Multi-media distribution, sources, and ecological risk of per- and poly-fluoroalkyl substances (PFAS) in the Weihe River Basin, China (Postprint)

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Abstract

Per- and poly-fluoroalkyl substances (PFAS) have garnered significant global attention due to their widespread presence and potential environmental and health risks. However, research on the occurrence and environmental behavior of PFAS across different media remains limited. We analyzed the occurrence, distribution, sources, and ecological risks of 32 PFAS across multiple media in the Weihe River, China. The concentrations of PFAS ranged from 5.89 to 472.84 ng/L in the pore water and from 9.93 to 459.50 ng/L in surface water, exhibiting significant spatial variability ($P<0.05$). In contrast, the PFAS concentration range in the sediments was 0.74–1.81 ng/g dry weight, with no pronounced spatial variation in solid-phase PFAS ($P>0.05$). Vertically, concentrations in 33.00% of pore water samples exceeded those in surface water, showing a heterogeneous vertical distribution with enrichment at depths of 40–60 cm. The physical-chemical characteristics of PFAS and the hydrological and sedimentary processes at the basin scale were responsible for PFAS partitioning between the aquatic environment and sediments. Four major sources were identified through integrated source apportionment: industrial and domestic wastewater (58.25%), aqueous film-forming foam (18.07%), combined input from household pollution and metal plating (8.70%), and stormwater runoff and landfill leachate (14.98%). The ecological risk assessment revealed negligible risks from short-chain PFAS in surface water and pore water, whereas long-chain PFAS posed low to moderate ecological risks. Furthermore, the discharge of PFAS from the Weihe River to the Yellow River was estimated up to 708.20 kg/a. This study provides critical data informing strategies for mitigating PFAS pollution in rivers across typical arid and semi-arid areas of China.

Full Text

Preamble

J Arid Land (2026) 18(4): 632–656 Multi-media distribution, sources, and ecological risk of per- and poly-fluoroalkyl substances (PFAS) in the Weihe River Basin, China TANG Bin 1,2,3,4 , SONG Jinxi 1,2,3,4* , LU Aoran 1,2,3,4 , ZHANG Zhuo 1,2,3,4 , MAO Ruichen YANG Chenxi 1,2,3,4 , LI Nan 1,2,3,4 , FENG Jiayuan 1,2,3,4 1 Xi' an Key Laboratory of Environmental Simulation and Ecological Health in the Yellow River Basin, Xi' an 710127, China; Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity, Xi' an 710127, China; College of Urban and Environmental Sciences, Northwest University, Xi' an 710127, China; Yellow River Institute of Shaanxi Province, Xi' an 710127, China; School of Water and Environment, Chang' an University, Xi' an 710054, China

Abstract

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Keywords

per- and poly-fluoroalkyl substances; multi-media distribution; source apportionment; ecological risk; Weihe River Citation:

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1 Introduction

Per- and poly-fluoroalkyl substances (PFAS) are a class of synthetic chemicals characterized by carbon–fluorine (C–F) bonds (Buck et al., 2011). Due to their remarkable hydrophobicity, chemical stability, and surface-active properties, PFAS are extensively used in consumer products and industrial applications, including food packaging, textiles, metal plating, and flame retardants (Miralles-Marco and Harrad, 2015; Glüge et al., 2020; Evich et al., 2022). The global production and widespread use of these substances have led to their release into various environmental media and biological systems, with detectable levels even in remote areas with minimal human activity (Cai et al., 2012; Cai et al., 2022; Chen et al., 2023). Given the potential irreversible toxic effects of prolonged exposure to PFAS on both the environment and living organisms, this contamination has garnered increasing attention. Some legacy PFAS compounds have been classified as persistent organic pollutants and are being phased out. Short-chain alternatives and emerging PFAS are increasingly replacing these legacy substances to meet industrial and domestic demands (UNEP, 2009, 2019). However, their widespread use across many areas has led to increasing environmental concentrations, posing new challenges to aquatic ecosystems. Consequently, a comprehensive assessment of the fate and ecological risks of both legacy and emerging PFAS in the environment is required.

Globally, many rivers continuously or intermittently receive pollutant inputs and play a critical role as primary receptors and sinks (Peralta-Maraver et al., 2018). Due to PFAS persistent accumulation in these ecosystems, surface water and sediments have become key media for studies assessing the characteristics of PFAS pollution and potential sources (Tao et al., 2024; Tang et al., 2025). However, the distribution and environmental fate of PFAS in hyporheic zones remain poorly understood. Pore water in the hyporheic zones of porous media plays a critical role in controlling the migration of pollutants within sediment matrices and facilitating exchange processes at the water–sediment interface (Jurado et al., 2007; Boano et al., 2014). Pore water can serve as a reservoir for hydrophobic organic contaminants (HOCs), such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), as well as amphiphilic contaminants like antibiotics (Maskaoui et al., 2002, 2005; Cheng et al., 2014). Therefore, a comprehensive understanding of the contamination characteristics and vertical distribution of PFAS compounds in pore water within hyporheic zones is essential.

The Weihe River, the largest tributary of the Yellow River, drains a basin area of approximately 13.48$×$10 . Flowing through the Gansu and Shaanxi provinces, the river plays a vital role in sustaining the livelihoods of tens of millions of people and serves as the economic lifeline of northwestern China (Chang et al., 2015). However, rapid urbanization and economic development along the riverbanks have led to unprecedented water pollution challenges in the Weihe River Basin, threatening the well-being of local communities. In response, management authorities have implemented Integrated River Basin Management (IRBM) initiatives throughout the main basin, including upgrades to wastewater treatment, rainwater-sewage separation systems, and ecological flow restoration efforts. While these actions have significantly improved traditional water quality indicators (DEEGS, 2025; DEESX, 2025). Despite considerable progress, the emergence of new contaminants, particularly PFAS, presents renewed challenges to water security in river basins (Xiao, 2017). Previous studies have reported PFAS contamination in surface waters of the Weihe River Basin (Zhou et al., 2019; Zhang et al., 2025), but data on PFAS pollution in sediments and pore water in hyporheic zones remain relatively scarce. Additionally, the spatial and vertical distribution characteristics of PFAS in the Weihe River remain unclear. Further clarification is needed regarding pollution sources and the risks to aquatic organisms. Therefore, an urgent assessment of PFAS contamination and potential risks across different media along the mainstream of the Weihe River is required to support basin-wide pollution control strategies.

