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# Exposure-Integrated Risk Prioritization of Legacy and Emerging PFAS: A Case Study of a Major River Basin in South Korea via High-Resolution Mass Spectrometry

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## Abstract

To the best of our knowledge, this is the first study to comprehensively investigate the exposure-integrated risk prioritization of legacy and emerging per- and polyfluoroalkyl substances (PFAS) in domestic freshwater networks, specifically the Geum River basin, South Korea. This was achieved by integrating the targeted analysis of 39 PFAS with high-resolution mass spectrometry (HRMS)-based suspect and non-target screening (SNTS) and quantitative structure-activity relationship (QSAR)-based hazard prioritization. Among the targeted analytes, 12 PFASs were ubiquitously detected at total concentrations varying widely (range: 7.20–86.2 ng/L, median: 31.5 ng/L). Tributary sites exhibited approximately 1.6-fold higher concentrations compared to mainstream sites. Perfluorobutane sulfonate (PFBS) emerged as the predominant compound, accounting for 19.1% of the total PFAS burden, reflecting localized emission profiles shifted toward short-chain alternatives. Furthermore, the SNTS workflow tentatively identified hydrogen-substituted PFBS (H-PFBS) (semi-quantified concentration: 7.08 ng/L), explicitly indicating a municipal wastewater footprint. Notably, the QSAR-based Toxicological Priority Index (ToxPi) identified long-chain PFAS, including perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), perfluorooctanesulfonic acid (PFOS), and perfluorooctanoic acid (PFOA), as having the highest intrinsic hazard potential. However, the exposure-integrated Risk Index (RI) drastically shifted the prioritization, identifying ubiquitous PFAS, including short-chain variants (PFBS and perfluorohexanoic acid (PFHxA)) and the legacy PFOA, as the highest management priorities due to their elevated environmental loading. Overall, this integrated framework bridges the critical gap between chemical identification and exposure-driven risks.


## 1. Introduction

Following consecutive global restrictions on legacy per- and polyfluoroalkyl substances (PFAS) (UNEP, 2022; UNEP, 2025), the chemical market has rapidly transitioned toward structurally diverse emerging alternatives. This industrial shift has increased reliance on fluorotelomer-based derivatives, which frequently serve as environmental precursors that transform into highly stable perfluoroalkyl acids (PFAAs) (Zhang et al., 2017; Yan et al., 2022), alongside ether-based variants exhibiting comparable or exceeding persistence and ecotoxicity to their predecessors (Shi et al., 2015; Wang et al., 2023; Wang et al., 2025). Consequently, recent monitoring efforts have demonstrated that the environmental loading of these emerging alternatives frequently eclipses that of legacy persistent organic pollutants (POPs) in global aquatic networks (Buck et al., 2011; Glüge et al., 2020; Xu et al., 2021; Brunn et al., 2023; Li et al., 2024).

Despite their escalating footprint, comprehensive characterization is severely constrained by the limited availability of authentic analytical standards, restricting conventional targeted analysis (Cousins et al., 2020). To overcome this bottleneck, high-resolution mass spectrometry (HRMS)-based suspect and non-target screening (SNTS) workflows have emerged as critical tools to tentatively identify unrecognized fluorinated entities (Hernández et al., 2012; Schymanski et al., 2014). However, chemical identification alone is insufficient. The long-term ecotoxicological impacts of newly identified PFAS remain poorly defined due to a critical scarcity of experimental persistence, bioaccumulation, and toxicity (PBT) data. To address these foundational gaps under major regulatory frameworks (Escher et al., 2023), quantitative structure-activity relationship (QSAR) models are increasingly employed to predict the physicochemical behavior of data-poor structures (Sosnowska et al., 2023; Karamertzanis et al., 2026). Furthermore, integrating QSAR-derived hazard metrics into the Toxicological Priority Index (ToxPi) framework offers a robust approach for multi-criteria risk prioritization (Liu et al., 2022; Hu et al., 2023; Chang et al., 2025).

In South Korea, widespread contamination of legacy and emerging PFAS has been documented across major aquatic systems (Lee et al., 2020; Yong et al., 2021; Lee et al., 2024; Min et al., 2025). However, the domestic application of such advanced screening and risk prioritization approaches remains critically scarce. To bridge this gap, it is imperative to apply these global trends domestically, particularly to the Geum River basin. Heavily influenced by a complex mixture of municipal wastewater discharges, agricultural runoff, and specific industrial activities, this major watershed urgently

requires comprehensive monitoring to investigate the domestic chemical transition (Naile et al., 2010; Hong et al., 2015; Min et al., 2025).

