

Monsoon Precipitation Regulates Priority Contaminant Sources, Quality, and Health Risks of Groundwater in a Rapidly Urbanizing Region

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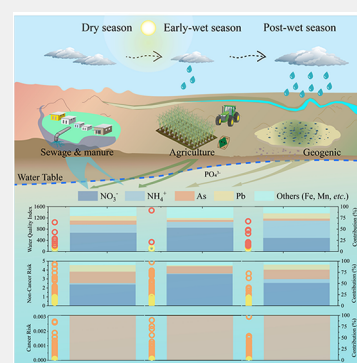
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ABSTRACT: Groundwater supplies ~50% of global domestic water yet faces intertwined geogenic and anthropogenic threats. The seasonal surge and shifts in priority groundwater contaminants in rapidly urbanizing regions, along with the specific sources driving these pulses, remain poorly understood. Addressing these knowledge gaps is critically important for improving water quality management, guiding sustainable water resource strategies, and mitigating health risks. We conducted triseason monitoring (dry, early wet, postwet) of 159 shallow domestic well samples across China's Pearl River Delta, integrating multi-isotopes ($\delta D-H_2O$, $\delta^{18}O-H_2O$, $\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$, $^{208}Pb/^{207}Pb$, and $^{206}Pb/^{207}Pb$) and Bayesian mixing, self-organizing maps (SOM), and positive matrix factorization (PMF). Water isotopes quantified a monsoon-paced shift from greater surface water influence in the dry season to precipitation-dominated recharge in the early wet season, linking hydroclimate to contaminant transport. Four contaminants (NO_3^- , NH_4^+ , As, and Pb) controlled water quality deterioration and health risk to the local population in the study and worldwide regions. The four priority contaminants peak asynchronously: nitrate maximizes in the early wet season and is dominated by sewage/manure inputs (mean 71%), whereas NH_4^+ increased postwet under more reducing, DOC-rich conditions. Lead was chiefly geogenic (granite weathering; mean 86%) yet showed stronger anthropogenic signatures postwet, and arsenic remained the dominant carcinogenic risk driver. The resulting connectivity-redox-risk cascade explains seasonal switching of risk composition and identifies sanitation upgrades, storm-resilient urban planning, legacy metal management, and seasonally adaptive monitoring as high-leverage interventions to safeguard groundwater.

KEYWORDS: groundwater quality, source apportionment, health risk assessment, seasonal variation, arsenic



1. INTRODUCTION

Groundwater constitutes approximately 99% of Earth's terrestrial liquid freshwater and supplies about half of global domestic water, underpinning drinking and irrigation needs, particularly in rapidly urbanizing regions.^{1–3} However, millions remain at risk from naturally occurring geogenic contaminants in groundwater, most notably arsenic (As) and fluoride (F).^{4,5} In many urbanizing basins, these hazards are compounded by anthropogenic nitrate (NO_3^-), ammonium (NH_4^+), and metal(loid)s (e.g., Pb) mobilized through shifts in recharge, redox, and flow pathways linked to surface water infiltration, aging infrastructure, and land use intensification.^{2,6,7} Hydrodynamic extremes (e.g., floods, drought) further destabilize groundwater quality by reorganizing transport and biogeochemical conditions.⁸ Together, these pressures complicate contaminant dynamics and impede progress toward the United Nations Sustainable Development Goals for clean water. However, the priority contaminants linked to water quality degradation, potential sources, and their corresponding health risks in rapidly urbanizing basins remain poorly understood.

Diagnostic tools exist, but face limits under urban groundwater complexity. Hydrogeochemical frameworks characterize water–rock interactions, and stoichiometric ratios (e.g., Cl/Br and NO_3^-/Cl) indicate surface water or wastewater influence.^{6,9} Machine-learning and receptor models (self-organizing map, SOM; positive matrix factorization, PMF) can help separate mixed sources.^{3,10} However, urbanization alters key solutes Cl^- and K^+ ,⁹ PO_4^{3-} ,¹¹ NO_3^- ,^{12–14} NH_4^+ ,² and heavy metal(loid)s (e.g., Pb^{15,16}) through diffuse and point inputs from sewage, industry, and legacy agriculture, disrupting canonical ratios and obscuring sources when statistical analysis tools are used alone.

Isotopic tracers sharpen source apportionment. Lead isotopes distinguish geogenic Pb from industrial and traffic

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emissions. For example, rock weathering-released Pb in groundwater can be clearly distinguished from automobile exhaust and industry.¹⁵ Dual NO_3^- isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$) resolve contributions from sewage/manure, soil-N, fertilizer, and deposition.^{1,12} Coupling isotopes with receptor models strengthens inference (e.g., > 50% sewage/manure NO_3^- in the Poyang Lake Basin).¹⁷ Despite these advances, integrated, seasonally resolved, multitracer source apportionment remains scarce in rapidly urbanizing aquifers where monsoon-driven recharge can rewire redox zonation and transport, shifting health-relevant contaminant pulses.

South China's Pearl River Delta (PRD), a monsoon-dominated, fast-urbanizing mega region, exhibits co-occurring geogenic hazards (As, NH_4^+) and anthropogenic pollution (NO_3^- , Pb) in groundwater and surface water.^{2,18} The documented global co-occurrence of geogenic As with NO_3^- , NH_4^+ , and Pb,^{3,9,19} together with intensifying hydroclimatic variability,²⁰ positions the PRD as an ideal natural laboratory for resolving how precipitation regimes and urban sources interact to shape groundwater risks.^{8,21}

Here, we investigated how monsoon hydroclimate and urbanization jointly regulate groundwater quality in the PRD using a triseason monitoring design (dry, early wet, postwet). We integrated stable isotopes ($\delta\text{D}-\text{H}_2\text{O}$, $\delta^{18}\text{O}-\text{H}_2\text{O}$, $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$), SOM, PMF, and Bayesian mixing to (1) identify priority contaminants linked to water quality degradation and health risk; (2) apportion natural versus anthropogenic sources with seasonal resolution; and (3) evaluate the role of monsoon-controlled recharge and redox in modulating contaminant pathways. Focusing on As, NO_3^- , NH_4^+ , and Pb, we provided a source-oriented framework that connects hydroclimatic seasonality to contaminant occurrence in a rapidly urbanizing aquifer. We further situated PRD findings within a global context to clarify management priorities in the As-affected aquifer. The framework is intended to inform targeted interventions, such as sanitation upgrades, storm-resilient land-water planning, and seasonally adaptive monitoring, to safeguard groundwater and public health.

2. MATERIALS AND METHODS

2.1. Study Region, Sampling, and Analysis

The composite alluvial PRD region in South China is characterized by a dense fluvial network and a subtropical monsoon climate with 1600–2300 mm annual precipitation, approximately 81%–85% of which falls during April–September. The PRD region is predominantly mantled by late Quaternary deposits comprising young marine sediment (above –20 m elevation) and young terrestrial units (–10 to –20 m). Groundwater occurs within granular and fissured aquifers and generally flows from the northwest/northeast toward the southeast coast, broadly following major river gradients. Recharge is primarily from precipitation, surface water infiltration (rivers, ponds), and agricultural irrigation.^{2,22} Shallow unconfined groundwater from widely distributed domestic wells is commonly used for cleaning and irrigation and, occasionally, for drinking. Geological and hydrogeological details were reported elsewhere.^{2,23}

We continuously collected 159 groundwater samples from 53 domestic wells (depth <14 m) via three times across three seasons: dry (January 2022, DRY), early wet (April 2021, WET-E), and postwet (September 2021, WET-P). Most wells are located within suburban residential areas for domestic use, where surface ponds or small rivers usually receive sewage discharge and may impact groundwater quality through surface water–groundwater interaction. Seasonal precipitation produced distinct groundwater levels below

land surface: DRY, 2.3–10.0 m (mean: 4.7 m); WET-E, 0.3–7.0 m (mean: 2.1 m); WET-P, 0.9–2.1 m (mean: 1.4 m). Concurrently, rainfall and surface waters (ponds, streams) were sampled.²⁰ Field measurements, including pH, dissolved oxygen (DO), oxidation–reduction potential (ORP), and temperature, were obtained in situ using a multiparameter water quality meter (HI9829). Major and trace elements were analyzed by ICP-OES (Agilent, 700 Series) and ICP-MS (Agilent, 8800), and As speciation by HPLC-AFS (PrinCen, Guangzhou, China), following our previous protocols,²⁴ with QA/QC and method detection limits summarized in the Supporting Information (Text S1 and Table S1). Anions (NO_3^- , Cl^- , and SO_4^{2-}) were measured by ion chromatography (DX As-DV, Dionex, US); NH_4^+ by Nesslerization; PO_4^{3-} by molybdenum–antimony antispectrophotometry; alkalinity by titration; F^- by Alizarin Complexone spectrophotometry (Mapada UV-1100); and TOC by the TOC autoanalyzer (TOC-L CPH CN200, Shimadzu).