Accordingly, we present a quantitative analysis of 32 PFAS in the Weihe River, northwestern China. The study aimed to: (1) investigate the occurrence and distribution characteristics of both legacy and emerging PFAS in multiple media, including surface water, pore water, and sediments;

(2) present an integrated multi-model source apportionment approach to identify and trace potential sources of PFAS; and (3) assess the environmental risks and the pollution load of PFAS to different trophic communities in the aquatic ecosystem, and estimate the mass load within the basin. By providing critical baseline data for the Weihe River, this study offers a framework for characterizing PFAS contamination and informs policy-driven mitigation strategies for emerging pollutants in arid and semi-arid environments. 2 Materials and methods

2.1 Study area and sampling

The Weihe River Basin (33°50′–37°18′N, 104°00′–110°20′E; Fig. 1 [Figure 1: see original paper]) is the primary artery for water and sediment transport in the Yellow River Basin and serves as a crucial water source for central and western China (Song et al., 2018). Geographically, its elevation gradient descends gradually from west to east. Numerous towns, industrial facilities, and agricultural activities are distributed along the river, increasing the likelihood of point-source

PFAS inputs. Between July and August 2024, surface water, sediment, and pore water samples were collected from 20 stations along the Weihe River. Nine upstream sites (W1-W9) were located in the Gansu Province, while six midstream sites (W10-W15) and five downstream sites (W16-W20) were located in the Shaanxi Province. Porewater samples were unavailable at some locations due to equipment malfunctions and flooding conditions. Detailed information on the sampling locations is presented in Figure 1.

All sampling containers were pre-rinsed with methanol, Milli-Q water, and river water from the sampling site. Surface water, pore water, and sediment samples were stored and transported to the laboratory in light-protected ice boxes. Water and sediment samples were stored at 4°C and -20°C, respectively, until analysis.

2.2 Chemicals and reagents

A total of 32 PFAS compounds were evaluated, including 11 perfluoroalkyl carboxylic acids, 8 perfluoroalkyl sulfonic acids, 3 fluorotelomer sulfonic acids, 3 polyfluoroalkyl ether sulfonates, 5 perfluoroalkyl ether carboxylic acids, and 2 perfluorooctane sulfonamidoacetic acids. All analytical standards and isotopically labeled internal standards, with purities >98.00%, were purchased from Wellington Laboratories Inc. (Guelph, Canada). Detailed information about the target compounds is provided in Table S1.

High-performance liquid chromatography (HPLC)-grade organic solvents, including methanol, acetonitrile, and methyl tert-butyl ether, were sourced from Thermo Fisher Scientific (Waltham, USA). Acetic acid and ammonium hydroxide were purchased from Alfa Aesar (Waltham, USA).

HPLC-grade ammonium acetate was supplied by Anpel Laboratory Technologies Co., Ltd. (Shanghai, China). Ultrapure water was obtained using a Milli-Q purification system (Burlington, USA).

2.3.1 Sample preparation and analysis

Pretreatment of PFAS in water and sediment samples was performed as previous methods (Zhou et al., 2023). Briefly, 1 ng of internal standard was added to each water sample, followed by extraction of the target PFAS using a weak anion exchange (WAX) solid-phase extraction cartridge (Waters Corporation, Midford, USA). The target analytes were sequentially eluted with an ammonia-methanol solution, methanol, ultrapure water, and ammonium acetate buffer. For sediment samples, 1 ng of internal standard and methanol were added and mixed thoroughly. The supernatant was obtained after ultrasonic-assisted extraction followed by high-speed centrifugation. This step was repeated three times; then, the combined extracts were subjected to the same solid-phase extraction (SPE) procedure as the water samples. The final extract was concentrated to approximately 200 μL.

Geographic distribution of sampling sites along the Weihe River (a). (b-d), field photographs depicting characteristic riverine environments across the upper, middle, and lower sections of the river.

All target PFAS concentrations were quantified using an ACQUITY Ultra Performance Liquid Chromatography (UPLC) system coupled with a Xevo TQ-S triple quadrupole mass spectrometer (Waters Corporation, Milford, USA). Chromatographic separation was performed on an ACQUITY UPLC BEH Shield RP18 column (Waters Corporation, Milford, USA). The mobile phases consisted of methanol and ammonium acetate, delivered using a gradient elution program at a flow rate of 0.2 mL/min.

Quality assurance (QA) and quality control (QC) No glassware or fluoropolymer materials were used during sample collection or pretreatment to prevent potential contamination. A procedural blank was included with each batch of 10 samples to monitor possible interferences during both preparation and instrumental analysis. After each batch was completed, a standard solution was injected to evaluate instrument stability and performance. Quantification was done using a mass-labeled internal standard calibration curve with seven concentration levels ranging from 0.5 to 100.0 ng/mL, demonstrating excellent linearity (>0.9800). The method detection limit (MDL) was determined by analyzing seven replicate samples at concentrations close to the estimated detection limit. Detailed information on the target analytes—including MDL values, method quantification limit (MQL), recovery, and detection frequency (DF)—is provided in Table S2. 2.4 Framework of source apportionment assessment Given the complexity of pollutant source resolution, we developed an integrated source

apportionment framework by combining multiple receptor modeling approaches. Diagnostic ratios (DRs) were applied to rapidly identify and characterize potential source categories and locations. Principal component analysis (PCA) was performed to identify the main components and evaluate the contributions of key pollution sources. Positive matrix factorization (PMF)—a multivariate receptor modeling tool commonly used to resolve source contributions and quantify the interrelationships among influencing factors—was employed as a complementary model to cross-validate the results, identify potentially overlooked sources, and quantify their contributions.

