably safe exposure threshold. Chronic ingestion at concentrations at or below the current USEPA MCL of 10 µg L⁻¹ has been associated with bladder, lung, and skin malignancies, cardiovascular disease, diabetes mellitus, and dermatological manifestations (Naujokas et al. 2013; National Research Council 2001). In the Ogallala Formation, arsenic enters groundwater primarily through reductive dissolution of iron oxyhydroxide minerals, a process activated under locally reducing redox conditions created by organic carbon availability, irrigation return flows, and fluctuating water-table elevations (Smedley and Kinniburgh 2002; McMahon et al. 2007; Whittemore et al. 2018). Because arsenic mobilization responds to localized sediment heterogeneity and microenvironmental redox chemistry rather than to broad regional geology, its occurrence across the High Plains is spatially discontinuous (Welch et al. 2000) and routinely undetected in the absence of systematic private-well monitoring.

The co-occurrence of nitrate and arsenic within the same aquifer system introduces hydrogeochemical complexity that single contaminant assessments cannot resolve. Nitrate-rich agricultural recharge sustains oxidizing redox conditions that suppress arsenic mobility while allowing nitrate to persist in solution; conversely, localized organic matter inputs or irrigation-induced saturation can establish reducing microenvironments that promote arsenic mobilization while denitrifying bacterial communities attenuate nitrate (McMahon and Chapelle 2008; Smedley and Kinniburgh 2002; Whittemore et al. 2018). These opposing redox dependencies mean that wells in close geographic proximity may exhibit elevated nitrate, elevated arsenic, or both simultaneously, a co-exposure scenario that requires integrated geochemical characterization and cumulative health risk modeling.

Three compounding knowledge gaps motivate the present study. First, prior groundwater investigations in western Kansas assess nitrate and arsenic as independent contaminants, precluding integrated evaluation of co-exposure, cumulative hazard, and the geochemical interactions governed by contrasting redox dynamics (Chaudhuri and Ale 2014; Whittemore et al. 2018). Second, existing assessments rely predominantly on regulatory compliance benchmarks and provide no mechanism for quantifying health risk borne by populations consuming water at sub-threshold but toxicologically relevant concentrations.

Risk-based indices calibrated to chronic daily intake and demographic-specific exposure parameters, standard in the international groundwater literature, remain underutilized in this region (Adimalla and Qian 2019). Third, the geographic structure of nitrate and arsenic contamination across western Kansas remains poorly resolved at the sub-county scale relevant to monitoring design.

Accordingly, this study characterizes the concentrations, geochemical controls, and demographically stratified health risks of nitrate and arsenic in 51 private domestic wells distributed across Ellis, Norton, Russell, and Decatur counties of the western Kansas High Plains. The specific objectives are to (i) quantify nitrate and arsenic concentrations and assess regulatory compliance against current and prospective lower thresholds; (ii) test whether contamination is structured at the county administrative scale; (iii) identify the dominant geochemical controls on contaminant occurrence using non-parametric correlation and principal component analysis; and (iv) quantify non-carcinogenic and carcinogenic health risk for adult and pediatric receptors using the USEPA Hazard Quotient (HQ) and Incremental Lifetime Cancer Risk (ILCR) frameworks, integrated through a composite Health Risk Water Quality Index (HQ-WQI).

2 Study area

The study area encompasses four contiguous counties in western Kansas, USA (Ellis, Norton, Russell, and Decatur) selected on the basis of three intersecting criteria: documented prior occurrence of nitrate and arsenic in High Plains Aquifer groundwater (Whitemore et al. 2018; McMahon et al. 2007), high density of private domestic well users without access to municipal supplies (Kansas Department of Agriculture 2022), and availability of a participating well-owner population through a postcard outreach programme. The counties span approximately 38.6°-39.9° N latitude and 100.7°-98.1° W longitude (Fig. 1) and represent the hydro-geologically heterogeneous north-central portion of the western Kansas High Plains, where agricultural land-use intensity and aquifer vulnerability are both high.

The counties overlie two primary aquifer units. The Ogallala Formation, composed of unconsolidated to weakly consolidated Miocene-Pliocene alluvial sediments (sand, gravel, silt, and clay), functions as a largely unconfined aquifer across the upland portions of all four counties (Gutentag et al. 1984; Kansas Geological Survey 2023). Quaternary alluvial deposits along the Saline and Solomon River drainages in Russell and Ellis counties form a secondary, hydraulically connected aquifer of varying thickness and permeability. Both units overlie Cretaceous chalk and shale bedrock. Water table depths range from less than 10 m in low lying alluvial settings to more than 60 m in upland Ogallala areas, with corresponding variability in contaminant travel times. Climate is semi-arid, and groundwater serves as the dominant source for drinking, irrigation, and livestock production.

Agricultural land use dominates the study area. Major crops include winter wheat and grain sorghum, both of which rely on synthetic nitrogen fertilization, with reported application rates of approximately 60–120 lb N acre⁻¹ (winter wheat) and 80–150 lb. N acre⁻¹ (grain sorghum) (Rogers et al. 2017; Kansas State University Extension 2022). Concentrated animal feeding operations are present in Ellis and Norton

counties. The combination of high nitrogen loading, permeable soils, and irrigation return flows promotes nitrate leaching into shallow groundwater (Chaudhuri and Ale 2014; Nolan and Hitt 2006), while the same hydrogeological conditions produce localized reducing microenvironments capable of mobilizing geogenic arsenic (Smedley and Kinniburgh 2002; McMahon et al. 2007).

3 Materials and methods

3.1 Sampling strategy and field protocols

Groundwater samples were collected from 51 private domestic wells and springs recruited through a voluntary participation programme, in which postcards offering free water quality testing were mailed to rural residential addresses in the four study counties. Of the 51 sampled sites, three were natural springs used as drinking water sources by participating households and were treated as functionally equivalent to wells for the health risk assessment. Site selection was therefore determined by respondent availability rather than by a probability based or spatially stratified design. This volunteer-based design introduces self-selection bias, and findings are interpreted as characterizing observed conditions at the 51 sites rather than as statistically representative regional prevalence estimates.

All wells were purged prior to sampling for a minimum of three well volumes or until field measured pH, specific conductance, dissolved oxygen, and turbidity stabilized within $\pm 10\%$ of three consecutive measurements (USEPA 2002), monitored using a calibrated multi-parameter meter. Sampling followed Eurofins Environment Testing protocols for container type and preservation. Samples for trace metal analysis (arsenic, iron, manganese, uranium) were collected in acid-washed polyethylene bottles preserved with concentrated nitric acid to pH < 2; samples for anion analysis (nitrate, chloride, sulfate, fluoride) were collected in unpreserved polyethylene bottles. All samples were stored at 4°C and transported to the laboratory within 24 h to meet holding-time requirements.

3.2 Laboratory analysis

Samples were submitted to Eurofins Environment Testing (St. Louis, Missouri, USA), accredited under the National Environmental Laboratory Accreditation Program and certified by the Kansas Department of Health and Environment for drinking-water analysis. Arsenic and uranium were quantified by inductively coupled plasma-mass spectrometry (ICP-MS) following USEPA Method 200.8 (method detection limits $0.5 \mu\text{g L}^{-1}$ and $0.1 \mu\text{g L}^{-1}$, respectively); iron and manganese by ICP-MS under the same method (method detection limits 0.05 mg L^{-1} and 0.005 mg L^{-1} , respectively). Nitrate (as NO_3^- -N) was determined by ion chromatography following USEPA Method 300.0 (method detection limit 0.05 mg L^{-1}). Major cations (Ca, Mg, Na, K) were determined by ICP-optical emission spectrometry following USEPA Method 200.7; major anions (Cl, SO_4 , F) by ion chromatography following USEPA Method 300.0. Field pH and specific conductance were measured in situ using calibrated electrochemical probes; total dissolved solids were determined gravimetrically following Standard Method 2540C; total hardness (as CaCO_3) was calculated from measured Ca and Mg using the standard formula. The laboratory implemented a comprehensive quality assurance and quality control programme including instrument calibration with NIST-traceable

reference standards, method and reagent blanks, laboratory control samples, matrix spike and matrix spike duplicates, and replicate sample analyses, all reported in the accompanying data package.