A one-way analysis of variance (ANOVA) was performed at a significance level of 0.05 for pairwise comparison of seasonal differences in groundwater chemistry parameters, with details provided in Text 1 and Table S2.

2.2. Water Quality Assessment and Health Risk Assessment

Groundwater quality was evaluated using the integrated weight water quality index (IWQI) coupled with entropy weighting.^{18,25} Seventeen groundwater parameters were included (Table S3). The IWQI of each sample was calculated according to eq 1:

$$\text{IWQI} = \sum_j^n W_j \times q_j \quad (1)$$

where W_j is the integrated weight coefficient of the j th parameter and q_j is the quality rating scale of each parameter. $j = 1, 2, 3, \dots, n$. The weight coefficients and quality rating scale of groundwater parameters were calculated by combining the G1 method and the entropy method, with details provided in Text S2 and Tables S3–S5.

Health risk in the local population from groundwater use was assessed using the USEPA framework for ingestion and dermal exposure based on comparative data from this work and previous global reports.^{26,27} Eight analytes (NO_3^- , NH_4^+ , As, Pb, Fe, Mn, F, and Cu) were evaluated for noncarcinogenic risk. Carcinogenic risk (CR) via oral exposure was estimated for As and Pb.²⁶ Given the high toxicity of As(III) with approximately 60 times higher than that of As(V), a speciation-aware risk assessment was performed (Text S3). A probabilistic Monte Carlo approach was adopted to propagate uncertainty in elemental concentration, ingestion rate (IR), and exposure frequency (EF).¹⁹ The body weights from different countries were updated accordingly in the framework, while the recommended exposure time was adopted from the USEPA model. Total hazard index (THI) and total carcinogenic risk (TCR) were summed, and the corresponding contribution of individual parameters in each sample was calculated after normalization. Methods for global data search strategy and synthesis procedures, noncarcinogenic risk, As speciation-adjusted carcinogenic risk, and Monte Carlo simulation are detailed in Text S3 and Tables S6 and S7.

2.3. Stable Isotope Analysis of δD and $\delta^{18}\text{O}$ in Water, Nitrate, and Pb

Stable isotopes of water ($\delta\text{D}-\text{H}_2\text{O}$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$) were measured using an isotopic liquid water and water vapor analyzer (L2130-i, Picarro) at the State Key Laboratory of Cryospheric Science and Frozen Soil Engineering, Chinese Academy of Sciences.²³ Isotope ratios are reported in ‰ relative to Vienna Standard Mean Ocean Water (VSMOW).²⁸ Calculation details are provided in Text S4. Long-term repeatability was <0.2‰ for δD and <0.08‰ for $\delta^{18}\text{O}$. Deuterium excess ($d\text{-excess} = \delta\text{D} - 8\delta^{18}\text{O}$) was calculated to evaluate precipitation effects and aid source attribution.²⁹

Groundwater samples (acidified with HCl) were analyzed for dual NO_3^- isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) using the denitrifier method,^{17,30} with details provided in Text S4. The analytical precision for international standard references (USGS34 and USGS35) was

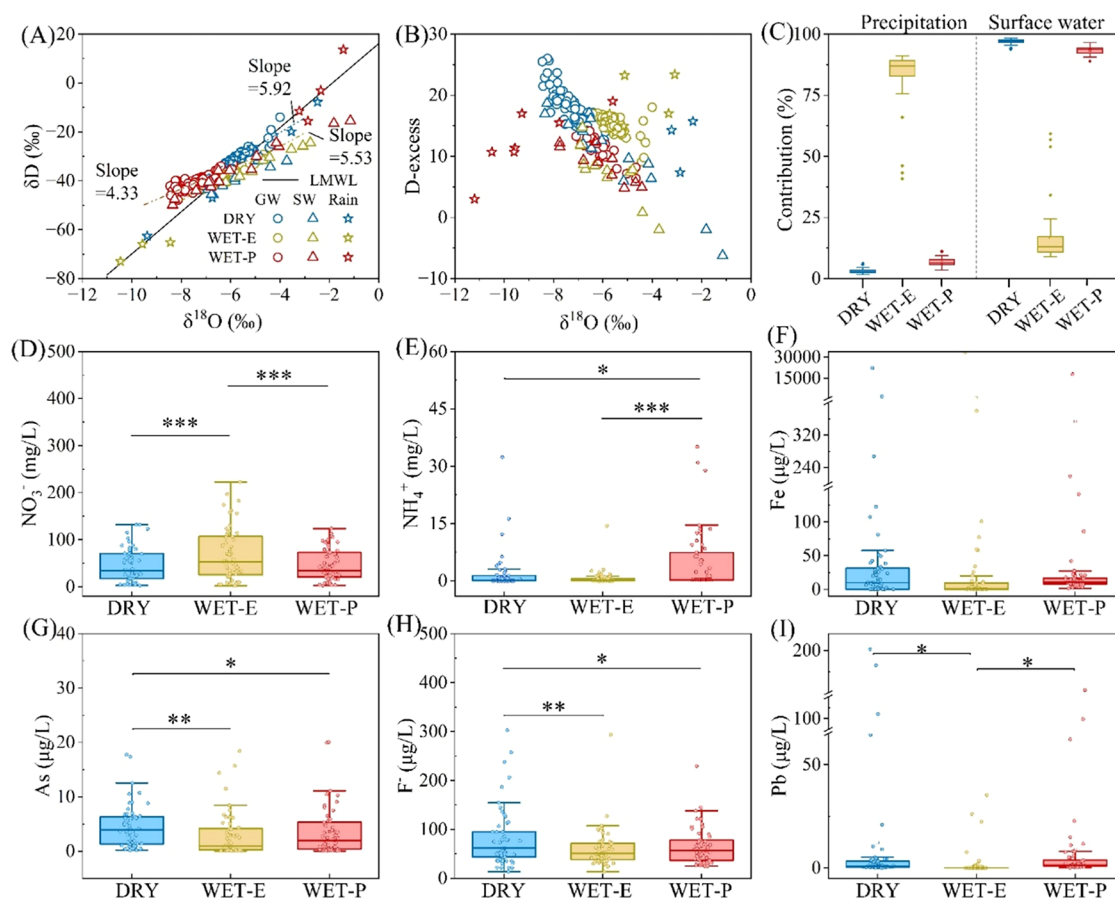


Figure 1. Seasonal variation in groundwater chemistry of the Pearl River Delta. (A) $\delta^2\text{H}$ – H_2O vs $\delta^{18}\text{O}$ – H_2O with local meteoric water line (LMWL, $\delta\text{D} = 8.60 \times \delta^{18}\text{O} + 16.15$).³⁷ (B) d-excess (d-excess = $\delta\text{D} - 8\delta^{18}\text{O}$). (C) MixSIAR water source apportionment (rain and surface water). Seasonal variations of (D) NO_3^- , (E) NH_4^+ , (F) Fe, (G) As, (H) F^- , and (I) Pb. Samples encompass three seasons: the dry season (January, DRY), the early wet season (April, WET-E), and the postmonsoon wet season (September, WET-P). Statistical significance is denoted by *p* values of 0.05 (*), 0.01 (**), and 0.001 (***).