Obtaining source distribution by DRs DRs are empirical metrics used to make preliminary inferences about potential contaminant sources based on the relative abundance of selected compounds. The compositional characteristics of PFAS have therefore been widely applied to infer possible sources of environmental contamination (Chen et al., 2016). We selected ratios such as sodium perfluorooctane sulfonate (PFOS)/ perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA)/PFOA, perfluorononanoic acid (PFNA)/PFOA, and perfluorobutanoic acid (PFBA)/PFOA as characteristic indicators with diagnostic significance. As PFOA is ubiquitous in aquatic environments, the concentrations of individual PFAS compound were normalized to the corresponding PFOA concentration at each sampling site, following the method of Chen et al. (2016).

Identifying the contribution of key sources by PCA For PCA, pollutant concentrations were used as the input variables. Principal components were extracted from the PFAS concentration data matrix using principal factor analysis with varimax rotation to identify source types.

Uncovering omitted potential sources by PMF Two datasets were used as inputs for the PMF model: a concentration matrix of 32$×$20 (comprising 32 individual PFAS and 20 sampling sites) and a corresponding uncertainty matrix of the same dimensions. The PMF v.5.0 algorithm was set to robust mode, with 100 iterations and a random initial seed. The number of factor range was set to 2–6, and the model reduces the species weight based on residual analysis and calculates the optimal results through iterative testing. The -value was used as the objective function, with factor scores indicating the strength of association between the variables in the original dataset and the specific factors. Ultimately, we selected a solution with four factors based on the comparison of -values, residual analysis, and the explanatory power of the factors. Uncertainty (Unc) was calculated following the model manual, where concentrations ≤MDL were estimated using Equation 1:

5 Unc

For target concentrations >MDL, Unc was calculated using Equation 2:

Error fraction Concentration where Error fraction is the relative uncertainty of the species concentration (%); and Concentration is the measured concentration of the species (ng/L or ng/g DW(dry weight)).

The PMF model was bootstrapped with 100 iterations, yielding an optimal four-factor solution robust =1482.2 and =1879.7.

2.5 Data analysis

The concentration ratio (CR) was calculated using Equation 3: where (ng/L) and (ng/L) are the concentrations of PFAS in the pore water and surface water, respectively.

The sediment-water partition coefficient (L/kg) and the carbon normalized partition coefficient (L/kg) were calculated using Equations 4 and 5 (Lee et al., 2020), respectively:

d sed w / 1000, K C C = × (4)

100 / where (ng/g DW) and (ng/L) are the concentrations of PFAS in sediment and surface water, respectively; and (%) is the percentage of organic carbon in the sediments.

The ecological risk of individual PFAS in surface water was assessed using the risk quotient (RQ) method, as defined in Equations 6 and 7:

MEC RQ , PNEC = (6)

50 50 / PNEC , AF LC EC = (7)

where MEC (ng/L) and PNEC (ng/L) are the measured environmental concentration and predicted no-effect concentration, respectively, of individual PFAS in surface water; (ng/L) and (ng/L) are the median effective concentration and the median lethal concentration, respectively; and AF is the assessment factor, typically set at 100 or 1000 based on chronic and acute toxicity data, respectively. All the toxicity values were obtained from the United States Environmental Protection Agency (US EPA) Ecological Structure Activity Relationships (ECOSAR) database.

Risk levels were classified into four categories: no risk ($RQ<0.010$), low risk ($0.010\leq RQ<0.100$), medium risk ($0.100\leq RQ<1.000$), and high risk (RQ$ $1.000).

The ecological risk of PFAS mixtures was assessed using the classical concentration addition (CA) model. Mixture risk quotients (RQ) for PFAS were calculated following previous methods (Thomaidi et al., 2020), as shown in Equation 8: where RQ is the ecological risk quotient of the individual PFAS; is the total number of detected PFAS; MEC (ng/L) and PNEC (ng/L) are the measured environmental concentration and predicted no-effect concentration of the individual PFAS, respectively.

The average annual runoff of the Weihe River at three representative locations—Tuoshi Station (upstream), Xianyang Station (midstream), and Tongguan Station (downstream)—is 16.53$$\times 1045.05\times 10, and 76.56\times$$10 , respectively. The Weihe River is the main recharge and transfer tributary of the Yellow River. The annual mass flux of PFAS transported by the river was calculated using Equation 9: water where M water (kg/a) is the annual mass of an individual PFAS; (ng/L) is the concentration of that PFAS at sampling location along the Weihe River; and /a) is the average annual runoff volume at that location.

2.6 Statistical analysis

Sampling maps and spatial variations in PFAS concentrations were generated using ArcMap v.10.5 software (ESRI, Redlands, USA). Other figures were created with Origin v.2025 software (OriginLab Corp, Northampton, USA) and R v.4.2.3 statistical software (R Core Team, R Foundation for Statistical Computing, Vienna, Austria). Significant differences were evaluated using the Mann-Whitney U test.

3 Results

3.1 Concentration and composition of PFAS Overall, 28 of 32 target PFAS were detected at least once in the Weihe River surface water samples (Fig. 2 [Figure 2: see original paper]). They included 19 legacy perfluoroalkyl acids (perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA)) and 9 emerging compounds (6:2 fluorotelomer sulfonic acid (6:2 FTS), 8:2 FTS, potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate

(9Cl-PF3ONS), Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS), perfluoro-4-oxapentanoic (PF4OPeA), perfluoro-5-oxahexanoic (PF5OHxA), perfluoro-3,6-dioxaheptanoic acid (3,6-OPFHpA), n-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA), and n-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA). The total PFAS concentration range across all sampling sites was 9.93–459.50 ng/L, with a median of 19.70 ng/L. In terms of composition, PFCAs with carbon chain lengths of 4–7 (C4-C7), 9–14 (C9–C14), and PFOA accounted for the majority of total PFAS in surface water, contributing 39.40%, 22.12%, and 22.15%, respectively.