Therefore, the primary objectives of this study were to: (1) comprehensively investigate the occurrence and spatial distribution of 39 targeted legacy and emerging PFAS across the Geum River basin; (2) screen and tentatively identify emerging PFAS variants utilizing an HRMS-based SNTS workflow; and (3) evaluate potential environmental risks by integrating QSAR-based PBT predictions with an exposure-based Risk Index (RI) assessment. This integrated approach bridges the critical gap between chemical identification and exposure-driven prioritization, warranting the need for a cautious interpretation of hazard-only assessments, and raising the need for continuous environmental management for fluorinated alternatives in aquatic ecosystems.

## 2. Materials and methods

# 2.1. Chemicals and materials

A total of 39 PFAS target analytes were included in this study, comprising 13 perfluoro carboxylic acids (PFCAs; C4–C14, C16, C18), 7 perfluoro sulfonic acids (PFSAs; C4–C10), and 19 precursor or alternative compounds. The precursor/alternative compounds consisted of perfluoro sulfonamides (FASAs), perfluoro sulfonamido acetic acids (FASAAs), fluorotelomer carboxylic acids (FTCAs), fluorotelomer unsaturated carboxylic acids (FTUCAs), fluorotelomer sulfonic acids (FTSs), fluorotelomer phosphate diesters (diPAPs), perfluoroether carboxylic acids (PFECAs), perfluoroether sulfonic acids (PFESAs). All native standards were obtained from Wellington Laboratories (Ontario, Canada). In addition, 25 isotope-labeled internal standards and four recovery standards were purchased from the same supplier. Detailed information on the target analytes and their corresponding isotope-labeled internal standards is summarized in Supplementary Information (Table S1). High performance liquid chromatography (HPLC)-grade methanol (MeOH) and ultrapure water were purchased from Honeywell (Charlotte, NC, USA). American Chemical Society (ACS)-grade ammonium hydroxide ($NH_4OH$) was obtained from Sigma-Aldrich (Darmstadt, Germany), and extra pure (EP)-grade ammonium acetate was obtained from Daejung Chemicals & Metals (Siheung, South Korea).

# 2.2. Sample collection

The Geum River, one of the four major rivers in South Korea, exhibits heterogeneous land-use characteristics along its watershed. Agricultural land use predominates in the upstream region, whereas urban and industrial areas are primarily concentrated in the middle and downstream reaches. Considering this spatial distribution of potential PFAS sources, surface water sampling was focused on the middle and downstream sections of the Geum River. Sampling was conducted between 20 and 22 May 2024 at a total of 12 sites (Fig. 1). Seven sites were located along the mainstream of the Geum River (M1–M7), extending from Daecheong Lake (M1) to the downstream reach (M7). In addition, five sites were selected in major tributaries (T1–T5) that are likely influenced by anthropogenic PFAS inputs. These regions encompass major urban areas, including Daejeon (T1–T2, M2), Sejong (T4, M3), and Cheongju (T3), where diverse potential PFAS sources are present, such as domestic wastewater, wastewater treatment plants (WWTPs), and industrial complexes such as semiconductor and paper industries. Tributaries in these areas, particularly the Miho River (T3–T4), have been reported to be influenced by industrial effluents and domestic discharges, which may contribute to contamination of the mainstream (Yeom et al., 2007; Yun et al., 2024). Downstream areas, including Gongju (M4), Buyeo (M5), Nonsan (T5, M6), and Gunsan (M7), exhibit mixed land-use characteristics and are subject to additional PFAS inputs from both domestic and industrial sources (Fig. 1). To minimize the influence of short-term hydrological variability, sampling was performed during a hydrologically stable period, with no precipitation recorded for at least five days prior to sample collection. Samples were collected using pre-cleaned 1 L and 2 L polypropylene bottles. The samples were immediately stored in iceboxes and maintained at temperatures below 4°C during transport to the laboratory. Upon arrival, all samples were stored at -20°C until further processing and analysis.