Iron (42 of 51 samples) and manganese (44 of 51 samples) frequently occurred below the analytical detection limit. For statistical calculations, half detection limit substitution ($0.025 \text{ mg L}^{-1} \text{ Fe}$; $0.0025 \text{ mg L}^{-1} \text{ Mn}$) was applied following standard USEPA guidance for censored environmental data (USEPA 2000). The censoring rate for these two parameters marginally exceeds the recommended 80% threshold; results involving Fe and Mn are therefore interpreted as indicative rather than definitive.

3.3 Statistical and multivariate analysis

Descriptive statistics (mean, median, minimum, maximum, standard deviation) were calculated for all measured parameters. The Shapiro-Wilk test confirmed strongly right skewed, non-normal distributions for both arsenic ($W = 0.643$, $p < 0.001$; skewness 2.63; excess kurtosis 12.27) and nitrate ($W = 0.595$, $p < 0.001$; skewness 2.31; excess kurtosis 6.11). Non-parametric methods were therefore used as the primary inferential framework. The Wilcoxon signed-rank test compared median contaminant concentrations against current MCL values. Spearman rank-order correlation (ρ) was used as the primary measure of association between contaminants and major ions; Pearson product-moment correlations (r) were calculated in parallel for descriptive completeness. The Kruskal-Wallis one-way analysis of variance by ranks (Kruskal and Wallis 1952) tested for inter-county differences (Ellis $n = 22$; Norton $n = 18$; Russell $n = 7$; Decatur $n = 4$ was excluded from inter-county comparison due to insufficient sample size); Dunn's post-hoc test with Bonferroni correction identified driving pairs where the Kruskal-Wallis test was significant. Statistical significance was assessed at $\alpha = 0.05$.

Principal component analysis (PCA) was performed on z-score-standardized values for 14 hydro-chemical parameters using the correlation matrix; components with eigenvalues ≥ 1 (Kaiser criterion) were retained. Hydro-chemical facies were characterized via a Piper trilinear diagram constructed from major ion concentrations converted to milliequivalents per litre. Geographic distributions of contaminant concentrations and Hazard Quotient values were displayed as proportional-symbol maps at the 51 georeferenced well locations; given uneven spatial distribution and sample density insufficient for reliable geostatistical interpolation, no spatial interpolation was applied (Adimalla and Qian 2019; Lapworth et al. 2017).

3.4 Health risk assessment

Quantitative health risk assessment followed the USEPA (1989) framework. For each contaminant and each receptor, chronic daily intake (CDI) through ingestion was calculated as Eq. (1):

$$CDI = (C \times IR \times EF \times ED) / (BW \times AT)$$

(1)

where C is the measured contaminant concentration in drinking water (mg L^{-1} ; arsenic was converted from $\mu\text{g L}^{-1}$), IR is the daily ingestion rate (L day^{-1}), EF is the exposure frequency (days year^{-1}), ED is the

exposure duration (years), BW is body weight (kg), and AT is the averaging time for non-carcinogenic risk (= ED × 365 days). Exposure parameters (Table 1) were drawn from the USEPA Exposure Factors Handbook (USEPA 1989, 2011) and are consistent with values widely applied in groundwater health risk studies (Adimalla and Qian 2019; Li et al. 2016).

Table 1

Exposure parameters and reference doses used in non-carcinogenic and carcinogenic health risk assessment for adult and pediatric receptors.

Parameter	Adult	Child	Units	Source
Ingestion rate (IR)	2.0	1.0	L day ⁻¹	USEPA 2011
Body weight (BW)	70	15	kg	USEPA 2011
Exposure duration (ED)	30	6	years	USEPA 1989
Exposure frequency (EF)	365	365	days year ⁻¹	USEPA 1989
Averaging time, non-carcinogenic (AT _{NC})	10,950	2,190	days	ED × 365
Averaging time, carcinogenic (AT _C)	25,550	25,550	days	USEPA 1989
Reference dose, As (RfD)	3 × 10 ⁻⁴	3 × 10 ⁻⁴	mg kg ⁻¹ day ⁻¹	USEPA IRIS
Reference dose, NO ₃ (RfD)	1.6	1.6	mg kg ⁻¹ day ⁻¹	USEPA IRIS
Oral slope factor, As (SF)	1.5	1.5	(mg kg ⁻¹ day ⁻¹) ⁻¹	USEPA IRIS 2024

Non-carcinogenic risk was quantified as the dimensionless Hazard Quotient (Eq. 2):

$$HQ = CDI / RfD$$

(2)

where RfD is the oral reference dose (USEPA IRIS): 0.0003 mg kg⁻¹ day⁻¹ for inorganic arsenic and 1.6 mg kg⁻¹ day⁻¹ for nitrate-N. Four HQ values were computed per well (HQ_{As,AD}; HQ_{As,N}; HQ_{NO3,AD}; HQ_{NO3,N} for adult and child receptors). HQ < 1 indicates intake below the reference dose; HQ ≥ 1 identifies wells warranting priority attention.

Because arsenic is a Group 1 human carcinogen with no demonstrably safe exposure threshold, an Incremental Lifetime Cancer Risk assessment was conducted (Eq. 3):

$$ILCR = CDI_{As} \times SF$$

(3)

where SF is the USEPA oral cancer slope factor for inorganic arsenic, $1.5 \text{ (mg kg}^{-1} \text{ day}^{-1})^{-1}$ (USEPA 2005), and CDI is computed with averaging time extended to the lifetime ($70 \text{ years} \times 365 = 25,550 \text{ days}$). Risk classifications follow the USEPA carcinogenic risk spectrum: de minimis ($< 1 \times 10^{-6}$), cautionary ($1 \times 10^{-6} - 1 \times 10^{-4}$), and unacceptable ($> 1 \times 10^{-4}$) (USEPA 1989).

A composite Health Risk Water Quality Index (HQ-WQI) was derived per well, following Adimalla (2019), as the sum of the child arsenic and child nitrate Hazard Quotients (Eq. 4):

$$\text{Composite child HQ} = \text{HQ}_{\text{As}} + \text{HQ}_{\text{N}}$$

(4)

Wells were classified into five categories based on the composite child HQ: very low (< 0.10), low ($0.10 - 0.49$), moderate ($0.50 - 0.99$), high ($1.00 - 2.00$), and very high (> 2.00). The pediatric receptor was selected as the basis for the composite index because children exhibit the highest Hazard Quotients across wells and contaminants and represent the most conservative, health-protective receptor.

To evaluate sensitivity of the compliance landscape to ongoing regulatory revision, prospective lower thresholds of 5 mg L^{-1} (nitrate-N) and $5 \mu\text{g L}^{-1}$ (arsenic), motivated by the epidemiological evidence cited in the Introduction, were applied as a counterfactual MCL scenario, and county-level compliance rates were recalculated.

4 Results and discussion

4.1 Hydrogeochemical baseline

Groundwater across the 51 sampled sites exhibited a neutral to slightly alkaline pH regime (range 7.0–8.1; mean 7.67; standard deviation 0.23), consistent with carbonate buffered Ogallala Formation aquifers. Specific conductance ranged from 404 to 2,190 $\mu\text{S cm}^{-1}$ (mean 938 $\mu\text{S cm}^{-1}$), and total dissolved solids ranged from 259 to 1,400 mg L^{-1} (mean 600 mg L^{-1}), with 26 of 51 wells (51.0%) exceeding the USEPA secondary standard of 500 mg L^{-1} . Calcium (mean 128 mg L^{-1}) and bicarbonate dominated the major-ion suite, and calcium-bicarbonate (Ca-HCO_3) was identified as the dominant hydro-chemical facies in the Piper trilinear diagram (Fig. 2), confirming carbonate dissolution as the primary control on baseline groundwater chemistry. A subset of wells in Ellis and Decatur counties plotted toward the Na–Cl field, indicating either cation exchange along extended flow paths or secondary contributions from evaporite dissolution and anthropogenic salinity; these wells corresponded spatially with the highest specific conductance and total dissolved solids in the dataset.