Furthermore, 13 of 32 target PFAS were detected in sediment samples. Among them, only 7 individual PFAS were frequently detected. While the DF of PFAS ranged from 5.00% to 85.00%, the majority of targeted emerging PFAS compounds were not detected, except for 6:2 FTS. Total PFAS concentration range in sediments was 0.74–1.81 ng/g DW, with a median of 1.18 ng/g DW.

In terms of composition, PFOA, C9–C14 PFCAs, and C4–C7 PFCAs accounted for 38.09%, 33.56%, and 19.04% of the total, respectively.

In pore water samples, 27 of 32 PFAS were detected, with DF range of 5.00%-100.00%. Total PFAS concentration range in pore water was 5.89–472.84 ng/L, with a median of 42.50 ng/L. The major constituents resembled those in surface water, with C4–C7 PFCAs, C9–C14 PFCAs, and PFOA accounting for 45.53%, 21.35%, and 20.43% of the total, respectively. 3.2 Spatial and vertical distribution of PFAS The highest total PFAS concentration in surface water occurred at site W15 (459.50 ng/L), Total concentration of per- and poly-fluoroalkyl substances (PFAS) and relative abundance in surface water (a, d), sediment (b, e), and pore water (c, f). C4–C7 PFCAs include PFBA, PFPeA, PFHxA, and PFHpA; C9–C14 PFCAs include PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA; C4–C7 PFSAs include PFBS, PFPeS, PFHxS, and PFHpS; C9-C12 PFSAs include PFNS, PFDS, and PFDoS. In Figure c and f, the same sampling site with numbers means different sampling depths.

The names of the abbreviations of these perfluorinated compounds are shown in Table S1.

followed by W20 (92.51 ng/L) and W16 (64.80 ng/L) sites, whereas the lowest levels were observed at W6 (9.93 ng/L) and W7 (10.13 ng/L) sites, together exhibiting pronounced spatial variability (Fig. 3a [Figure 3: see original paper]). PFAS concentrations differed significantly between downstream and upstream sites (Mann-Whitney U test; <0.001), with a general trend of midstream>downstream>upstream.

Notably, after excluding the extreme outlier at site W15, the average total PFAS concentration at the remaining five midstream sites (W10–W14) was

16.08 ($±$4.28) ng/L, which was comparable Distribution of total PFAS in the surface water (a), sediment (b), and pore water (c) of the Weihe River.

Seasonal variations within different sub-basins are indicated in the violin plots (d–f). ns, non-significance; *, <0.050 level;* **, <0.001 level.

to the upstream level. These results suggest that the apparent midstream peak is driven by localized sources rather than regional contamination. The spatial distribution of PFAS concentration reflects the influence of anthropogenic activities and regional economic development. PFAS distribution in the Weihe River is primarily governed by localized land-use patterns. Low levels at upstream sites (W1–W9) are attributed to the predominance of forest and grassland areas characterized by minimal anthropogenic disturbance. In contrast, the downstream enrichment is driven by intense urban and agricultural activities, which facilitate wastewater discharge. A sharp peak occurred at site W15, situated between Xianyang and Xi’ an cities. This hot spot is likely sustained by concentrated industrial emissions and high population density within this metropolitan corridor.

PFAS concentrations in sediments were relatively uniform across sampling sites, with no significant spatial variation in total PFAS (>0.050; Fig. 3b). This uniformity may reflect the fact that sediment-bound PFAS represent long-term accumulation processes, capturing more stable historical inputs rather than recent discharges. The spatial distribution of PFAS in pore water exhibited significant differences between upstream and downstream regions (<0.050; Fig. 3c).

The elevated concentration at site W15, located in the midstream transition zone, was the main contributor to the higher average PFAS concentrations in the middle reaches. Consistent with surface water trends, PFAS concentrations in pore water were relatively higher in the downstream region and at site W15. Furthermore, CR values of PFAS were calculated to evaluate differences between pore water and surface water for individual PFAS compounds (Table S3). Only 33.00% of the samples had higher PFAS concentrations in pore water than in surface water (CR>0.000), whereas 64.00% of the samples had higher concentrations in surface water (CR<0.000). compounds with DF below 60.00%. Although PFAS concentrations in surface water exceed those in pore water at most sampling points, this difference tended to diminish with increasing depth (up to 60 cm) along the vertical profile (Fig. 4a [Figure 4: see original paper]). Most PFAS monomers exhibited elevated concentrations at depths of 40–60 cm. Furthermore, short-chain PFAS tended to accumulate in deeper sediment layers, whereas long-chain PFAS were predominantly enriched in surface sediments (Fig. 4b). This pattern is likely attributable to the greater mobility of short-chain PFAS.

Notably, site W18 showed the highest concentrations in 0–20 cm depth, likely due to the predominance of fine-grained sediments (<0.075 mm) in the surface layer at this location (Fig. 3.3 Distribution of PFAS between water and sediments is a key parameter for evaluating the transport potential of contaminants within the hyporheic zone. Owing to the limited DF of individual PFAS in both water and sediment, values were calculated for only 8 compounds, i.e., perfluorohexanoic acid (PFHxA), PFHpA, PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), and PFOS. A decreasing trend was observed in these values for PFNA and PFUnDA (Fig. 5 [Figure 5: see original paper]). This nonlinear growth trend likely reflects a combination of factors, including the structural characteristics of PFAS molecules, particle size, and environmental conditions.