0.25‰ for $\delta^{15}\text{N}$ – NO_3^- and 0.5‰ for $\delta^{18}\text{O}$ – NO_3^- . Source endmember data for NO_3^- and Pb contamination (e.g., agricultural fertilizer use, sewage/manure sources, and industrial emissions for NO_3^-) were compiled from previous studies.^{17,31}

Lead isotopes in groundwater were analyzed using ICP-MS (Agilent Technologies 7700 series).³² Recoveries for NIST SRM 981 were 97.1%–102.8% for ^{204}Pb , 98.8%–102.8% for ^{206}Pb , 96.6%–101.2% for ^{207}Pb , and 98.0%–104.6% for ^{208}Pb . The relative standard deviations (triplicates) were $\leq 2.2\%$ for individual isotopes and $\leq 0.6\%$ for $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$. Candidate Pb sources included the commonly reported industrial emissions, leaded gasoline, agricultural fertilizers, and local crustal background, which have been used in the investigation of Pb sources in soils of the study region.^{32–34} Local background was additionally characterized using soil collected at 170 cm depth from an uncontaminated field.³⁵

Source contributions to groundwater NO_3^- and Pb were quantified using a Bayesian stable-isotope mixing model (MixSIAR in R).²³ Model configuration and isotope data handling are described in Text S4.

2.4. Source Apportionment Using Self-Organizing Maps (SOM) and Positive Matrix Factor (PMF) Analysis

Potential sources and process controls were explored using SOM and PMF.³ Variables characterizing rock–water interaction, major/trace elements, and IWQI were included in SOM (MATLAB 2018a; SOM Toolbox 2.1). Neuron count (63) followed the heuristic eq $5\sqrt{N}$, where *N* is the sample size, arranged on a 7×9 hexagonal lattice; preprocessing and training settings are described in Text S5.

PMF was applied to resolve contributing factors to groundwater chemistry, with factor number selected based on environmental interpretability and bivariate diagnostics.^{17,36} Variable reliability was assessed using signal-to-noise ratios (concentration/uncertainty); data preparation, uncertainty estimation, and model performance criteria are provided in Text S5 and Table S8. Integrating isotopic constraints with SOM and PMF results enabled triangulation of sources and identification of the variables that are most influential to groundwater quality.

3. RESULT AND DISCUSSION

3.1. Hydrogeochemical Evidence for Seasonally Reconfigured Groundwater–Surface Water Connectivity

Multiseasonal monitoring reveals that the PRD shallow aquifer operates as a hydroclimate-sensitive system whose recharge pathways and biogeochemical conditions are reorganized across the monsoon cycle (Figure 1). Stable water isotopes (δD and $\delta^{18}\text{O}$) provide direct constraints on recharge sources and mixing (Figure 1A,B). Groundwater δD and $\delta^{18}\text{O}$ values ($\delta\text{D}_{\text{gw}}$: -47.8‰ to -14.0‰ , mean: -36.2‰ ; $\delta^{18}\text{O}_{\text{gw}}$: -8.4‰ to -4.0‰ , mean: -6.4‰) cluster near the LMWL (Figure 1A and Table S9), confirming a dominant meteoric origin.³⁷ However, groundwater plots with a lower apparent slope (Figure 1A) and elevated d-excess (Figure 1B) relative to local rain, indicating that recharge is not purely direct rainfall infiltration but incorporates an evaporated surface water

component enriched in $\delta^{18}\text{O}$.²⁹ The consistent decline in $\delta^{18}\text{O}$ with increasing $\delta^{18}\text{O}$ (Figure 1B) further supports evaporative enrichment prior to recharge.³⁸

MixSIAR modeling quantifies a monsoon-paced switch in effective recharge sources. In the dry season, precipitation contributions are minimal (1.6%–6.2%, mean: 3.0%) (Figure 1C), concurrent with the deepest water tables, pointing to a stronger relative influence of surface water interaction and stored groundwater. In the WET-E, precipitation dominates (40.8%–91.1%, mean: 83.3%) (Figure 1C), consistent with rapid vertical percolation and convergence of rainfall and groundwater isotopic signatures.³⁸ In WET-P, modeled precipitation contributions decreased (3.5%–11.1%, mean: 6.7%). This apparent reduction is plausibly explained by delayed drainage and strong mixing within saturated soils/sediments and surface waters that have already been isotopically modified by rainfall, such that rainfall influence is expressed indirectly through mixed surface water recharge.^{38,39} Together, the isotope evidence supports the central premise of this study, i.e., monsoon seasonality rewires hydrologic connectivity, thereby reshaping transport pathways, redox evolution, and the timing of contaminant pulses.

The aquifer is characterized by circumneutral pH conditions (4.75–8.23, mean: 6.84) and predominantly oxic environments (ORP: –66.70 to 483.80 mV, mean: 183.50 mV) (Figure S1). Seasonal fluctuations in DO dynamics were pronounced, with significantly higher concentrations during the dry period (Figure S1). Groundwater DO levels in the cold dry season can be enhanced by the low temperature and more recharge from surface water.^{21,40} The highest DOC levels occurred at the end of the wet season, resulting from the continuous input of surface-derived terrestrial organic matter alongside recharge from precipitation and surface water.⁴¹ Additionally, more extensive organic matter mineralization probably occurred during the wet season, leading to further exhaustion of oxygen.⁴⁰

3.2. Monsoon Seasonality Drives Nitrate Flushing and Late-Season Reductive Accumulation

Across the 17 evaluated parameters, nitrogen species and redox-sensitive elements emerge as the principal drivers of groundwater vulnerability. Nitrate ranges from 1.8–222.4 mg/L (mean: 53.6 mg/L), and NH_4^+ ranges from nondetectable (ND) to 35.0 mg/L (mean: 2.5 mg/L) (Figure 1 and Table S10). Eighty-two percent of groundwater samples exceeded the Chinese drinking water guideline for NO_3^- (10 mg/L), while 38% exceeded the recommended NH_4^+ threshold (0.5 mg/L). Seasonally, NO_3^- is significantly elevated in WET-E (Figure 1D), whereas NH_4^+ is strongly enriched in WET-P (Figure 1E). Generally, groundwater NO_3^- originates from sewage/manure, soil leaching, and fertilizer, while NH_4^+ accumulates from organic matter decomposition under a reducing environment.^{42,43} The contrast in NO_3^- and NH_4^+ seasonal variation is consistent with two distinct but coupled monsoon processes in which rapid recharge drives early season “ NO_3^- flushing” from soils and leaking sanitation sources, followed by late-season “reductive accumulation” under sustained wetting and higher DOC that promotes oxygen depletion, organic matter mineralization, and NH_4^+ persistence/production.^{7,14}

Five potentially toxic elements (Fe, Mn, As, F, and Pb, Figure 1F) show heterogeneous but diagnostically meaningful patterns. Fe (ND–33.4 mg/L, mean: 0.5 mg/L) and Mn (ND–1.1 mg/L, mean: 0.1 mg/L) (Table S10) exceeded

guideline thresholds in 4% and 16% of samples, respectively. These redox-sensitive elements provide process information beyond water quality, and their covariation with DOC and NH_4^+ helps identify zones/times of enhanced reduction.

Arsenic concentrations ranged from ND to 20.1 $\mu\text{g/L}$ (Figure 1G and Table S10), with 9% of samples exceeding the safe drinking water standard (10 $\mu\text{g/L}$). Compared to historical reports (up to 560 $\mu\text{g/L}$),²² the current distribution indicates lower regional As levels. The decline in groundwater As concentrations appears to be controlled by the prevailing oxidizing conditions,²⁴ as indicated by high redox potential values. The predominance of As(V) (mean: 82%) over As(III) (mean: 18%) and generally positive redox potential values suggest that oxidizing conditions constrain As mobility. Meanwhile, phosphate (0.002–2.29 mg/L, mean: 0.47 mg/L) is lower than previously reported (0.08–8.6 mg/L, mean: 2.11 mg/L),⁴⁴ plausibly reflecting strengthened wastewater P controls.⁴⁵ Lower PO_4^{3-} may reduce competitive As desorption, further suppressing dissolved As.²⁴ Importantly, this does not eliminate risk; even relatively modest As concentrations can dominate carcinogenic risk, as discussed in Section 3.3.