4.2 Arsenic: distribution, geochemical controls, and non-carcinogenic risk

Arsenic concentrations ranged from below the analytical detection limit ($0.5 \mu\text{g L}^{-1}$) to $19.0 \mu\text{g L}^{-1}$ (mean $3.88 \mu\text{g L}^{-1}$; standard deviation $2.98 \mu\text{g L}^{-1}$; median $3.30 \mu\text{g L}^{-1}$). The distribution was strongly right skewed (skewness 2.63; excess kurtosis 12.27), driven by a single high concentration outlier in Norton County (well NT-19; $19.0 \mu\text{g L}^{-1}$), which was the sole exceedance of the USEPA MCL of $10 \mu\text{g L}^{-1}$ (2.0% of the sampled population). The Wilcoxon signed-rank test confirmed that the median arsenic concentration was significantly below the MCL ($W = 31$, $p < 0.001$). Wells with arsenic $> 5 \mu\text{g L}^{-1}$ in Norton County formed a spatially coherent cluster spanning approximately 30 km, consistent with localized geogenic mobilization rather than random distribution.

Spearman and Pearson correlation analyses (Fig. 3a) confirmed the geochemical interpretation. The Pearson correlation between arsenic and iron was $r = +0.407$ ($p = 0.003$), the strongest linear association in the dataset, providing direct statistical evidence of co-mobilization through reductive dissolution of iron oxyhydroxide phases. Spearman correlations between arsenic and pH ($\rho_s = +0.328$, $p = 0.019$) and between arsenic and fluoride ($\rho_s = +0.327$, $p = 0.019$) are consistent with alkaline-pathway geogenic enrichment: under elevated pH, surface desorption of arsenate from mineral surfaces intensifies, and fluoride mobilization from calcium–fluoride mineral phases that host arsenic in volcanic-ash-derived Ogallala sediments proceeds through analogous pH-dependent mechanisms (Smedley and Kinniburgh 2002). All other arsenic–major-ion associations were non-significant ($p > 0.05$), indicating that arsenic mobility is decoupled from bulk groundwater chemistry and governed by localized redox heterogeneity at the sub-well scale.

The Kruskal–Wallis test detected no statistically significant difference in arsenic concentrations among Ellis, Norton, and Russell counties ($H = 3.19$, $p = 0.203$; Dunn's pairwise adjusted $p > 0.05$ for all three comparisons; Table 2). This non-significant inter-county result is analytically important: it falsifies the implicit assumption underlying county-level compliance monitoring that contamination is structured at the administrative county scale. Instead, arsenic occurrence is controlled at the sub-county, well-specific level by local sediment facies, organic carbon availability, and micro-scale redox conditions, the hydrogeological heterogeneity that well-by-well monitoring is designed to detect and that county-level surveys systematically miss.

Adult arsenic Hazard Quotients ranged from 0 to 1.81 (mean 0.370; standard deviation 0.284), and child Hazard Quotients ranged from 0 to 4.22 (mean 0.863; standard deviation 0.663). One well, NT-19 in Norton County, exceeded $HQ \geq 1$ for both adult (1.81) and child (4.22) receptors, constituting the sole well at which arsenic ingestion through drinking water posed an unacceptable non-carcinogenic risk under the USEPA framework. A second Norton County well ($7.6 \mu\text{g L}^{-1}$) produced child $HQ = 1.44$, an additional pediatric concern below the current MCL. The child arsenic Hazard Quotient distribution (median 0.734) substantially exceeded the adult distribution (median 0.315) across all 51 sites, reflecting the proportionally greater body-weight-normalized daily intake assigned to the pediatric receptor, a pattern that holds even when individual well concentrations remain below regulatory thresholds (Naujokas et al. 2013; National Research Council 2001).

Table 2

Kruskal–Wallis one-way analysis of variance by ranks for arsenic and nitrate-N concentrations among study counties, with Dunn's post-hoc pairwise comparisons (Bonferroni-corrected). The non-parametric tests were applied because both variables violated normality (Shapiro–Wilk $p < 0.001$). Decatur ($n = 4$) was excluded from inter-county comparison owing to insufficient sample size.

Test	Variable	H (χ^2)	df	p-value	Conclusion
Kruskal–Wallis	Arsenic ($\mu\text{g L}^{-1}$)	3.19	2	0.203	Not significant
Kruskal–Wallis	Nitrate-N (mg L^{-1})	2.17	2	0.338	Not significant
Dunn's pairwise (Bonferroni)	Comparison	Z	—	Adj. p	Significance
Arsenic	Ellis vs. Norton	0.84	—	> 0.05	Not significant
Arsenic	Ellis vs. Russell	0.61	—	> 0.05	Not significant
Arsenic	Norton vs. Russell	1.12	—	> 0.05	Not significant
Nitrate-N	Ellis vs. Norton	1.03	—	> 0.05	Not significant
Nitrate-N	Ellis vs. Russell	0.74	—	> 0.05	Not significant
Nitrate-N	Norton vs. Russell	0.48	—	> 0.05	Not significant

4.3 Nitrate: distribution, anthropogenic sources, and non-carcinogenic risk

Nitrate-N concentrations ranged from 0.0 to 25.2 mg L^{-1} (mean 5.41 mg L^{-1} ; standard deviation 5.04 mg L^{-1} ; median 4.01 mg L^{-1}), with five wells (9.8%) exceeding the USEPA MCL of 10 mg L^{-1} (maxima 10.2, 13.8, 19.3, 21.5, and 25.2 mg L^{-1}). The exceedance wells are distributed across Norton ($n = 3$) and Ellis ($n = 2$) counties, spatially consistent with the highest intensity of irrigated cropland and documented nitrogen fertilizer application rates (Chaudhuri and Ale 2014). The Wilcoxon signed-rank test confirmed that the median nitrate-N concentration was significantly below the MCL ($W = 45$, $p < 0.001$). Application of the prospective 5 mg L^{-1} threshold reclassified 21 of 51 wells (41.2%) as exceeding the health protective benchmark, including 11 Ellis and 3 Norton county wells in the 5–10 mg L^{-1} range that Schullehner et al. (2018) and Temkin et al. (2019) associate with elevated colorectal cancer risk and adverse reproductive outcomes.

Spearman correlation analysis (Fig. 4c) revealed statistically significant positive associations between nitrate-N and specific conductance ($\rho_s = +0.287$, $p = 0.041$), total dissolved solids ($\rho_s = +0.287$, $p = 0.041$), calcium ($\rho_s = +0.291$, $p = 0.038$), chloride ($\rho_s = +0.290$, $p = 0.039$), and total hardness ($\rho_s = +0.285$, $p = 0.043$), consistent with co-loading of nitrate and major ions through agricultural return flows and septic effluent infiltration (Nolan and Hitt 2006; Ransom et al. 2022). Significant negative correlations of nitrate with pH ($\rho_s = -0.325$, $p = 0.020$) and manganese ($\rho_s = -0.332$, $p = 0.018$) are geochemically diagnostic: nitrate persists in solution under oxidizing conditions that suppress reductive

mobilization of redox-sensitive metals, while wells with elevated manganese and lower nitrate reflect reducing microenvironments where denitrification attenuates the nitrate pool. This opposing redox signal is illustrated in the As–nitrate–Fe bubble plot (Fig. 4b), where wells with the highest dissolved iron cluster in the upper-left reducing zone (high As, low NO_3) and the lower-right oxidizing zone (low As, high NO_3) is populated only by small bubbles. The detection of total coliforms in 10 of 51 wells and *Escherichia coli* in 3 of 51 wells provides additional evidence that localized organic matter inputs from septic systems or livestock waste contribute to both microbial contamination and the establishment of reducing microenvironments.