## 2.3. Sample pretreatment

Surface water samples were extracted following a previously reported method with minor modifications (Chang et al., 2025). Briefly, 500 mL of each sample was filtered through a glass microfiber filter (GF/F, 0.7 μm, GVS, Italy) and spiked with 5 ng of isotope-labeled internal standards. The filtered samples were extracted using solid-phase extraction (SPE) with Oasis WAX cartridges (150 mg, 6 cc; Waters, USA). Prior to sample loading, the cartridges were sequentially conditioned with 5 mL of 0.1% $NH_4OH$ in MeOH, then 5 mL of MeOH, and 5 mL of pure water. The samples were then loaded onto the cartridges at a flow rate of approximately 10 mL/min. After sample loading, the cartridges were washed with 6 mL of 25 mM ammonium acetate and dried under vacuum for 60 min. Target compounds were subsequently eluted with 4 mL of MeOH followed by 4 mL of 0.1% $NH_4OH$ in MeOH. The combined elutes were concentrated to approximately 200 μL under a gentle stream of nitrogen. A recovery standard (5 ng) was then added, and the extract was reconstituted to a final volume of 1 mL with MeOH prior to instrumental analysis.

## 2.4. Instrumental analysis

Target and suspect PFAS analysis was conducted using liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS). Chromatographic separation was achieved using a Vanquish Flex ultra-high performance liquid chromatography (UHPLC) system (Thermo Fisher Scientific, USA) equipped with a C18 column (Hypersil GOLD™, 4.6 mm × 50 mm, 3 μm, Thermo Scientific, USA) and a guard column (ZORBAX Eclipse XDB-C8, 2.1 mm × 12.5 mm, 5 μm, Agilent Technologies, USA). The UHPLC system was coupled to an Orbitrap Exploris 120 mass spectrometer (Thermo Fisher Scientific, USA). The mobile phase consisted of (A) 10 mM ammonium acetate in water/MeOH (9:1, v/v) and (B) 10 mM ammonium acetate in MeOH. Mass spectrometric detection was performed using electrospray ionization (ESI) in negative ion mode. Data were acquired in full-scan and data-dependent acquisition (DDA) modes to obtain high-resolution $MS^1$ spectra and corresponding $MS^2$ fragmentation data. Detailed LC gradient conditions and instrument parameters are provided in Table S2.

## 2.5 Suspect and non-target screening workflow for unknown PFAS

Suspect and non-target screening of PFAS was performed using Compound Discoverer v3.4 (Thermo Fisher Scientific). Raw LC-Orbitrap/MS data were processed using the built-in PFAS Unknown ID workflow with several parameter modifications. The HRMS data were first preprocessed through noise reduction, peak detection, retention time alignment, and gap filing to generate a comprehensive feature list. The detected features were subsequently filtered using the following criteria: peak intensity ≥ $1 \times 10^5$, signal-to-noise ratio (S/N) ≥ 3, abundance at least three times higher than that observed in procedural blanks, and mass accuracy within ± 5 ppm. Structural confidence levels were assigned according to the framework proposed by Schymanski et al. (2014), with PFAS-specific considerations described by Charbonnet et al. (2022). Features initially identified solely on the basis of accurate mass were classified as Level 5 candidates, whereas those supported by molecular formula assignment and isotope pattern evaluation were categorized as Level 4. Further structural characterization was performed through spectral matching and annotation using mzCloud, FluoroMatch, FISH scoring, and PFAS-specific databases, including the PFAS Duke list. Homologous PFAS series were additionally examined through network-based analysis. Features exhibiting at least two informative fragment ions in $MS^2$ spectra, sufficient for substructure elucidation, were assigned to Level 3. Higher-confidence Level 2 annotations were achieved when additional diagnostic fragment ions enabled determination of functional group positions, thereby providing greater structural specificity. This multi-tiered workflow allowed systematic and robust identification of both known and emerging PFAS in complex environmental samples.

## 2.6. Semi-quantification and risk prioritization

Semi-quantitative concentrations were calculated for PFAS lacking authentic standards to enable comparison with target PFAS and to facilitate subsequent risk prioritization analyses. Following the approach of Liu et al. (2024), concentrations

were estimated using a structural similarity-based surrogate method, which approximates concentrations based on the structural similarity between unknown compounds and known PFAS with available standards. To implement this approach, PFAS structures were converted into Simplified Molecular Input Line Entry System (SMILES) format, and pairwise structural similarities were calculated as Tanimoto coefficients using the RDKit library in Python (Jupyter Notebook 7.0.8). Compounds with Tanimoto coefficients ≥ 0.5 were considered structurally similar and were therefore selected as surrogate compounds for semi-quantification. Semi-quantitative concentrations were then derived by applying the concentration–intensity relationship of the matched surrogate PFAS to the measured peak intensity of the unknown PFAS, assuming comparable instrumental responses among structurally similar compounds.