Seasonal patterns reinforce the hydrologic-redox coupling. Mean As concentrations are higher in DRY (4.6 $\mu\text{g/L}$) than in wet seasons (3.3 $\mu\text{g/L}$), consistent with the Fe seasonal pattern (Figure 1F). The consistent pattern of As and Fe in the dry season is explained by the significantly lower redox potential observed (Figure S4). This likely reflects a combination of (i) dilution by rainfall recharge in the wet season,⁴⁶ and (ii) oxygen delivery during early wet recharge that inhibits Fe(oxyhydr)oxide reduction and facilitates the oxidation of Fe(II) and As(III).⁴⁷ Because As(V) is more strongly adsorbed, dissolved As decreases under these conditions.⁴⁸ Conversely, longer residence times and weaker recharge influence (late wet $\rightarrow$ dry) can sustain reductive dissolution of Fe (oxyhydr)oxides and release of sorbed As.^{41,49}

An interesting but decoupled seasonal pattern was observed for both As and NH_4^+ , despite their co-occurrence under reducing conditions. Although As and NH_4^+ are both prevalent during simultaneous methanogenesis and Fe reduction in reducing groundwaters, As concentrations do not always correlate with NH_4^+ levels, depending on the diversity, structural composition, and degradation degrees of organic matter.^{50,51} In addition, As mobilization may be driven by NH_4^+ oxidation coupled to Fe(III) reduction in unconfined and semiconfined aquifers.⁵¹ The complex organic matter-promoted reactions responsible for As and NH_4^+ enrichment during surface water–groundwater interactions, where oxygen from river or precipitation infiltration is frequently consumed by organic matter oxidation, warrant further investigation.

Fluoride remains consistently low (0.013–0.302 mg/L; mean: 0.069 mg/L) with minimal seasonal variability (Figure 1H), and most samples fall well below Chinese (1.0 mg/L) and WHO guideline values (1.5 mg/L).^{25,52} Low F concentrations are consistent with fluorite (CaF_2) precipitation favored by circumneutral pH conditions and relatively elevated Ca.^{53,54}

Lead is widespread and occasionally high (ND–202 $\mu\text{g/L}$; mean: 7.7 $\mu\text{g/L}$) (Figure 1I), with 10% of the samples exceeding the drinking water guideline value of 10 $\mu\text{g/L}$ and 13% exceeding local background (2.6–5.9 $\mu\text{g/L}$).^{25,55,56} This pattern of frequent low-to-moderate Pb with sporadic spikes suggests a system where a dominant geogenic baseline is

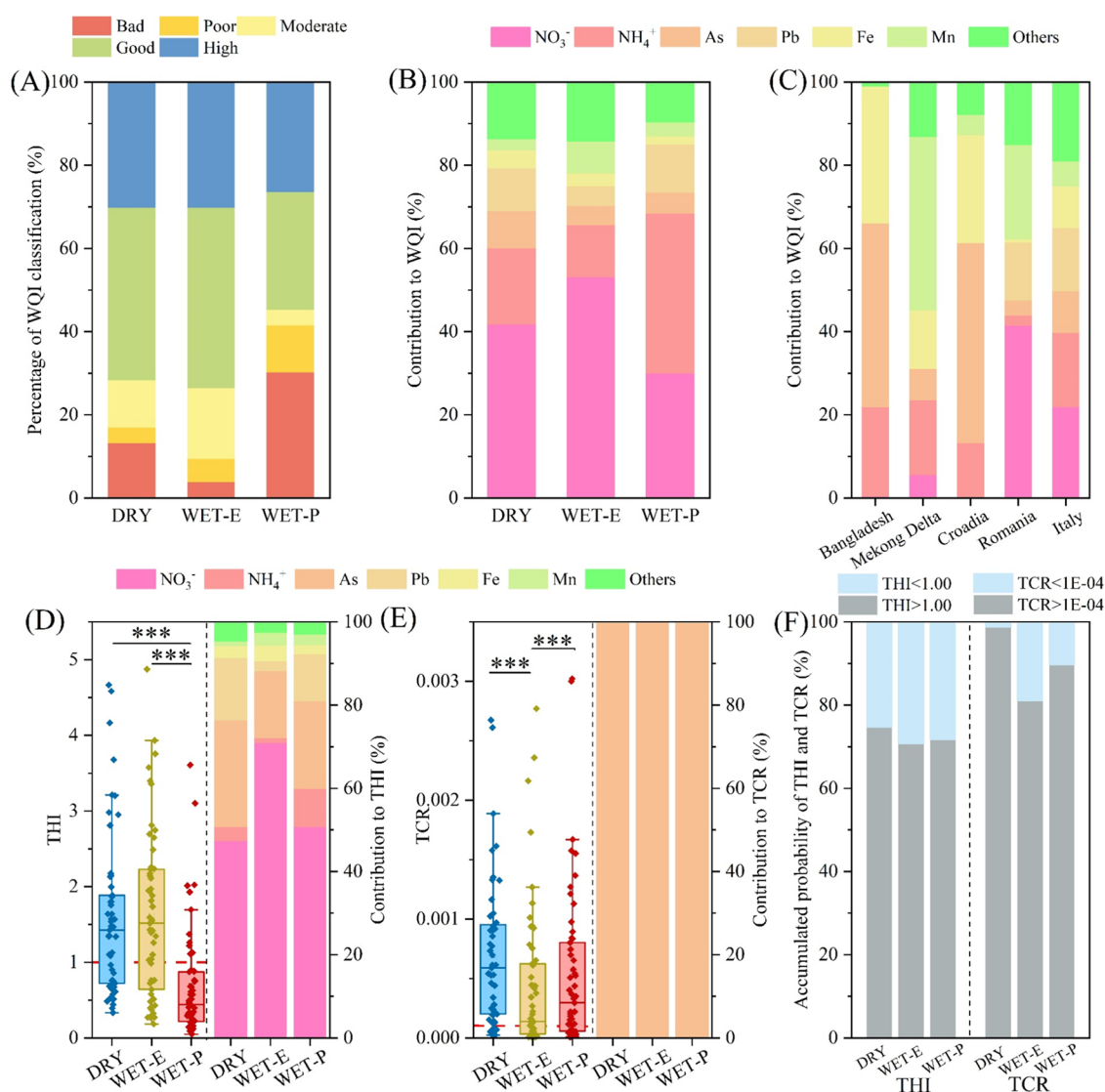


Figure 2. Groundwater quality and health risk assessment across three seasons. (A) Water quality and (B) average parameter contributions in the Pearl River Delta. (C) Average parameter contributions from previous publications (Text S3). Monte Carlo estimates (mean values) of (D) total THI and (E) TCR to adults and seasonal accumulative probability of THI and TCR (F). Three seasons: the dry season (January, DRY), the early wet season (April, WET-E), and the postmonsoon wet season (September, WET-P). Statistical significance is denoted by *p* values of 0.05 (*), 0.01 (**), and 0.001 (***).

punctuated by episodic mobilization of anthropogenic legacy Pb, a hypothesis tested by Pb isotopes in Section 3.4.

3.3. Monsoon Timing Shifts Peak Water Quality Deterioration and Health Risk Dominance

IWQI results show that water quality is acceptable in many wells but degrades systematically by the postwet period (Figure 2A). “Good” water comprised 43% (WET-E) and 42% (DRY) of samples, but declined significantly to 28% in WET-P. Conversely, WET-P has 41% of samples classified as “Poor/Bad”, compared to 9% (WET-E) and 17% (DRY). This significant late-wet deterioration indicates that prolonged monsoon conditions increase the probability of adverse groundwater quality, likely by cumulatively enhancing transport of contaminants into shallow aquifers and producing reducing conditions that mobilize redox-sensitive constituents from long-term precipitation events.

Across seasons, four crucial contaminants, including NO₃⁻, NH₄⁺, Pb, and As, dominate IWQI deterioration (Figure 2B).