The Kruskal-Wallis test detected no statistically significant difference in nitrate-N concentrations among Ellis, Norton, and Russell counties ($H = 2.17$, $p = 0.338$; all Dunn's adjusted $p > 0.05$; Table 2), consistent with sub-county heterogeneity in well construction, land-use intensity, soil permeability, and proximity to nitrogen application zones.

Adult nitrate Hazard Quotients ranged from 0 to 0.451 (mean 0.098), with no exceedances of $\text{HQ} = 1$. Child Hazard Quotients ranged from 0 to 1.05 (mean 0.228; median 0.167); HQ exceeded 1 at five wells (10.2, 13.8, 19.3, 21.5, and 25.2 mg L^{-1} nitrate-N), all in Norton and Ellis counties (Fig. 4a). The well with 25.2 mg L^{-1} nitrate-N yielded the maximum nitrate child HQ of 1.05 and raised acute methemoglobinemia concern for infant consumers in addition to chronic carcinogenic risk (USEPA 2011; Schullehner et al. 2018). The pattern, in which children experience $\text{HQ} \geq 1$ at substantially more wells than adults, is consistent with the physiological exposure model and demonstrates the demographic differential that compliance-based monitoring frameworks cannot detect.

4.4 Multivariate Hydrogeochemistry: Principal Component Analysis

Principal component analysis on z-score-standardized values for 14 hydro-chemical parameters retained five components with eigenvalues ≥ 1 , collectively explaining 86.4% of total variance (Fig. 5). Three components are analytically informative.

PC1 (42.2% of variance) was dominated by strong negative loadings on total dissolved solids (-0.395), specific conductance (-0.395), calcium (-0.356), hardness (-0.359), sulfate (-0.332), and chloride (-0.341), representing the primary mineralization gradient driven by water–rock interaction and evaporite dissolution. Wells scoring low on PC1 exhibit high salinity attributable to extended residence time and lithological exposure to carbonate and sulfate formations; wells scoring high on PC1 represent recently recharged, lower-salinity groundwater.

PC2 (16.0% of variance) was characterized by negative loadings on fluoride (-0.489), pH (-0.311), and arsenic (-0.359), contrasted with a positive loading on nitrate ($+0.247$). This component captures a geogenic enrichment / anthropogenic contamination axis: high negative PC2 scores identify wells where alkaline geogenic conditions promote co-mobilization of arsenic and fluoride from volcanic-ash-derived

sediment phases, while positive scores index the anthropogenic nitrate signal. The opposing positions of arsenic and nitrate on PC2 provide multivariate confirmation of the competing redox dependencies developed in Sects. 4.2 and 4.3.

PC3 (10.9% of variance) carries strong negative loadings on arsenic (-0.490) and iron (-0.475), representing the redox differentiation axis most directly relevant to arsenic health risk. Sites scoring low on PC3 are those where reducing microenvironments drive concurrent iron oxyhydroxide dissolution and arsenic release, the geochemical mechanism responsible for the elevated arsenic concentrations in Norton County. The PC3 loading pattern corroborates the Pearson As–Fe correlation ($r = +0.407$, $p = 0.003$) and confirms that reductive dissolution of iron oxyhydroxide phases is the dominant proximal mechanism of arsenic mobilization in this system, operating independently of the bulk mineralization gradient captured by PC1.

Together, PC1, PC2, and PC3 establish that groundwater chemistry in the four-county study domain is governed by three geochemical processes operating on partially independent axes: a primary salinity gradient (carbonate and evaporite dissolution), a geogenic-enrichment process (alkaline pH control on F and As), and a redox gradient differentiating reducing (As- and Fe-mobilizing) from oxidizing (NO_3^- -retaining) conditions. These three processes generate the observed co-contamination landscape: spatially clustered geogenic arsenic, diffusely distributed anthropogenic nitrate, and localized co-occurrence at wells where intermediate redox conditions allow both contaminants to coexist in solution.

4.5 Composite Health Risk Water Quality Index and ILCR

The composite child Hazard Quotient ($\text{HQ}_{\text{As}} + \text{HQ}_{\text{NO}_3\text{-N}}$) integrated arsenic and nitrate risk into a single site level classification (Fig. 6). One well (2.0%) was classified very low risk; five (9.8%) low; 17 (33.3%) moderate; 26 (51.0%) high; and 2 (3.9%, both in Norton County) very high. Norton County well NT-19 ($19.0 \mu\text{g L}^{-1}$ As; $10.2 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$) generated $\text{HQ}_{\text{As}} = 4.22$ and $\text{HQ}_{\text{NO}_3\text{-N}} = 1.81$, the highest overall risk in the dataset and the sole well exceeding the current arsenic MCL. A second Norton well ($7.6 \mu\text{g L}^{-1}$ As; $10.2 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$) produced composite child $\text{HQ} = 2.12$, driven by the combined arsenic and nitrate burden. In aggregate, 43 of 51 wells (84.3%) fell within Risk Categories 3–5, indicating that moderate-to-high composite non-carcinogenic risk for the pediatric receptor is the predominant groundwater condition across the study domain.

This finding is strikingly inconsistent with the regulatory compliance picture: 46 of 51 wells (90.2%) are fully compliant with current USEPA MCLs for both arsenic and nitrate, yet the HQ-WQI analysis classifies only six wells (11.8%) as genuinely low risk. The 74-percentage point divergence between regulatory compliance and health risk-based assessment is most pronounced for the pediatric receptor, for whom sub-MCL concentrations routinely produce HQ values in the moderate to high range. This compliance risk divergence constitutes the central evidence base for the monitoring policy recommendations advanced in Sect. 5.

The Incremental Lifetime Cancer Risk assessment supplemented the non-carcinogenic analysis. Adult ILCR values ranged from 0 (four wells below detection) to 3.49×10^{-4} (mean 7.13×10^{-5} ; standard deviation 5.22×10^{-5}). Thirteen wells (25.5%) yielded adult ILCR exceeding the unacceptable threshold of 1×10^{-4} , corresponding to dissolved arsenic above approximately $5.4 \mu\text{g L}^{-1}$; NT-19 recorded the highest adult ILCR at 3.49×10^{-4} ($3.49 \times$ the threshold). An additional 34 wells (66.7%) fell within the cautionary range (1×10^{-6} – 1×10^{-4}), and four wells (7.8%) fell below the de minimis threshold. For the child receptor, ILCR ranged from 0 to 1.63×10^{-4} (mean 3.33×10^{-5}). The child CDI is approximately 46.7% of the adult CDI, reflecting the shorter exposure duration and lower ingestion rate; consequently, NT-19 was the sole well exceeding 1×10^{-4} for children, and 46 wells (90.2%) fell within the cautionary range.

These ILCR results extend carcinogenic concern well beyond the single MCL exceeding site and establish arsenic ingestion as a spatially distributed, quantifiable public health hazard. The broader child cautionary footprint underscores that developmental stage exposure to even low arsenic concentrations contributes measurable carcinogenic risk, and that NT-19 represents a severe exceedance warranting priority remedial attention for households with young children.

4.6 Prospective regulatory threshold analysis

The current USEPA MCLs for arsenic ($10 \mu\text{g L}^{-1}$) and nitrate-N (10 mg L^{-1}) were not established as the most health protective thresholds technically achievable but as regulatory compromises among analytical feasibility, treatment cost, and the epidemiological knowledge base available at the time of promulgation (National Research Council 1999, 2001; USEPA 2001). Subsequent epidemiological evidence (Schullehner et al. 2018; Ward et al. 2018; Temkin et al. 2019; Naujokas et al. 2013) has generated sustained scientific and regulatory momentum toward prospective threshold reductions to 5 mg L^{-1} (nitrate-N) and $5 \mu\text{g L}^{-1}$ (arsenic). The present dataset permits a direct, empirically grounded evaluation of what such revisions would mean for the western Kansas private well population (Table 3).