To evaluate the relative risks of detected PFAS, a risk-based prioritization approach integrating chemical hazard and environmental exposure was applied following previous studies (Hu et al., 2023; Chang et al., 2025). Chemical hazard was quantified using the ToxPi, which integrates persistence (P), bioaccumulation (B), and toxicity (T) attributes derived from structure-based predictive models. Persistence was evaluated using biodegradation-related indicators, including outputs from BIOWIN models representing rapid biodegradation probability, ultimate biodegradation timeframe, and biodegradability potential. Bioaccumulation potential was assessed using predicted partitioning and accumulation descriptors, including bioconcentration factors and log $K_{OW}$ values. Toxicity attributes included both ecological and human health endpoints, such as acute aquatic toxicity, carcinogenicity, mutagenicity, developmental toxicity, endocrine-related effects, repeated-dose toxicity, and acute oral toxicity predicted using QSAR-based tools. Detailed model information and prediction platforms are provided in Table S3. All predicted parameters were normalized prior to integration using x, log(x), or inverse transformations depending on endpoint directionality to ensure that higher scores consistently reflected greater PBT concern. Equal weighting (1/3) was assigned to persistence, bioaccumulation, and toxicity components to avoid bias toward any single category. The normalized attributes were subsequently integrated to generate composite ToxPi scores representing overall chemical hazard.

Environmental exposure was estimated using detection frequency (DF) and maximum observed concentration. To minimize the influence of extreme values while incorporating occurrence frequency, exposure was calculated using normalized concentrations combined with detection frequency as follows (Eq. (1)):

$$Exposure_i = DF_i \times \frac{C_i - C_{min}}{C_{max} - C_{min}} \text{ (Eq. 1)}$$

where $C_i$ represents the maximum concentration of PFAS *i*, and $C_{min}$ and $C_{max}$ denote the minimum and maximum concentrations among all detected PFAS, respectively. Exposure values were subsequently normalized to a 0–1 range to allow comparison across compounds (Eq. (2)):

$$Exposure_{norm,\,i} = \frac{Exposure_i - Exposure_{min}}{Exposure_{max} - Exposure_{min}} \text{ (Eq. 2)}$$

Finally, the risk index (RI) was calculated by integrating hazard and exposure (Eq. (3)):

$$RI = ToxPi\ Score \times Exposure_{norm,i} \text{ (Eq. 3)}$$

Based on RI values, PFAS were classified into four priority levels: high (RI > 0.1), medium (0.01 < RI ≤ 0.1), low (0.001 < RI ≤ 0.01), and insignificant priority (RI ≤ 0.001).

## 2.7. Quality assurance (QA) and quality control (QC)

To minimize background PFAS contamination during sampling and sample preparation, all sample bottles and laboratory apparatus were made of polypropylene (PP). Procedural blanks processed using the same pretreatment protocol were analyzed together with samples to assess potential background contamination. All target PFAS in the blank samples were lower than the method detection limits (MDLs). To prevent background contamination originating from the LC system and

mobile phases, a PFAS delay column (Hypersil GOLD™, 4.6 mm × 50 mm, 1.9 µm, Thermo Scientific, USA) and PEEK solvent lines were used. The PFAS concentrations in the surface water samples were all within the analyte-specific calibration ranges, as summarized in Table S4. Linear calibrations exhibited good correlation coefficients ($r^2 > 0.99$), and relative standard deviations (RSDs) for standards were within ± 15%. Accuracy, precision, and MDLs were evaluated using 5 ng matrix-spiked samples. With the exception of PFDS (58.7%), the recoveries of U.S. Environmental Protection Agency (EPA) Method target PFAS were within acceptable ranges (US EPA, 2024). For PFAS not included in EPA Method 1633, recoveries of 8:2 diPAP and FOUEA fell within the commonly applied acceptance range of 70–130% (US EPA, 2018)), whereas FBSA (163.5%) and FHxSA (157.4%) exhibited elevated recoveries. Precision, expressed as RSDs, was below 15% for all analytes. MDLs were calculated based on seven replicate analyses, by multiplying the standard deviation of the spiked replicates by the Student's *t*-value (3.14) at the 99% confidence level. The details of individual PFAS accuracy and precision are listed in Table S4. Mass calibration of the Orbitrap mass spectrometer was performed at least once per week to ensure stable mass accuracy throughout the analytical period.