Nitrogen species (NO₃⁻ and NH₄⁺) are the largest contributors, accounting for 60%–68% of IWQI degradation (Figure 2B). The increase in poor-quality groundwater during WET-P (Figure 2A) aligns with NH₄⁺ enrichment, implying that monitoring restricted to dry or early wet periods would systematically underestimate late-monsoon vulnerability. This codominance of nitrogen species (Figure 2C) is consistent with observations from other geogenic-As regions where NO₃⁻ and NH₄⁺ frequently co-occur and strongly shape overall groundwater quality.^{57–59}

Metal(loid)s, including As, Pb, Fe, and Mn, collectively contributed to 20%–26% of water deterioration, although declining metal(loid) concentrations have been reported recently.⁴⁹ Arsenic (5%–9%) and Pb (5%–12%) consistently rank among the top contributors, and Mn (3%–9%) and Fe (2%–5%) contribute less, while seasonal-precipitation-driven redox processes regulate the relative contributions from As and NH₄⁺ (Figure 2B). The global synthesis of groundwater (Figure 2C) highlights that Pb, although less emphasized in

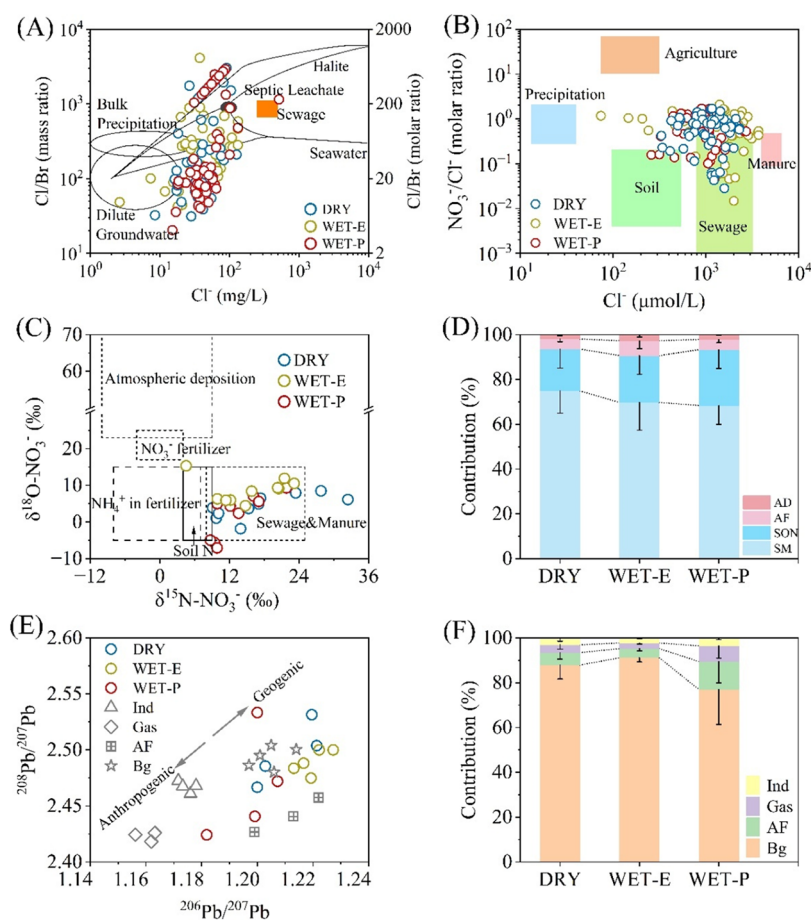


Figure 3. Source apportionment of nitrate and Pb in groundwater across three seasons. (A) Cl/Br vs Cl^- with mixing lines for dilute groundwater (Cl^- : 1.4 mg/L, Cl/Br: 110), seawater (Cl^- : 19296 mg/L, Cl/Br: 288), sewage (Cl^- : 400 mg/L, Cl/Br: 700), septic-tank effluents (Cl^- : 126 mg/L, Cl/Br: 1561),⁹ and halite.⁶ (B) $\text{NO}_3^-/\text{Cl}^-$ vs Cl^- showing NO_3^- sources end-members (manure, sewage, soil, precipitation, and agriculture).^{13,17} (C) Dual isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$ vs $\delta^{18}\text{O}-\text{NO}_3^-$) and (D) MixSIAR results for NO_3^- sources (atmospheric deposition (AD), agricultural fertilizer (AF), soil nitrogen (SON), and sewage/manure (SM)).^{12,13} (E) Pb stable Pb isotopes ($^{208}\text{Pb}/^{207}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$) and (F) MixSIAR results for Pb sources (industrial emissions (Ind), leaded-gasoline (Gas), agricultural fertilizer (AF), and background local crust (Bg)).^{32–34} Samples span three seasons: the dry season (January, DRY), the early wet season (April, WET-E), and the postmonsoon wet season (September, WET-P).

classic geogenic-As narratives, appears repeatedly as a non-negligible cocontaminant in northwestern Romania,⁵⁸ northern Italy,⁵⁹ and the Mekong Delta⁶⁰ to groundwater quality deterioration. This persistence is compatible with long-lived soil/road-dust Pb reservoirs and continued remobilization decades after phase-out of leaded gasoline.⁶¹

Monte Carlo health risk assessment for adults reveals widespread exceedances and strong seasonal structure (Figure 2D–F). The mean total noncarcinogenic hazard index (THI) is 1.58 (>1), with significantly seasonal difference in means of 1.62 (WET-E) $\approx$ 1.59 (DRY) > 0.69 (WET-P) (Figure 2D). Nitrate dominates noncarcinogenic risk year-round (71% in WET-E > 51% in WET-P > 47% in DRY), consistent with early wet-season NO_3^- flushing and sustained NO_3^- presence across seasons. The secondary contributors included As (16–26%), Pb (2–15%), and NH_4^+ (1–9%) (Figure 2D), indicating that monsoon seasonality shifts not only concentrations but the composition of risk.

Carcinogenic risk from As and Pb is high (mean 5.6×10^{-4}), exceeding the benchmark of 1.0×10^{-4} , with significantly seasonal differences in seasonal means of DRY (6.95×10^{-4}) $\approx$ WET-P (5.41×10^{-4}) > WET-E (4.43×10^{-4}) (Figure 2E). Approximately 71% of groundwater samples exceeded the carcinogenic threshold. Importantly, As speciation matters:

assuming all As is present as As(III) would overestimate the health risk because the less toxic As(V) form was dominant. Even after speciation adjustment (Text S3), As contributes >99% of carcinogenic risk, confirming As as the primary cancer risk driver.

Overall, Monte Carlo simulations indicated that >72% and >90% of the local population may face noncarcinogenic and carcinogenic risks above thresholds, respectively (Figure 2F). The dry season yields the highest carcinogenic risk exceedance probability (99%) due to higher mean As concentrations. A subset of wells shows extreme outcomes, with maximum HI and CR exceeding thresholds by more than 4.5-fold and more than 30-fold, respectively, underscoring the need for hotspot-targeted intervention rather than uniform management.

3.4. Isotopes Resolve Monsoon-Shifting Sources of Nitrate and Pb

Given the strong health relevance of NO_3^- and Pb, we applied conservative tracers and isotopes to separate natural versus anthropogenic influences. Cl/Br ratios and $\text{NO}_3^-/\text{Cl}^-$ relationships (Figure 3A,B) indicate mixed recharge and contamination pathways.^{6,9} Most samples fall within or near mixing fields for dilute groundwater, precipitation, sewage, and septic leachate (Figure 3A), implicating sanitation-related inputs.