Under a prospective $5 \mu\text{g L}^{-1}$ arsenic threshold, 14 of 51 wells (27.5%) would exceed the benchmark, a 13.7-fold increase over the 1 well (2.0%) currently non-compliant at $10 \mu\text{g L}^{-1}$. Prospective arsenic exceedances concentrate in Norton (6 wells; 33.3% of county sample) and Decatur (4 wells) counties, identifying these counties as facing disproportionate management burden under any future revision. Under a prospective 5 mg L^{-1} nitrate-N threshold, 21 of 51 wells (41.2%) would exceed the benchmark, a 4.2-fold increase over the 5 wells (9.8%) currently non-compliant; Ellis County carries the greatest nitrate burden under this scenario, with 11 of 22 wells (50.0%) exceeding 5 mg L^{-1} , consistent with its combination of high irrigated cropland area and concentrated animal feeding operation density. Combined, the prospective dual-threshold scenario reclassifies 27 of 51 wells (52.9%) as non-compliant, compared with 6 wells (11.8%) under current MCLs, indicating that the current regulatory framework materially underestimates the proportion of households exposed to concentrations associated with chronic disease risk in the epidemiological literature.

Table 3

County-level well compliance under current USEPA Maximum Contaminant Levels and prospective lower thresholds for arsenic and nitrate-N. "Prop." denotes the proposed prospective threshold; all current MCL exceedances are a strict subset of prospective exceedances.

County	n	As > 5 $\mu\text{g L}^{-1}$ (Prop.)	As > 10 $\mu\text{g L}^{-1}$ (MCL)	NO ₃ > 5 mg L ⁻¹ (Prop.)	NO ₃ > 10 mg L ⁻¹ (MCL)
Ellis	22	4 (18.2%)	0 (0%)	11 (50.0%)	4 (18.2%)
Norton	18	6 (33.3%)	1 (5.6%)	3 (16.7%)	3 (16.7%)
Russell	7	0 (0%)	0 (0%)	1 (14.3%)	0 (0%)
Decatur	4	4 (100%)	0 (0%)	3 (75.0%)	1 (25.0%)
Total	51	14 (27.5%)	1 (2.0%)	21 (41.2%)	5 (9.8%)

5 Conclusions and recommendations

This study provides the first integrated geochemical and demographically stratified health risk assessment of nitrate and arsenic co-occurrence across 51 private domestic wells and springs in the western Kansas High Plains Aquifer. Five principal conclusions emerge from the combined evidence.

First, nitrate-N and arsenic occur at concentrations that, while predominantly compliant with current USEPA MCLs (90.2% compliance), are associated through the Hazard Quotient and Incremental Lifetime Cancer Risk frameworks with substantial pediatric and adult risk. Composite child HQ-WQI classifies 84.3% of wells as moderate-to-very-high risk, and adult ILCR identifies 25.5% of wells as exceeding the unacceptable carcinogenic threshold. The 74-percentage-point divergence between regulatory compliance and risk-based classification represents a systematic mismatch between protections afforded by the existing regulatory framework and the chronic disease burden documented in the contemporary epidemiological literature.

Second, contamination is not structured at the county administrative scale. Kruskal-Wallis tests detected no significant inter-county differences for either contaminant (As $H = 3.19$, $p = 0.20$; NO₃ $H = 2.17$, $p = 0.34$), and Dunn's pairwise comparisons confirmed the result. Contamination is structured at the well scale by local sediment heterogeneity, redox conditions, and land-use proximity, an outcome that county-level compliance surveys are structurally incapable of resolving.

Third, geochemical controls on arsenic and nitrate are mechanistically distinct and partially opposing. Arsenic correlates with iron ($r = +0.41$), pH, and fluoride, consistent with reductive dissolution of iron oxyhydroxides under alkaline-reducing microenvironments; nitrate correlates with calcium, chloride, total dissolved solids, and specific conductance, and inversely with pH and manganese, consistent with diffuse agricultural loading sustained under oxidizing conditions. The principal component analysis confirmed three independent geochemical axes (mineralization, geogenic As–F enrichment, and Fe–As

redox), and the bubble visualization of As versus NO₃ with Fe as size demonstrates the opposing redox signal directly.

Fourth, application of prospective lower thresholds (5 mg L⁻¹ NO₃-N; 5 µg L⁻¹ As) reclassifies 52.9% of sampled wells as non-compliant, compared with 11.8% under current MCLs. This counterfactual analysis localizes within the western Kansas study domain the regulatory implications of MCL revision currently under active scientific and policy deliberation.

Fifth, the findings carry implications beyond the study domain. The integrated source–pathway–receptor methodology employed here, combining geochemical characterization, demographically stratified CDI–HQ–ILCR risk assessment, HQ–WQI composite classification, and prospective regulatory threshold analysis, provides a replicable, policy-relevant template for analogous investigations across the High Plains Aquifer system and in other rural agricultural landscapes worldwide where private domestic well dependence persists outside regulated public water supply infrastructure.

Several limitations qualify the interpretation. The volunteer-based sampling design precludes formal extrapolation to the broader regional well population; the cross-sectional, single-campaign design limits temporal representativeness; the analytical suite excluded pesticides, pharmaceuticals, and volatile organic compounds; and the absence of stable isotope data (δ¹⁵N–NO₃, δ¹⁸O–NO₃, δ²H, δ¹⁸O) precludes definitive nitrate source attribution. Future investigations should employ probability-based sampling designs stratified by land-use category and aquifer setting; longitudinal monitoring at sentinel sub-sets of high-risk wells; stable isotope analysis for nitrate source attribution; and explicit investigation of mixture toxicity for the nitrate–arsenic co-exposure scenario.

Translated into management priorities, the results recommend (i) immediate provision of point-of-use reverse osmosis treatment and quarterly re-testing at the two Norton County wells classified as very high risk; (ii) voluntary well-testing programmes for households with children under six years across Ellis and Norton counties, designed against the prospective 5 mg L⁻¹ NO₃ and 5 µg L⁻¹ As benchmarks; (iii) administrative mechanisms (e.g., property-transfer testing requirements) to bring private wells in counties with documented exceedance history under formal monitoring; and (iv) strengthened nutrient management requirements for agricultural operations overlying the unconfined Ogallala Formation in the highest-loading sub-county areas. The compliance–risk divergence demonstrated here is reproducible from the same dataset only by integrated, demographically stratified, multi-contaminant risk assessment, and constitutes the empirical case for risk-informed private well governance in the High Plains Aquifer.

Declarations

Competing interests

The authors declare that they have no competing financial or non-financial interests relevant to the content of this article.

Ethics approval and consent to participate

This study did not involve any experimental procedures on human participants, human biological samples, or personally identifiable health data; hence, human-subject ethical approval or informed consent was not applicable. Participation was limited to voluntary granting of physical access to private wells for the collection of groundwater samples for analysis of drinking water quality. The analytical results were returned to the participating households for their own information and were used in aggregate for academic research.

Clinical trial number

not applicable.

Consent to publish declaration: not applicable.

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Author Contribution

J.K.O. conceptualized the study, performed the geochemical analyses, statistical modelling (correlation, Kruskal–Wallis, principal component analysis), Hazard Quotient, Incremental Lifetime Cancer Risk, and HQ-WQI calculations, generated the figures and tables, and wrote the original manuscript. T.S. supervised the project, contributed to study design, and critically revised the manuscript. J.S. provided the field-collected groundwater chemistry dataset, methodological guidance on sampling protocols and reviewed the manuscript. R.L. contributed to the geographic information system analysis. All authors read and approved the final version.