## 3.1. Regional and global PFAS levels

Total concentrations of $\sum_{39}$ PFAS in the Geum River basin ranged from 7.20 to 86.2 ng/L, with a median value of 31.5 ng/L. In comparison with other major river systems in South Korea, the concentration levels in the Geum River were generally within a similar or slightly lower range (Table 1). Specifically, the concentrations observed in this study were lower than those reported for the Namhan River (6.10–882 ng/L, median: 229 ng/L) (Lee et al., 2024) and the Nakdong River (4.15–1,554 ng/L, median: 32.0 ng/L) (Sim et al., 2021). This trend was also consistent with recent multi-river assessments by Hung et al. (2025), which reported higher concentrations for the Nakdong River (5.1–199 ng/L, median: 69.6 ng/L) and the Yeongsan River (3.69–69.1 ng/L, median: 51.5 ng/L). In contrast, the Namhan River exhibited a lower concentration (5.28–20.0 ng/L, median: 13.3 ng/L) than observed in the Geum River. On a global scale, PFAS levels in the Geum River were higher than those found in relatively pristine aquatic environments, such as Sweden (1.00–60.0 ng/L, median: 4.00 ng/L) (Nguyen et al., 2017) and Canada (0.64–26.0 ng/L, median: 12.0 ng/L) (Teymoorian et al., 2025a). Conversely, these levels were comparable to or lower than those observed in anthropogenically impacted systems, including the Czech Republic (7.63–68.0 ng/L, median: 17.8 ng/L) (Zarębska et al., 2024), France (13.4–219 ng/L, median: 35.7 ng/L) (Teymoorian et al., 2025b), and Australia (ND–526 ng/L, median: 63.5 ng/L) (Paige et al., 2024). These comparable or lower concentrations may partly reflect differences in PFAS management strategies and historical emission patterns, including strengthened PFAS regulations (Table S5). Notably, the concentrations in the Geum River remained orders of magnitude lower than the highly elevated levels documented in China (13.2–403,000 ng/L, median: 178 ng/L) (Liu et al., 2025), which may be associated with differences in historical industrial activities and regulatory implementation (Table S5).

Table 1
Comparison of PFAS concentrations in the Geum River with other studies

| Sampling area | Sampling year | Sample size (n) | Target PFAS | Median (ng/L) | Range (ng/L) | Reference |
|---|---|---|---|---|---|---|
| Geum river | 2024 | 12 | 39 | 31.5 | 7.20–86.2 | This Study |
| Namhan river | 2023 | 7 | 24 | 229 | 6.10–882 | Lee et al., 2024 |
| Namhan river | 2019 | 3 | 13 | 13.3 | 5.28–20.0 | Hung et al., 2025 |
| Nakdong river | 2019 | 15 | 27 | - | - | Yong et al., 2021 |
| Nakdong river | 2019 | 36 | 27 | 32.0 | 4.15–1,554 | Sim et al., 2021 |
| Nakdong river | 2019 | 10 | 13 | 69.6 | 5.1–199 | Hung et al., 2025 |
| Nakdong river | 2021 | 15 | 41 | - | 13.3–189 | Kang et al., 2025 |
| Yeongsan river | 2019 | 8 | 13 | 51.5 | 3.69–69.1 | Hung et al., 2025 |
| Sweden | 2013 | 40 | 26 | 4.00 | 1.00–60.0 | Nguyen et al., 2017 |
| Czech Republic | 2023 | 20 | 25 | 17.8 | 7.63–68.0 | Zarębska et al., 2024 |
| Australia | 2020 | 64 | 33 | 63.5 | ND[1)]–526 | Paige et al., 2024 |
| China | 2023 | 30 | 25 | 178 | 13.2–403,000 | Liu et al., 2025 |
| Canada (mainstream) | 2018–2021 | 250 | 77 | 12.0 | 0.64–26.0 | Teymoorian et al., 2025a |
| Canada (tributary) | 2018–2021 | 197 | 77 | 6.00 | ND–3,614 | Teymoorian et al., 2025a |
| France | 2023–2024 | 17 | 77 | 35.7 | 13.4–219 | Teymoorian et al., 2025b |

[1)]: Not detected (below method detection limit)