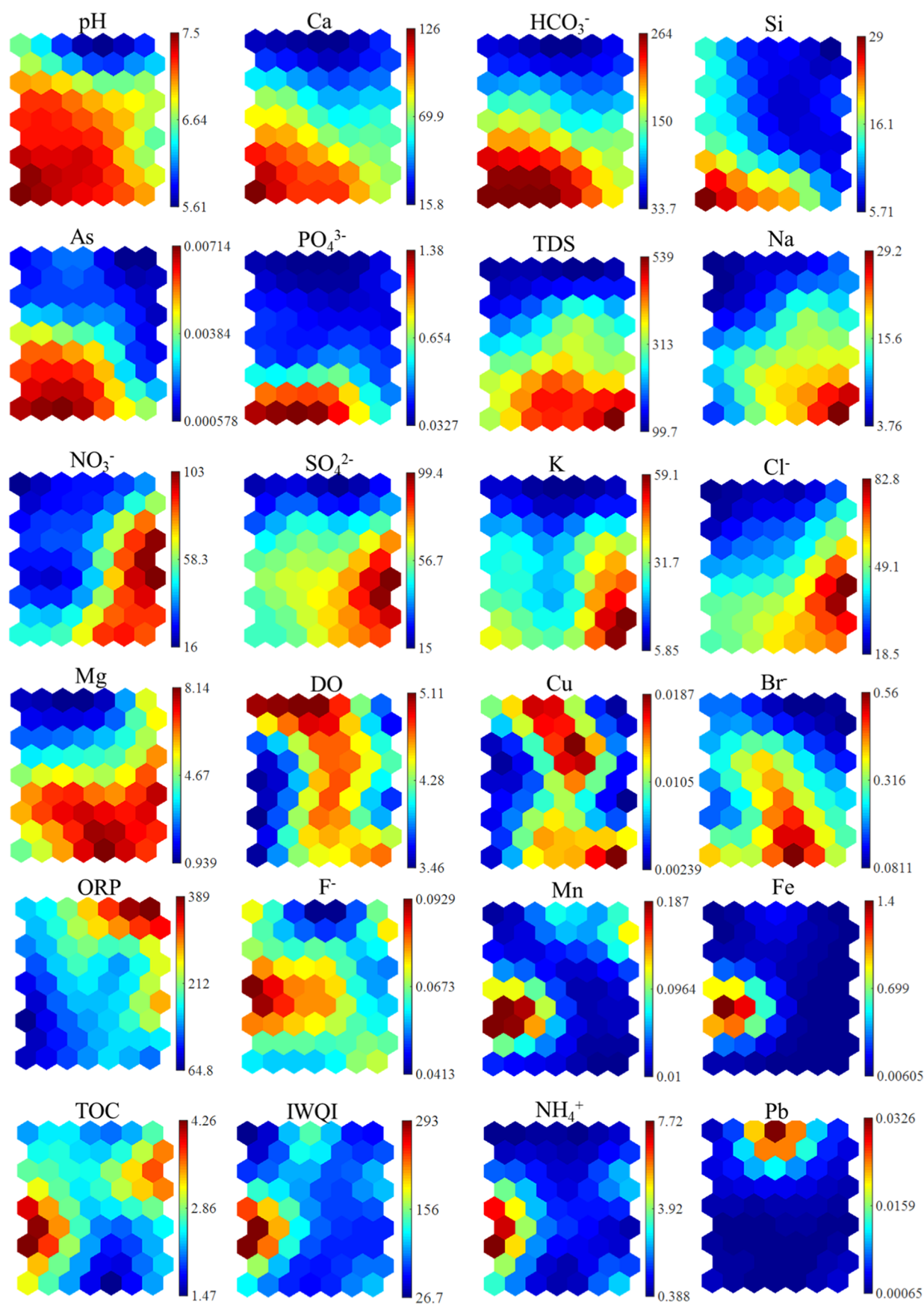


Figure 4. SOM matrix showing the clustering of groundwater variables into three partitions: (1) HCO_3^- , Si, PO_4^{3-} , As, Ca, and pH; (2) TDS, NO_3^- , SO_4^{2-} , Cl^- , Na, and K; (3) Fe, Mn, F, NH_4^+ , TOC, and IWQI.

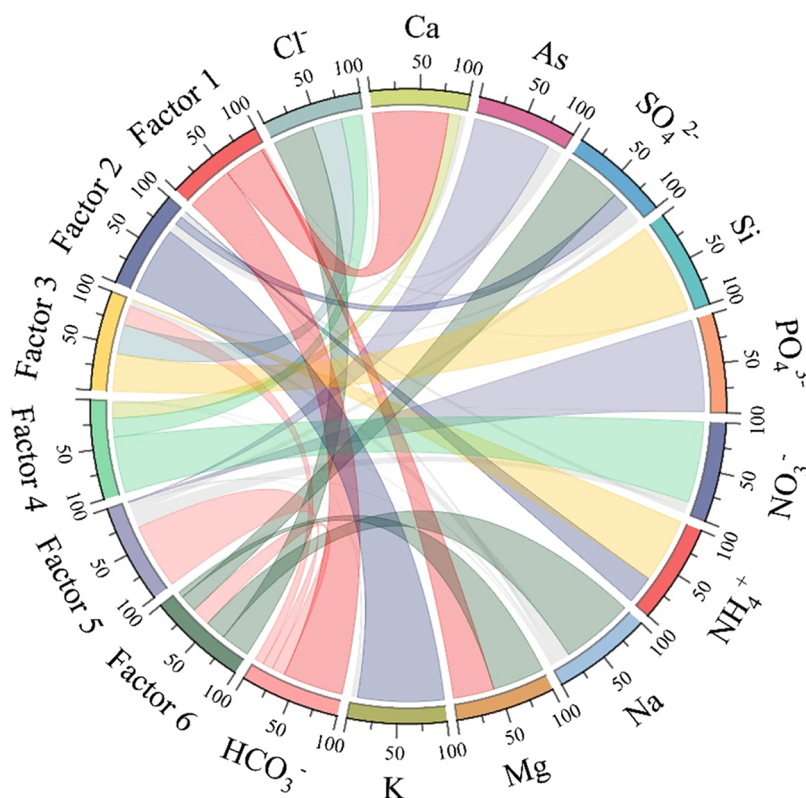


Figure 5. Circos plot of source contributions (%) to groundwater components in the Pearl River Delta. Sources include rock–groundwater interactions (calcium/dolomite dissolution, F1; silicate weathering, F3; mirabilite/gaylussite/halite dissolution, F6), agricultural activities (F2), manure/sewage runoff (F4), and reducing mineral dissolution (F5). Bandwidth is proportional to the source contribution percentage. For example, F4 comprises 60% NO_3^- , 20% Cl^- , 20% Ca, and trace Na and P; NO_3^- receives 0% from F1, 5.1 from F2, 70% from F4, and 20% from F5.

Several wells with low Cl^-/Br^- (<110) and Cl^- (<10 mg/L) (Figure 3A) likely reflect relatively uncontaminated rain/surface water recharge.⁴¹ Negligible seawater intrusion across the sampled wells is consistent with previous studies.^{23,62}

Dual NO_3^- isotopes ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) show clear seasonal shifts. Dry season samples are more enriched ($\delta^{15}\text{N}_{\text{NO}_3}$ 9.11‰–32.42‰; mean 17.62‰; $\delta^{18}\text{O}_{\text{NO}_3}$ –1.83‰–8.47‰; mean 4.31‰) than wet season samples ($\delta^{15}\text{N}_{\text{NO}_3}$ 3.47‰–21.81‰; mean: 9.65‰; $\delta^{18}\text{O}_{\text{NO}_3}$ –7.05‰–9.31‰; mean 1.77‰) (Figure 3C), consistent with sewage/manure influence and seasonally varying mixing/leaching. MixSIAR quantifies that sewage/manure contributes 43%–90% (mean 71%) of groundwater NO_3^- , followed by soil-N (7%–36%, mean: 22%), atmospheric deposition (<6%, mean: 2%), and fertilizer (<16%, mean: 5%) (Figure 3D). This dominance implicates septic leakage and inadequate sanitation as the most actionable control on NO_3^- risk in peri-urban PRD.⁶³ The slight increase in soil-N and fertilizer-N contributions during wet seasons is consistent with rainfall-enhanced flushing of legacy soil NO_3^- and fertilizer inputs.⁶⁴ Similarly, NO_3^- in groundwater of an urbanized valley of Monterrey, Mexico, primarily originated from soil nitrogen and sewage.¹ A strong fertilizer contribution in an early wet season sample (16%) indicates that intense rainfall can trigger episodic agricultural NO_3^- pulses even when average fertilizer influence is small. This result is consistent with the observed higher contribution from fertilizer to groundwater NO_3^- observed in the Tarom watershed, North-West Iran, in later spring compared to later autumn, especially in regions with more than 75% agricultural land.¹² The minimal deposition

signal aligns with the documented decline in atmospheric nitrogen deposition in China.⁶⁵ Collectively, the isotope evidence supports a monsoon-driven model in which rainfall accelerates vertical transport from sanitation and soils into shallow groundwater, producing early wet season NO_3^- maxima.