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Data Availability

The processed groundwater chemistry dataset (51 wells; 14 hydro-chemical parameters), Hazard Quotient and Incremental Lifetime Cancer Risk calculations, and Spearman and Pearson correlation matrices that support the findings of this study are available from the corresponding author upon reasonable request. Raw analytical data packages from Eurofins Environment Testing are held under standard laboratory client-confidentiality terms; redacted summary tables, with personally identifying location information removed, can be released to facilitate replication and meta-analysis. The full groundwater chemistry dataset, sampling metadata, and analytical results supporting this study are also archived in the Fort Hays State University Scholars Repository as part of the corresponding author's M.S. thesis (Owusu 2024, <https://scholars.fhsu.edu/theses/3304/>).

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Figures

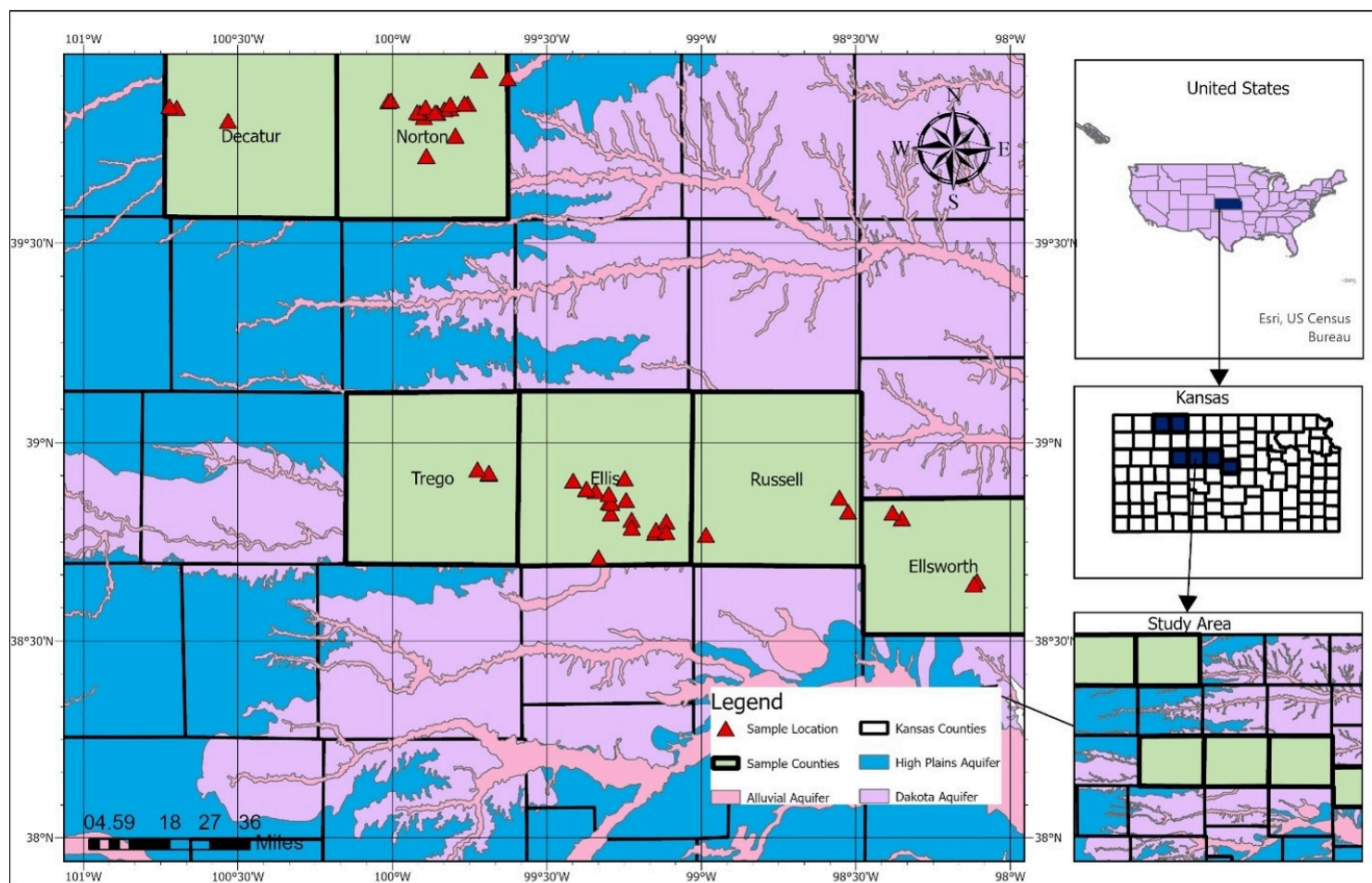


Figure 1

Location of the 51 sampled private wells and springs across Ellis, Norton, Russell, and Decatur counties, western Kansas, USA. Sampling extent is overlaid on the High Plains Aquifer extent. The inset shows the position of the study area within the contiguous United States. Map projection: NAD 1983 State Plane Kansas North; coordinate reference: WGS 84.

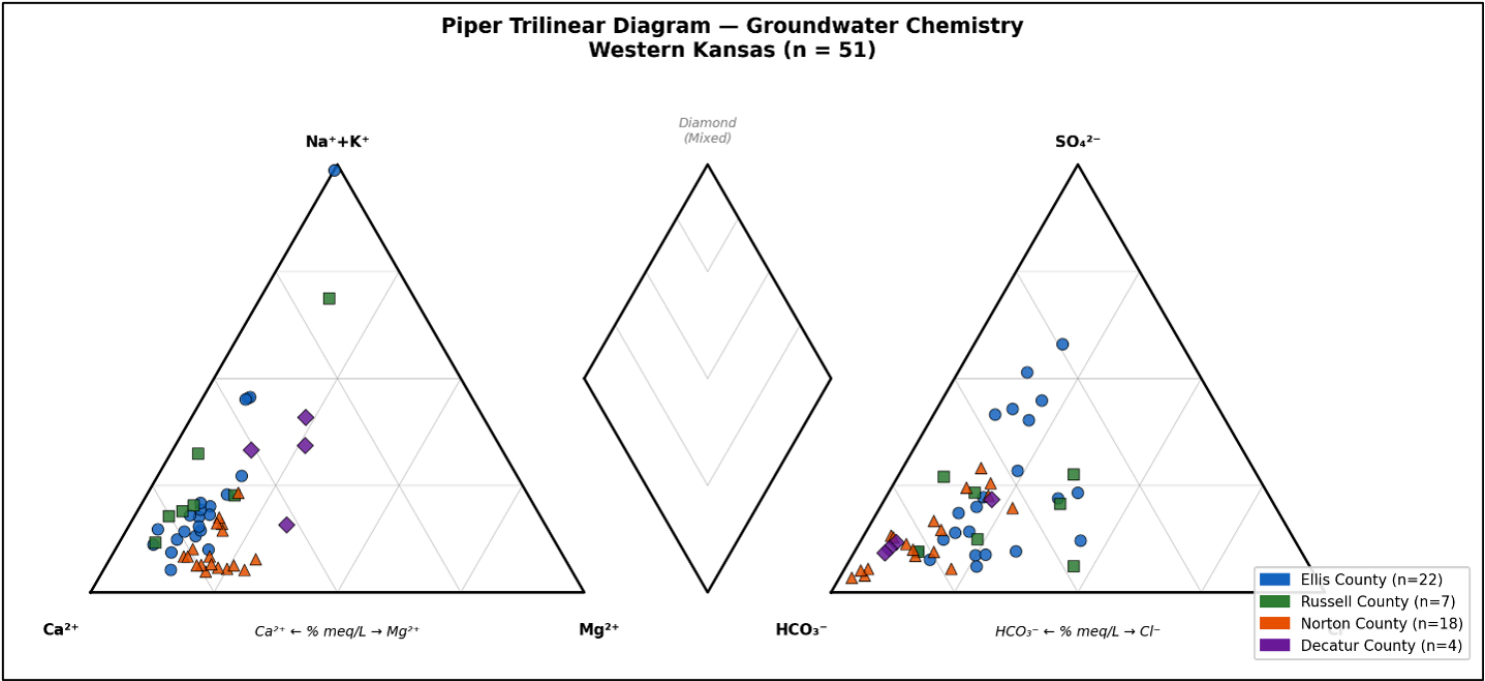


Figure 2

Piper trilinear diagram of major-ion chemistry for 51 groundwater samples from the western Kansas High Plains Aquifer. The Ca–HCO₃ facies dominates (lower-right quadrant of the central diamond), consistent with carbonate aquifer dissolution in the Ogallala Formation. A subset of Ellis and Decatur county wells plot toward the Na–Cl facies, indicating ion-exchange or evaporite influence.