3.4 Source apportionment

3.4.1 Evaluating potential pollution source distribution through ratio analysis ranges for PFOS/PFOA, PFHpA/PFOA, PFNA/PFOA, and PFBA/PFOA ratios were 0.0080-1.0200, 0.0290-1.1410, 0.0530-1.1780, and 0.0010-0.1120, respectively. Generally, a PFOS/ PFOA ratio greater than 1.0000 indicates the potential presence of point source pollution. Values exceeding 1.0000 were observed at site W20 (Tongguan Station), where the PFNA/PFOA ratio was 1.1780, indicating point source PFAS contamination at this site. Furthermore, no significant relationship was found between PFBA/PFOA and PFOS/PFOA ratios (=0.0108, >0.050),

Vertical concentration profiles of individual PFAS in the water (a1-a9) and sediment (b1-b6) samples of the Weihe River. (a1), PFBA; (a2), PFPeA; (a3), PFHxA; (a4), PFHpA; (a5), PFOA; (a6), PFNA; (a7), PFDA; (a8), PFBS; (a9), PFOS; (b1), PFHxA; (b2), PFHpA; (b3), PFOA; (b4), PFNA; (b5), PFDA; (b6), PFOS. The names of the abbreviations of these perfluorinated compounds are shown in Table S1. indicating substantial differences in the potential sources of PFAS from agricultural and domestic waste, as well as farm sewage, reflecting considerable variability in environmental processes. A weak relationship between PFNA/PFOA and PFOS/PFOA ratios (=0.2138, =0.040) suggests that industrial waste, wastewater treatment plant discharges, and the degradation of fluorotelomer alcohols (FTOHs) may be significant sources of PFAS in the environment. Conversely, the lack of a significant relationship between PFHpA/PFOA and PFOS/PFOA ratios (=0.0010, >0.050) further indicates that industrial and domestic sources within the watershed, rather than atmospheric deposition, are likely the primary contributors to PFAS contamination in surface waters.

Sorption coefficients log (a) and log (b) of PFAS in the Weihe River. Boxes indicate the IQR (interquartile range, 25 to 75 percentiles). The median value is shown as a line within the box. The square is shown as the mean value. Whiskers extend to the most extreme value within 1.5×IQR. The data distribution is represented by black diamonds and normal fit curves. The names of the abbreviations of these perfluorinated compounds are shown in Table S1.

Identification of critical sources using PCA Monomeric compounds with detection rates below 50.00% were excluded from the statistical analysis. Figure

6b [Figure 6: see original paper] presents the PCA results for PFAS concentrations in Weihe River surface water. Surface water PFAS samples can be categorized into two principal components (PCs): PC1 and PC2, with contribution percentages of 50.10% and 25.30%, respectively, yielding a cumulative variance of 75.40%. PC1 was dominated by several PFAS compounds, including PFOA, PFHxA, PFNA, PFHpA, perfluoropentanoic acid (PFPeA), potassium perfluorobutane sulfonate (PFBS), PFDA, and PFBA. PC2 was primarily influenced by long-chain PFAS and emerging PFESA compounds, including PFUnDA, PFDoDA, perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), PFDS, 11Cl-PF3OUdS, and 9Cl-PF3ONS.

Tracking missing potential sources using PMF Factor 4 (FC4) representing the largest share (58.25%), followed by Factor 1 (FC1; 18.07%), Factor 2 (FC2; 14.98%), and Factor 3 (FC3; 8.70%). These results are consistent with PCA findings. For instance, FC1 was dominated by PFHxS, PFOS, and 6:2 FTS. FC3 aligned with PC2 and was characterized by long-chain PFAS and polyfluoroalkyl ether sulfonates, whereas FC4 corresponded to PC1, comprising both long- and short-chain PFAS from mixed pollution sources.

PFDA was additionally identified as a key marker compound and was classified under FC2.

3.5 Ecological risk assessment

Ecological risks of 26 PFAS to three representative organisms in the Weihe River Basin were evaluated using toxicity data from the Ecotoxicology Knowledgebase (ECOTOX). With the exception of long-chain compounds PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA, individual PFAS posed negligible risks to surface waters. In sediments from hyporheic zones, long-chain PFAS presented low to moderate risks to green algae, daphnids, and fish across all sampling sites (Fig. 7 [Figure 7: see original paper]). values in surface water from the Weihe River were relatively high. Specifically, 55.00% of sampling sites exhibited low risk levels for green algae (0.011–0.031), while risks for daphnids (0.017–0.152) and fish (0.016–0.163) ranged from low to moderate across all sites (Fig. 7a).

Similarly, in sediment samples, 33.00% of sites exhibited low RQ values (0.028–0.062), whereas risks for daphnids (0.014–0.437) and fish (0.013–0.491) were consistently low to moderate across all sites. These findings suggest that regulatory agencies should, in line with the

Source analysis of PFAS. (a), diagnostic ratios of PFOS/PFOA, PFBA/PFOA, PFHpA/PFOA, and PFNA/PFOA; (b), principal component analysis (PCA) result; (c), source apportionment results of PFAS with the positive matrix factorization (PMF) model. FC1-FC4 are the four primary factors contributing to PFAS contamination. The names of the abbreviations of these perfluorinated compounds are shown in Table S1. precautionary principle, strengthen oversight of PFAS mixtures in aquatic environments, particularly in high-risk river sections such as site W15. The potential impacts on sensitive species warrant sustained close attention.

Risks to green algae (1.95$×10–9.05×10)*werenegligible, andriskstodaphnids*(1.61×10–6.85×10); *andfish*(2.27
*chaincompoundsposedhigherrisksthantheirshort−chainanalogues, reflectingtheirgreaterinherenttoxicity.*1
Most target PFAS monomers in the pore water did not pose significant ecological risks.