Pb isotopes indicate that Pb is primarily geogenic but not purely geogenic (Figure 3E). Groundwater samples ($^{206}/^{207}\text{Pb}$: 1.182–1.227; $^{208}/^{207}\text{Pb}$ 2.424–2.533) span fields consistent with local crust/uncontaminated soil and anthropogenic sources (legacy leaded gasoline, industrial emissions). MixSIAR results show a dominant rock weathering contribution (55%–94%, mean: 86%), with smaller inputs from fertilizers (2%–26%, mean: 7%), leaded gasoline legacy (2%–15%, mean: 4%), and industry (<5%) (Figure 3F). The dominant geogenic signal is consistent with Pb mobilization through granite weathering in groundwater from the Maheshwaram watershed, India.¹⁵ Similarly, mineral weathering and industrial/agricultural pollution can both contribute to elevated Pb concentrations in Nigerian groundwater.⁶⁶ However, anthropogenic contributions increase in WET-P, consistent with enhanced transport of Pb stored in agricultural soils and road dust under prolonged rainfall and higher infiltration/runoff connectivity.¹⁶ These findings provide a novel approach to characterizing sources of the unexpected occurrence of Pb in groundwater as the limited reports from Northwestern Romania and Northern Italy.^{58,59} Thus, even a primarily geogenic Pb system can exhibit seasonally amplified anthropogenic signatures, reinforcing the value of late-wet

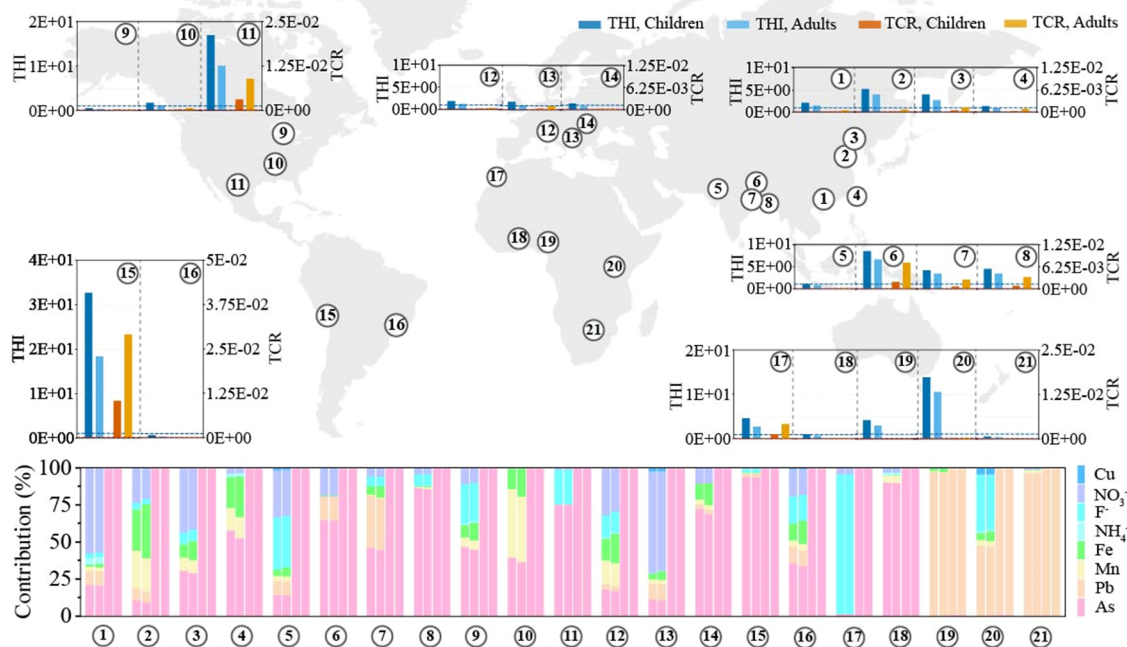


Figure 6. Average probability distributions of total hazard index (THI) and total carcinogenic risk (TCR) for both children and adults in global groundwater (Table S11). Contaminant contributions are shown in the lower panel (detailed in Tables S12–S15).

monitoring and source-specific mitigation (e.g., managing soil/road-dust mobilization and fertilizer-associated Pb).

3.5. SOM, PMF, and Isotopes Converge on a Seasonal Connectivity-Redox-Risk Cascade

Integrating SOM and PMF provides a mechanistic synthesis that links the hydroclimate seasonality to contaminant dynamics. SOM identifies three coherent partitions (Figure 4), and PMF resolves six interpretable factors (Figure 5), enabling separation of natural geochemical baselines from anthropogenic solute inputs and redox-drive mobilization.

The first SOM partition comprising HCO_3^- , Si, PO_4^{3-} , As, Ca, and pH (Figure 4) reflects mineral controls on solute release/retention. PMF Factor 5 aligns with this partition and is enriched in HCO_3^- (70%), NO_3^- (17%), SO_4^{2-} (8%), PO_4^{3-} (1%), and As (<1%), accounting for 99% of PO_4^{3-} and 84% of As variance (Figure 5). The strong PO_4^{3-} loading makes this factor a sensitive indicator of redox-mediated mineral processes. Elevated PO_4^{3-} concentrations during WET-E, alongside lower ORP, support reductive dissolution of Fe (oxyhydr)oxides, releasing PO_4^{3-} and mobilizing As.⁶⁷ The copresence of HCO_3^- suggests concurrent organic matter mineralization.⁵¹ Competitive desorption by PO_4^{3-} provides an additional pathway for As mobilization where PO_4^{3-} is elevated.^{4,24} Minor wastewater/manure contributions to PO_4^{3-} are plausible and consistent with NO_3^- coloadings.⁴⁴ Future PO_4^{3-} -P isotope analysis would strengthen discrimination of wastewater versus fertilizer P sources in urban aquifers.¹¹

Anthropogenic nitrogen signatures are captured by Factor 2 (K: 73%, Ca: 10%, SO_4^{2-} : 10%, and NO_3^- : 5%) and Factor 4 (NO_3^- : 61%, Cl^- : 20%, Ca: 17%) (Figure 5). Factor 2 accounted for 93% of K, 6% of Ca, 19% of SO_4^{2-} , 5% of NO_3^- , and 30% of NH_4^+ , while Factor 4 accounted for the presence of 87% of NO_3^- , 22% of Cl^- , and 13% of Ca. The occurrence of K and the co-occurrence of NO_3^- and Cl^- served as reliable conservative tracers for detecting the recharge of agricultural

emissions and wastewater, respectively, to urban groundwater systems.⁹ Therefore, compared to Factor 2, the much higher loading of Factor 4 on NO_3^- can be explained by sewage/manure, which dominated NO_3^- presence in groundwater, as supported by dual NO_3^- isotopes. Parameters in both PMF factors resemble the second SOM partition (NO_3^- , SO_4^{2-} , Cl^- , Na, K, and TDS, Figure 4), showing the coexisting impact of manure, sewage, and agricultural activities. In rapidly urbanizing suburban areas of the study region, sewage infiltration to groundwater has been exacerbated by inadequate sanitation systems,³⁷ as evidenced by the widespread discharge of household waste into local ponds and streams.

Natural geochemical baselines are resolved by Factors 1 (HCO_3^- : 51%, Ca: 44%), 3 (Si: 40%, Cl^- : 32%, HCO_3^- : 21%), and 6 (Cl^- : 31%, Na: 22%, HCO_3^- : 20%, SO_4^{2-} : 18%), which represent carbonate dissolution, silicate weathering, and dissolution of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$), and halite (NaCl) (Figure 5). These factors explain most major ion variance, reaffirming that mineral dissolution establishes the background chemistry against which monsoon-driven contaminant pulses occur. Compared with SOM, PMF provided finer separation of specific dissolution pathways, highlighting the value of combining pattern recognition and quantitative receptor modeling.

Finally, the third SOM partition groups Fe, Mn, F, NH_4^+ , TOC, and IWQI (Figure 4), revealing that redox-sensitive metals, organic carbon, and NH_4^+ covary with overall water quality. Their weak expression in PMF results reflects greater variability and uncertainty typical of redox-sensitive parameters and indices.¹⁰ The postwet increase in NH_4^+ , together with Fe/Mn behavior, is consistent with organic matter decomposition under lower redox potential, promoting NH_4^+ accumulation.^{43,56} Additional isotope analysis would help confirm the dynamic sources of NH_4^+ in groundwater highly impacted by surface water recharge.^{50,68} This convergence

across methods supports a unified mechanism in which monsoon-driven connectivity increases early wet-season NO_3^- transport, while prolonged wetting and elevated DOC shift the system toward reduction, amplifying NH_4^+ and redox-sensitive metal dynamics and driving the observed late-season deterioration in water quality and risk.