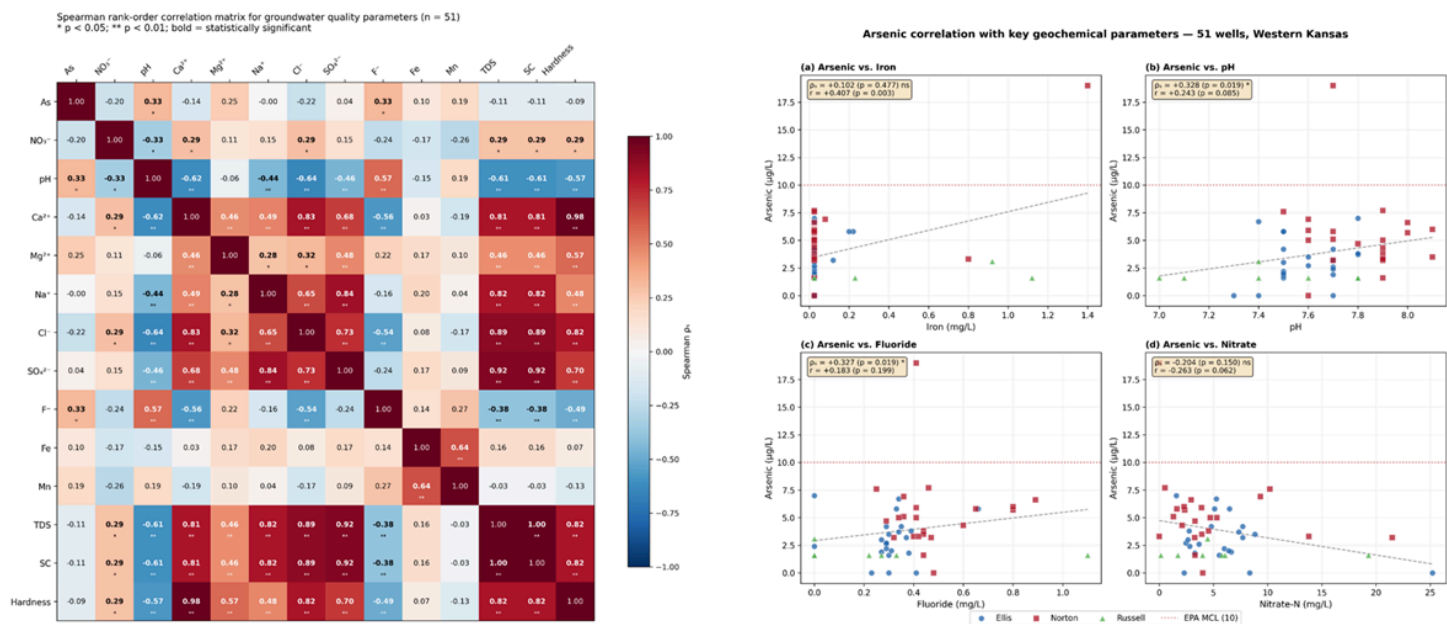


Figure 3

(a) Spearman rank-order correlation heatmap for the 14 measured groundwater quality parameters (n = 51); colour intensity indicates correlation strength (red = positive, blue = negative); asterisks denote statistical significance (* p < 0.05; ** p < 0.01). (b) Scatter plots of arsenic against key geochemical parameters: iron, pH, fluoride, and nitrate-N, colour-coded by county. Dashed red line = USEPA MCL (10 $\mu\text{g L}^{-1}$). Significant Spearman associations (As–Fe, As–pH, As–F) are diagnostic of redox- and pH-controlled geogenic mobilization.

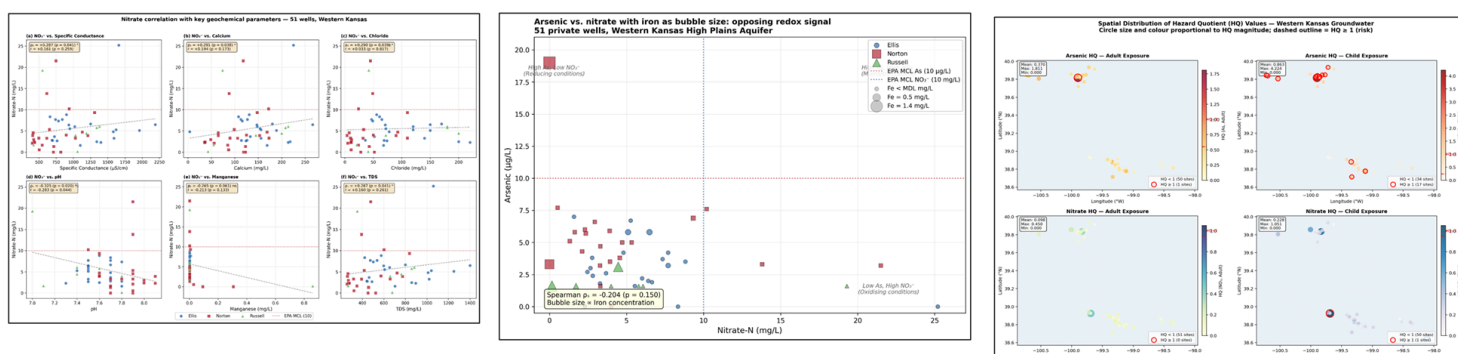


Figure 4

(a) Spatial distribution of arsenic and nitrate-N concentrations across 51 sampled wells; circle size and colour intensity scale with concentration. Red outlines mark wells exceeding USEPA Maximum Contaminant Levels. (b) Arsenic versus nitrate-N concentration with iron concentration as bubble size, illustrating the opposing redox signal: large bubbles (high Fe) cluster in the upper-left reducing zone (high As, low NO₃), and the lower-right oxidizing zone (low As, high NO₃) is populated only by small bubbles. (c) Scatter plots of nitrate-N concentration versus key geochemical parameters: (a) Specific

conductance, (b) Calcium, (c) Chloride, (d) pH, (e) Manganese, and (f) TDS, color-coded by county. Dashed red line = EPA MCL (10 mg/L). Significant Spearman correlations include SC, Ca, Cl, TDS, pH, and Mn. n = 51 wells.