However, 6 compounds, i.e., PFOA, PFNA, PFUnDA, PFDoDA, PFTrDA, and PFTeDA posed ecological risks at least at one sampling site. Among them, PFTrDA (green algae: 7.94$×10–1.39×10; *daphnids* : 6.25×10–1.09×10; *andfish* : 6.25×10–1.09×10)*andPFTeDA*(*greenalgae* : 4.26×10–6.40×10; *daphnids* : 4.00×10−2.48×10; *andfish* : 5.00×10–3.10×$ 10) were associated with moderate ecological risks (Fig. 7b).

Mixture risk quotients (RQ) and individual ecological risks for PFAS. (a), total RQ in surface water (a1) and pore water (a2) across all sampling sites; (b), individual ecological risk quotient (RQ) for green algae (b1 and b2), daphnids (b3 and b4), and fish (b5 and b6) in surface water and pore water, respectively. The names of the abbreviations of these perfluorinated compounds are shown in Table S1.

3.6 Mass loads to the Weihe River

By combining the 5-a average runoff from upper, middle, and lower sections of the Weihe River with PFAS concentrations at the nearest sampling sites (W10, W15, and W20), we estimated the annual mass load of PFAS in the three reaches of the river using Equation 9. Total fluxes in the upper, middle, and lower reaches were 18.75, 2070.00, and 708.20 kg/a, respectively (Table S4).

Mass loadings in the three sections followed the trend: long-chain PFAS>short-chain PFAS>emerging PFAS. Long-chain PFAS accounted for the majority of the mass load during high-flow periods, while the usage of short-chain substitutes gradually increased across the basin, with the contribution of short-chain PFAS reaching 44.60% at the Xianyang Station in the middle reaches. Emerging PFAS accounted for 3.52%, 2.97%, and 1.24% of the total PFAS loads in the upper, middle, and lower reaches, respectively. These results indicate that while the use of short-chain substitutes is gradually increasing in the Weihe River basin, the growth contribution of emerging substitutes remains limited.

4.1 PFAS pollution in the Weihe River

We examined the total PFAS concentrations and spatial distribution at 20 stations along the Weihe River. Relatively high concentrations of alternative PFAS —PFPeA, PFHxA, and PFBS—were observed in the Weihe River Basin, with their proportions increasing compared with traditional long-chain homologs. In contrast, emerging PFAS contributed only 3.20% to the overall total PFAS composition. The global ban on the production and use of conventional long-chain

PFAS has likely promoted the increasing prevalence of short-chain and emerging alternatives in the environment (Liu et al., 2019; Li et al., 2020a). Although the overall PFAS contamination in the Weihe River remains relatively low, the anomalous concentrations detected at site W15 suggest the presence of localized point-source pollution.

The dominance of long-chain homologues in sediments reflects their strong affinity for the solid-phase particles, driven by high associated with carbon chain length and functional group characteristics (Higgins and Luthy, 2006; Li et al., 2022). Among short-chain PFAS, only PFHxA exhibited elevated levels, while others such as PFBA, PFPeA, and PFBS were rarely detected, which may be attributed to the high mobility of short-chain PFAS and the use of alternatives in the basin. Meanwhile, the distribution patterns within the hyporheic zone were likely influenced by a major flood event during sampling, as seasonal flooding is known to dilute contaminant concentrations and perturb sediment–water exchange dynamics (Yamazaki et al., 2025). To the best of our knowledge, researchers regarding the concentration and environmental behavior of PFAS in hyporheic zone are limited. Our findings contrast with that of Gao et al. (2020): specifically, concentrations of most PFAS in surface water were higher than those in pore water, with the exceptions of PFOA, PFNA, and PFOS. This result indicates that external loading to surface water remains a primary pathway for PFAS contamination in the Weihe River.

Vertical distribution results indicate that the fate of PFAS in pore water is governed by multiple interactive factors. Surface–groundwater interaction serves as a key mechanism driving environmental migration, where flow velocity-mediated hydrodynamic processes dictate the intensity and depth of PFAS release, further influenced by carbon chain length and sediment grain size (Yu et al., 2024). Benthic organisms act as ecosystem engineers, modifying the physical- chemical environment of the hyporheic zone through bioturbation and patch heterogeneities (Peralta-Maraver et al., 2018), thereby influencing the adsorption-desorption processes of PFAS.

Additionally, the pore water/surface water ratio and concentration gradients are primary drivers of desorption (Reif et al., 2022). Specifically, lower pore water loads provide additional adsorption potential, whereas higher loads increase the risk of re-release. Consequently, PFAS accumulated in sediments are a persistent threat to water quality, potentially migrating downstream into aquifers even after primary sources are controlled.

4.2 Environmental effects on PFAS distribution The adsorption affinity of PFAS is primarily governed by their structural characteristics, with and log generally increasing alongside carbon chain length (Lee et al., 2020; Chen et al., 2023). The primary factors influencing sediment adsorption include steric hindrance and hydrophobic interactions. Steric hindrance increases with carbon chain length, thereby inhibiting sediment adsorption of PFAS (Guelfo and Higgins, 2013), while hydrophobic interactions strengthen with increasing chain length, further enhancing adsorption capacity (Higgins and Luthy, 2006). Beyond molecular structure, sediment grain size and mineral-surface electrostatic interactions are key mechanisms driving PFAS adsorption. Specifically, finer particles provide larger specific surface areas and pore volumes that enhance solid-phase retention, significantly increasing values (Hubert et al., 2023; Hu et al., 2025). Concurrently, charged mineral surfaces modulate adsorption–desorption via electrostatic attraction or repulsion of PFAS functional groups (Fig. S2), contributing to the spatial variability of partitioning coefficients within the heterogeneous sedimentary environments of the Weihe River.