3.6. Global Groundwater Reanalysis from Geogenic Arsenic-Tainted Regions Reveals Synergistic Contaminants and Monsoon-Driven Health Risks

Arsenic, a group 1 carcinogen, remains a pervasive geogenic groundwater contaminant worldwide and continues to affect millions of people. Although synergistic contaminants driven by geogenic or anthropogenic processes have been widely reported, their potential threat to population health is often neglected.

To address this, we compiled and analyzed global groundwater data from typical As-contaminated regions to prioritize the crucial contaminants threatening potential population health (Figure 6 and Tables S11–S15). A Monte Carlo health risk assessment of adults and children revealed that risks from groundwater contaminants far exceed recommended levels for local populations, particularly in northern Chile, northern Mexico, Ghana, Bangladesh, India, and China. This overarching finding underscores the need for crucial groundwater protection strategies, especially in regions characterized by extreme hydrodynamic conditions and severe surface water contamination.

How urbanization and infrastructure deficits convert geogenic-As aquifers into multicontaminant systems is a topic of growing interest. Consistent with our study, non-negligible contributions of three priority contaminants, including NO_3^- , NH_4^+ , and Pb, along with additional Fe, Mn, and F, to the noncarcinogenic health risk were identified, in addition to As. The general contributions of coexisting Fe and Mn to health risk were predictable in geogenic-As groundwater, as the reducing aquifer conditions favor reductive processes of Fe and Mn (hydr)oxides.^{7,14}

Furthermore, the produced NH_4^+ from the mineralization of nitrogen-bearing organic matter in reducing environments plays a notable role in noncarcinogenic health risk, particular in some regions, including the Songnen Plain and Taiwan of China, the Mississippi River Basin in the USA, and Milan Metropolitan in Italy (Figure 6). Fluoride-associated risk is prevalent in some regions, including Bist-Doab in India, southwest Michigan, Mhamid Oasis in Morocco, and Arusha in Tanzania (Figure 6). This is largely induced by high pH and alkalinity, which favor the replacement of exchangeable F^- in fluoride-rich minerals and are further exacerbated by longer residence time.^{54,69}

Beyond the potential contribution from geogenic contaminants, an increasing contribution of NO_3^- was observed in global groundwater, such as in the PRD of our work, the Yellow River Delta of China, northern Bangladesh, northwest India, Brazil, North Italy, and Northwest Romania (Figure 6). Nitrogen pollution arises from diffuse and ubiquitous sources and is amplified by incomplete or aging sanitation networks in rapidly developing regions, where sewer coverage, septic integrity, and wastewater containment are insufficient. This pattern was confirmed by the strong sewage/manure signal in NO_3^- isotopes.

Pb emerges as a non-negligible cocontaminant whose behavior is consistent with a primarily geogenic baseline

punctuated by seasonally enhanced anthropogenic contributions. Co-occurrence of carcinogen Pb in geogenic-As settings was significant in India, Bangladesh, Romania, northern Italy, and Canada (Figure 6), yet remains under-recognized in groundwater surveillance. Cu and Cd have been scarcely reported in some regional groundwater and likely reflect industrial impact.⁵⁸ These compiled priority contaminants collectively shape overall water quality deterioration and (non)carcinogenic risk and pose a compounded burden in which geogenic baseline contamination is increasingly overprinted by human-derived solute loading, particularly in rapidly urbanizing regions.

Besides identifying the priority contaminants, another key perspective of our work is that monsoon hydroclimate governs not only how much contamination occurs but also when specific risks peak. The coupled connectivity-redox-risk cascade identified here suggests that early wet-season recharge increases vertical connectivity and drives NO_3^- flushing from soils and sanitation-impacted recharge. Conversely, prolonged wetting later in the monsoon shifts aquifers toward more reducing conditions that favor NH_4^+ persistence/production and mobilization of redox-sensitive metals. This seasonal reorganization of dominant species implies that monitoring restricted to dry or early wet campaigns can systematically underestimate late-monsoon deterioration and misidentify the priority constituents for mitigation. Practically, risk-based groundwater management in monsoon regions should therefore include targeted late-wet sampling, with parallel tracking of nitrogen species, DOC, and redox indicators (e.g., Fe/Mn, ORP) to anticipate transitions in vulnerability.

Our isotope evidence, together with the observed wet season strengthening of anthropogenic signatures, indicates that legacy Pb stored in agricultural soils and road dust can be mobilized during sustained rainfall and increased runoff infiltration connectivity. This points to a broader, climate-sensitive exposure pathway: the intensification of heavy rainfall events could increase episodic transport of legacy metals to shallow aquifers even decades after source controls (e.g., leaded gasoline phase out). Accordingly, Pb monitoring should be strengthened in rapidly urbanizing, monsoon-influenced aquifers, particularly during late wet conditions when mobilization potential is highest.

Finally, the study highlights the value of combining receptor models (SOM/PMF) with isotopic tracers to separate background water–rock controls from anthropogenic loading and redox-driven mobilization. Such multilines-of-evidence frameworks are increasingly necessary for sustainable groundwater management under rapid land use change and a shifting climate, because they identify not only contaminant occurrence but also the dominant processes and seasons that should be targeted for monitoring, mitigation, and risk communication.

4. CONCLUSIONS AND FUTURE PERSPECTIVES

This study integrated multi-isotope tracers ($\delta\text{D-H}_2\text{O}$, $\delta^{18}\text{O-H}_2\text{O}$, $\delta^{15}\text{N-NO}_3^-$, $\delta^{18}\text{O-NO}_3^-$, and Pb isotopes), Bayesian mixing, self-organizing maps, and positive matrix factorization (PMF) to disentangle sources, processes, and seasonal dynamics. Water isotope mixing indicates a seasonal shift from surface water influence (dry season) to precipitation-dominated recharge (early wet), followed by postwet mixing and storage effects, changes that reorganize contaminant pathways and redox zonation. The work identified four priority contaminants, namely, NO_3^- , NH_4^+ , As, and Pb, that jointly

control groundwater quality (IWQI) and health risks. Nitrate is predominantly derived from sewage/manure (mean 71%), with rainfall-enhanced leaching of legacy soil-N and fertilizers during wet seasons. Ammonium accumulates under reducing postwet conditions, probably via organic matter degradation. Lead is chiefly geogenic (mean 86%) via granite weathering, yet gains measurable anthropogenic contributions from fertilizer residues and legacy leaded-gasoline during storm periods. Arsenic reflects sedimentary mineral dissolution and PO_4^{3-} -facilitated competitive desorption, with wet-season dilution and oxidation lowering dissolved As. Water quality deteriorates markedly in the postwet season. Probabilistic health risk assessment (Monte Carlo) indicates that >72% and >90% of the local population likely face noncarcinogenic and carcinogenic risk exceedances, respectively, with As dominating carcinogenic risk even after speciation-aware adjustment. A global synthesis underscores that in geogenic-As regions, co-occurrence with NO_3^- , NH_4^+ , and Pb is widespread, amplifying the need for seasonally adaptive monitoring.

Several limitations of this study should be acknowledged. First, it is critical to emphasize that the assessment addresses health risk only from a screening perspective rather than providing definitive toxicological conclusions. The risk estimates derived from the USEPA model serve as an initial warning signal rather than a substitute for actual in vivo or clinical toxicity outcomes. Second, our current understanding of groundwater priority pollutants, particularly emerging contaminants of persistent concern, remains poorly understood. A more in-depth and region-specific investigation, integrating long-term monitoring data and advanced toxicological profiling, is urgently needed to refine the priority list and reduce the uncertainties inherent in this screening-level exercise.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/envhealth.6c00427>.

Analysis of metal(loid)s in groundwater, QA/QC, and ANOVA test. Groundwater quality evaluation method using the integrated-weight water quality index (IWQI) by the G1 method. Health risk assessment. Isotope analysis and the Bayesian stable isotope mixing model (MixSIAR) details. The details of SOM and PMF model analysis. (PDF)

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Notes

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