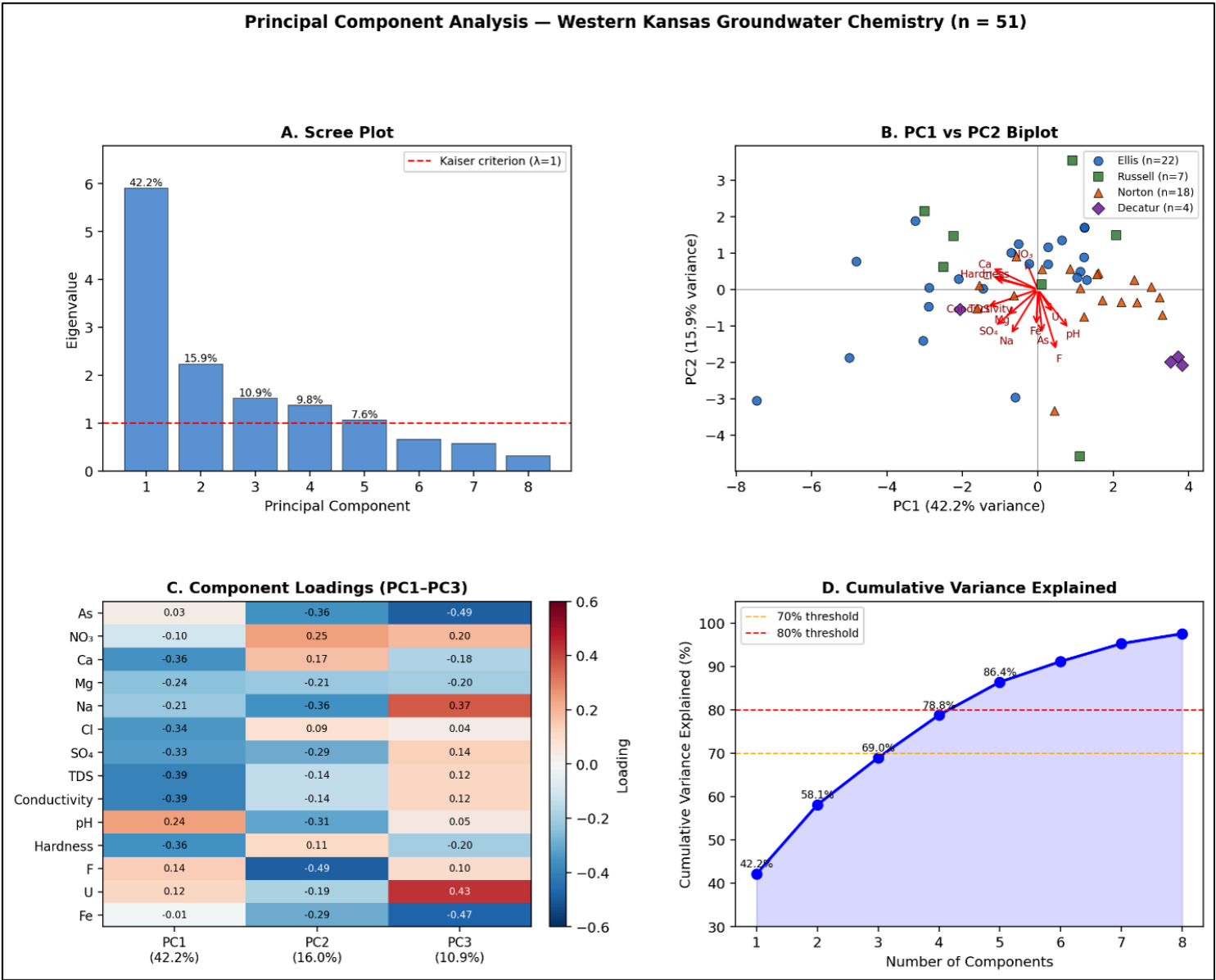


Figure 5

Principal component analysis biplot of 14 hydro-chemical parameters from 51 groundwater samples, western Kansas High Plains Aquifer. PC1 (42.2 % variance) = mineralization gradient; PC2 (16.0 %) = geogenic As–F–pH enrichment versus anthropogenic nitrate; PC3 (10.9 %) = Fe–As redox gradient. Five components collectively explain 86.4 % of total variance. Loadings and scores were computed from z-score-standardized data; axes are unrotated principal components.

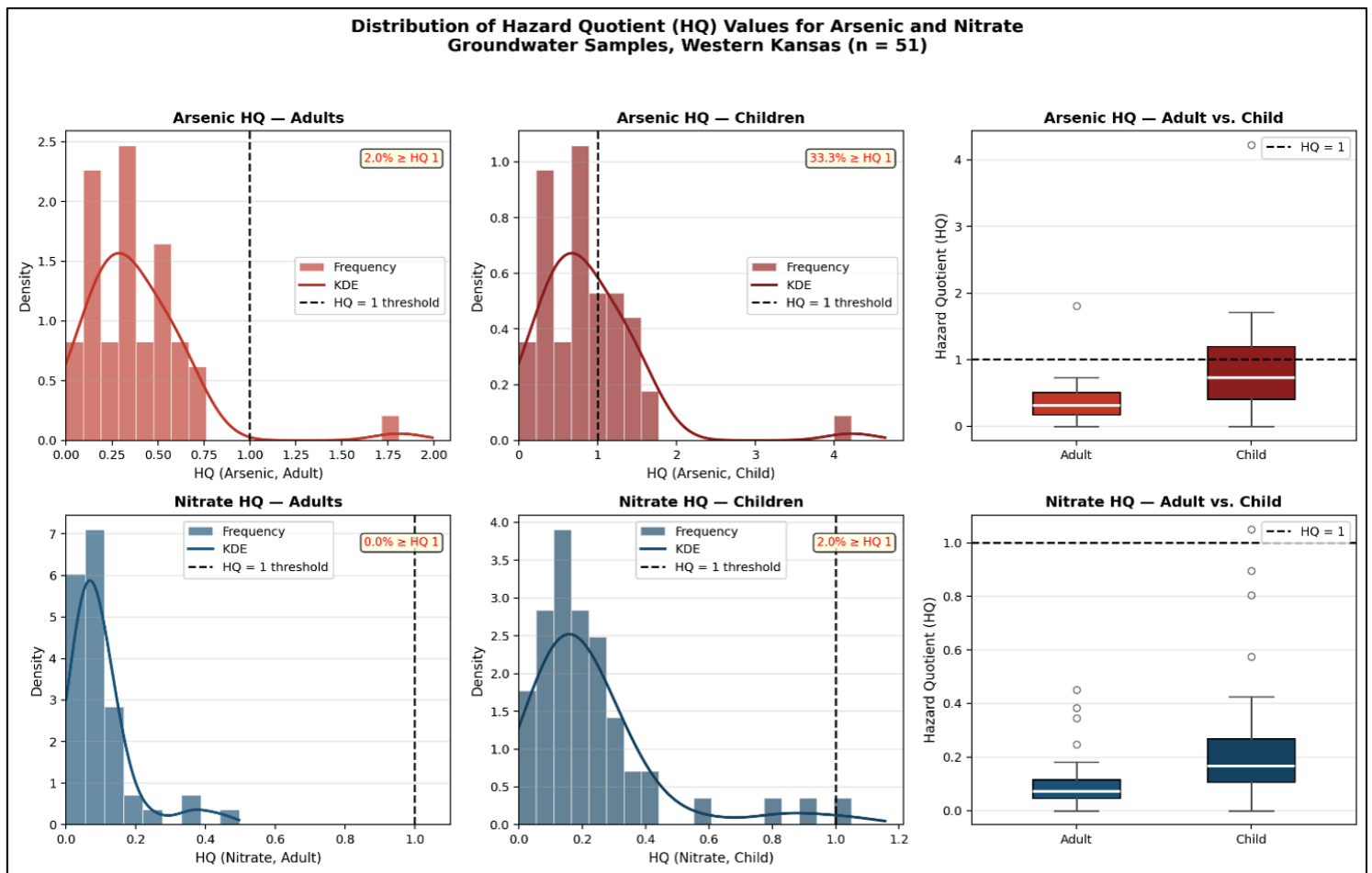


Figure 6

(a) Frequency distributions and box plots of non-carcinogenic Hazard Quotient (HQ) values for arsenic and nitrate-N across adult and child receptors at 51 wells; vertical dashed line at HQ = 1 = USEPA non-carcinogenic risk threshold. (b) Composite Health Risk Water Quality Index (HQ-WQI) classification of the 51 wells. (c) Adult and child Incremental Lifetime Cancer Risk (ILCR) distribution; horizontal dashed line at 1×10^{-4} = unacceptable carcinogenic risk threshold. Descriptive statistics: As adult mean HQ = $0.370 (\pm 0.284)$; As child mean HQ = $0.863 (\pm 0.663)$; NO_3 adult mean HQ = $0.098 (\pm 0.090)$; NO_3 child mean HQ = $0.228 (\pm 0.210)$.