Environmental factors and changes in hydrological processes play a significant role in the interfacial distribution of PFAS. While long-chain PFAS typically exhibit a strong affinity for organic-rich solid media (Ghaznavi et al., 2025), the lack of significant correlation between PFAS concentrations and TOC in this study (>0.050) suggests that low contaminant levels in the upper and middle reaches may limit organic carbon-driven enrichment. Furthermore, intense hydrological activities may enhance terrestrial inputs and elevate aqueous PFAS concentrations (Lougkovois et al., 2025), facilitating their transport via resuspended sediments and suspended particles (Zushi et al., 2012; Liu et al., 2015). These processes likely induce interfacial perturbations, altering local partitioning patterns and thereby intensifying spatial heterogeneity. 4.3 Anthropogenic activities effects on PFAS pollution We employed a multi-approach assessment framework to identify the main sources of PFAS contamination in the Weihe River. Ratio analysis of typical PFAS in environmental samples provides valuable insights into potential pollution sources, particularly for rapid screening of impacted areas. For example, PFBA and PFHpA are commonly used as indicators of domestic wastewater, agricultural effluent, and precipitation-related inputs (Wang et al., 2012; Chen et al., 2016). Similarly, PFNA is associated with 8:2 FTOH feedstocks and is often used to trace emissions and degradation of fluoropolymers (Buck et al., 2011).

The PCA results effectively identified potential pollution sources. Compounds associated with PC1 indicated combined inputs from industrial and domestic wastewater, including fluoropolymer manufacturing, food packaging, textile production, as well as emissions from household waste (Li et al., 2023; Riaz et al., 2023). Domestic pollution and metal electroplating are identified as the major contributors to PC2. Reportedly, long-chain PFAS accumulate significantly in consumer and recreational products, such as outdoor textiles, and gloves (Li et al., 2023; Liu et al., 2024).

Additionally, compounds such as 9Cl-PF3ONS and 11Cl-PF3OUdS have been used as PFOS replacements in the electroplating industry, where they function as commercial mist suppressants (Wang et al., 2013).

The results of the PMF analysis showed strong consistency with PCA, with both methods identifying similar pollutant composition patterns. In the PMF model, FC1 was closely associated with AFFF applications and electroplating activities. Historically, PFHxS and PFOS were extensively utilized in aqueous film-forming foams (AFFF), metal plating, and as surfactants (Li et al., 2023).

Recently, 6:2 FTS has been increasingly introduced as an alternative (Hamid et al., 2020). In contrast, the PMF model identified FC2, characterized by PFDA, which has been previously reported to be enriched in storm water runoff, landfill leachate, and industrial wastewater (Lin et al., 2009; Zushi and Masunaga, 2009; Perkola and Sainio, 2013). Overall, both methodologies consistently identified various industrial wastewater, domestic sewage, surfactants, and AFFF as the predominant potential sources of PFAS in the surface water of the Weihe River,

while the PMF model further highlighted the potential impacts of stormwater runoff and landfill leachate. These findings underscore the value of an integrated multi-model approach in enhancing the reliability of source apportionment results. 4.4 Risk assessment and riverine mass discharges Short-chain PFAS exhibited lower ecological risk compared with long-chain PFAS. Despite their relatively low concentrations, both PFTrDA and PFTeDA posed greater ecological risks due to their higher inherent toxicity. Although the direct risks from short-chain alternatives appear minimal, focusing solely on immediate impacts may overlook their long-term threats to groundwater systems and public health (Li et al., 2020b; Riaz et al., 2023), thereby raising significant concerns regarding ‘regrettable substitution’ (Dosunmu et al., 2025). Notably, benthic organisms inhabiting the hyporheic zone may bioaccumulate PFAS from sediments and subsequently transfer them to higher trophic level aquatic organisms through the benthic food web (Munoz et al., 2017; Diao et al., 2022). Given the adverse impacts on aquatic biota under long-term exposure scenarios, it is imperative to implement strict oversight of PFAS alternatives until their safety profiles are fully characterized.

Furthermore, PFAS in surface water typically occur as complex mixtures rather than as isolated monomers. These mixtures may exert synergistic effects, potentially elevating ecological risks beyond those associated with individual compounds (Pan et al., 2020). Although concentration addition models may underestimate risks by overlooking potential chemical interactions (Heys et al., 2016), the RQ results for the Weihe River nevertheless remain concerning. In the absence of empirical toxicity data, ECOSAR offers a convenient screening-level assessment of aquatic toxicity. However, its predictions entail inherent uncertainties due to its reliance on specific algorithms and limited training datasets (EPA, 2012; Massarsky et al., 2022). Regardless of the safety margins typically inherent in screening-level evaluations, the incorporation of experimental toxicity data remains critical for enhancing the accuracy and reliability of future assessments.

The calculated PFAS discharge at the river outlet exhibits a substantial increase compared with the flux reported in 2017 (239.00 kg/a) (Zhou et al., 2019). PFAS concentrations in most environmental matrices are rising globally, a trend likely driven by the increased use of alternative PFAS (Land et al., 2018). Although the production of long-chain compounds such as PFOA and PFOS have been phased out under global agreements, the manufacturing centers of fluorochemical feedstocks have shifted toward the East Asian regions. This industrial relocation presents ongoing challenges for managing PFAS contamination in local aquatic environments.

This ongoing input originates from both large-scale fluorochemical enterprises and numerous small workshops engaged in the manufacture of long-chain PFAS (Li et al., 2025).

4.5 Limitations

We collected surface water, pore water, and sediment samples from the Weihe River during the high-flow season of 2024 to analyze the spatial occurrence and distribution patterns of PFAS across multiple media. While these findings provide essential baseline insights, the lack of multi-seasonal data remains a primary limitation. Given that seasonal variations in PFAS distribution have been widely observed, the absence of a temporal dimension may introduce uncertainties into the estimation of source contributions, ecological risks, and discharge loads.

Therefore, monitoring pollutants across different seasons warrant further exploration.

5 Conclusions

This study elucidates the multi-media distribution and transport mechanisms of PFAS within the Weihe River Basin. Our findings demonstrate that PFAS distribution patterns was primarily governed by water exchange dynamics, with the hyporheic zone acting as a critical reservoir for vertical migration. The partitioning behavior at the sediment-water interface was largely controlled by compound molecular structures, local sedimentary characteristics, and hydrological

factors, which collectively contributed to non-linear responses. Source apportionment underscores the predominant role of industrial discharge, domestic sewage, surfactants, and AFFFs as key contributors, also highlighting potential inputs from stormwater runoff and landfill leachate.

Additionally, although individual ecological risks remain low, the cumulative effect of long-chain PFCAs necessitates a shift toward mixture-based risk assessments.

In summary, we advocate for a dual-track mitigation strategy, which integrates long-term monitoring programs and comprehensive emission inventories with stringent source controls and advanced wastewater treatment technologies to reduce the PFAS mass flux into the Yellow River.

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SONG Jinxi; Visualization: MAO Ruichen, FENG Jiayuan. All authors approved the manuscript.

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Appendix

Table S1 List of target perfluorinated compounds monitored, abbreviations, names, and chemical formulas Abbreviation Formula Perfluoroalkyl carboxylic acids (PFCA) Perfluorobutanoic acid PFPeA Perfluoropentanoic acid PFHxA Perfluorohexanoic acid PFHpA Perfluoroheptanoic acid Perfluorooctanoic acid Perfluorononanoic acid Perfluorodecanoic acid PFUnDA Perfluoroundecanoic acid PFDoDA Perfluorododecanoic acid PFTrDA Perfluorotridecanoic acid PFTeDA Perfluorotetradecanoic acid Perfluoroalkyl sulfonic acids (PFSA) Potassium perfluorobutane sulfonate PFPeS Sodium perfluoropentane sulfonate PFHxS Sodium perfluorohexane sulfonate PFHpS Sodium perfluoroheptane sulfonate Sodium perfluorooctane sulfonate Sodium perfluorononane sulfonate Sodium perfluorodecane sulfonate PFDoS Sodium perfluorododecane sulfonate Fluorotelomer sulfonic acids (FTSA) 4:2 FTS 4:2 fluorotelomer sulfonate sodium 6:2 FTS 6:2 fluorotelomer sulfonate sodium 8:2 FTS 8:2 fluorotelomer sulfonate sodium Polyfluoroalkyl ether sulfonates (PFESA)

PFEESA Potassium perfluoro (2-ethoxyethane) sulfonate 9Cl-PF3ONS Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate 11Cl-PF3OUdS Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate Perfluoroalkyl ether carboxylic acids (PFECA) HFPO-DA Hexafluoropropylene oxide dimer acid NADONA Sodium 4,8-dioxa-3H-perfluorononanoate PF4OPeA Perfluoro-4-oxapentanoic acid PF5OHxA Perfluoro-5-oxahexanoic acid 3,6-OPFHpA Perfluoro-3,6-dioxaheptanoic acid Perfluorooctane sulfonamidoacetic acids (FOSAA) N-MeFOSAA N-methylperfluoro-1-octanesulfonamidoacetic acid N-EtFOSAA N-ethylperfluoro-1-octanesulfonamidoacetic acid

Table S2 Method of detection limit (MDL), method of quantification limit (MQL), recovery, and detection frequency (DF) of individual per- and poly-fluoroalkyl substances (PFAS) in water and sediment Compound Recovery (%) Water Sediment MDL (ng/L) MQL (ng/L) DF (%) MDL (ng/g DW) MQL (ng/g DW) DF (%) 122.80$±6.90*PFPeA*126.50±8.10*PFHxA*115.00±5.70*PFHpA*80.80±6.40101.80±8.10101.
2*FTS*121.90±4.706 : 2*FTS*127.70±7.108 : 2*FTS*127.40±10.30*PFEESA*112.50±3.709*Cl*−
*PF*3*ONS*152.30±9.6011*Cl*−*PF*3*OUdS*75.40±7.30*HFPO*−*DA*132.30±6.10*NaDONA*119.50±11.20*PF*4*OPe*
*OPFHpA*117.10±5.70*N* − *MeFOSAA*89.80±6.20*N* − *EtFOSAA*89.20±$10.30

Note: Mean±SD; n =3.

Table S3 Distribution of concentration ratio (CR) between pore water and surface water for detected PFAS Compound (20 cm) (40 cm) (60 cm) (20 cm) (40 cm) (60 cm) (20 cm) (40 cm) PFPeA PFHxA PFHpA Compound (60 cm) (20 cm) (40 cm) (60 cm) (20 cm) (40 cm) (60 cm) Median 0.269 0.170 PFPeA 0.714 0.241 0.440 PFHxA 0.759 0.334 0.760 PFHpA 0.555 0.198 0.560 0.598 0.300 0.105 0.210 0.259 Note: The same sampling site with numbers means different sampling depths. Values with bold indicate that pore water concentrations are higher than those in surface water.

Fig. S1 Cumulative weight curves of sediment grain size for various sampling sites. (a), W12; (b), W15; (c), W17; (d), W18; (e), W19.

Table S4 Estimated mass load of PFAS discharged from the Weihe River to the Yellow River Component Concentration (ng/L) Mass load (kg/a) Upstream Midstream Downstream Upstream Midstream Downstream PFPeA PFHxA PFHpA PFUnDA PFDoDA PFTrDA PFTeDA PFHxS PFHpS 6:2 FTS 9Cl-PF3ONS 11Cl-PF3OUdS PF4OPeA PF5OHxA 3,6-OPFHpA N-MeFOSAA N-EtFOSAA Long-chain PFAS (kg/a) Short-chain PFAS (kg/a) Emerging PFAS (kg/a) Total PFAS (kg/a) Note: ' '-'' means no data.

Fig. S2 Conceptual model of per- and poly-fluoroalkyl substances (PFAS) interactions with sediments.

Mechanisms include hydrogen bonding, electrostatic attraction and repulsion, and hydrophobic interactions.

Molecular model adapted is referenced from Lyu et al. (2022).

Note: Figure translations are in progress. See original paper for figures.