## 3.2. Homologue composition and congener profiles of individual PFAS

Among the 39 target PFAS analyzed, 12 compounds were detected in the Geum River, including seven PFCAs, four PFSAs, and one FTS (Fig. 2). PFCAs emerged as the dominant homologue group, contributing 65.1% of the total PFAS mass, followed by PFSAs (33.7%) and FTSs (1.1%). This composition pattern aligns with observations in other industrialized river systems of Korea (Sim et al., 2021; Jeong et al., 2025). At the individual compound level, PFBS—a well-known replacement of PFOS (Qi et al., 2018)—was the most predominant, exhibiting the largest composition share (0.57–31.6 ng/L, 19.1%). This predominance reflects the shifting trend toward alternative compounds in Korean aquatic environments (Hong et al., 2015). Other major contributors showed comparable concentration ranges and shares, including PFHxA (1.11–15.2 ng/L, 16.0%), PFOA (1.40–12.5 ng/L, 14.9%), and PFPeA (0.40–11.3 ng/L, 12.8%). Regulated legacy PFAS, such as PFOS (0.80–4.43 ng/L) and PFHxS (0.35–7.33 ng/L), as well as short-chain alternatives like PFBA (1.09–11.0 ng/L) and PFHpA (0.58–4.20 ng/L), also fell within similar concentration brackets. Given their structural similarities and persistent nature, the widespread occurrence of these short-chain homologues warrants continuous monitoring. In contrast, minor contribution and lower concentration ranges were observed for PFNA (0.54–1.51 ng/L, 2.9%), 6:2 FTS (not detected [ND]–3.31 ng/L, 1.13%), PFPeS (ND–0.42 ng/L, 0.57%), and PFDA (ND–0.48 ng/L, 0.43%).

While most targeted PFAS were ubiquitously distributed across the basin with detection frequencies exceeding 90%, suggesting diffuse pollution sources, PFDA (41.7%) and 6:2 FTS (25%) exhibited relatively restricted distribution profiles.

## 3.3. Spatial contamination profiles and identification of emerging alternative PFASs

Total PFAS concentrations were higher in the tributaries of the Geum River (T1–T5; mean: 43.1 ng/L) than in the mainstream (M1–M7; mean: 26.9 ng/L) by a factor of approximately 1.61 (Fig. S1). In the tributaries, spatial gradients strictly tracked urban and industrial density, rising sharply from T1 (12.2 ng/L) to T2 (41.7 ng/L) in the Daejeon metropolitan area, and from T3 (25.6 ng/L) to T4 (86.2 ng/L) within the Cheongju–Sejong industrial corridor (Fig. 3). The peak concentration at T4 is heavily tied to its hydrological proximity to four upstream industrial complexes featuring semiconductor and textile manufacturing facilities—sectors highly notorious for alternative PFAS usage (Byrne et al., 2024; Jia et al., 2025). In the mainstream, stepwise concentration increments were observed immediately downstream of major tributary confluences (e.g., M1 [7.20 ng/L] to M2 [17.2 ng/L], M2 to M3 [38.7 ng/L], and M5 [29.3 ng/L] to M6 [31.5 ng/L]), confirming that tributary inputs dictate the mainstream chemical profile. Conversely, the subsequent decline and stabilization of concentrations observed between M3 to M5 suggest that self-purification mechanisms, primarily driven by dilution and downstream mixing, successfully buffered the high-density tributary inputs.

PFCAs remained the dominant homologue group (> 50%) across most sampling sites, with the notable exception of T4. At T4, PFSAs predominated (51.6%), driven almost entirely by PFBS, which constituted 36.7% of the total PFAS mass. The spatial fingerprint of this tributary was clearly visible in the mainstream: the PFBS mixing ratio doubled from 8.94% upstream of the confluence (M1–M3) to 19.7% downstream (M4–M7). Mass load estimations further corroborated this spatial link, indicating that the T4 tributary accounted for approximately 71% of the PFBS mass load delivered to the lowest downstream reach (M7; see Table S6 for detailed load calculations).

SNTS tentatively identified hydrogen-substituted PFBS (H-PFBS) at site T2 with Level 3 confidence (Fig. S2). Its semi-quantified concentration reached 7.08 ng/L, notably surpassing PFBS concentration (4.74 ng/L) measured at the same site. H-PFAS structures are widely recognized as transformation products generated via microbially mediated defluorination or sequential H/F exchange reactions (Zhang et al., 2025), and have been frequently detected in waste-reception environments like drinking water (Qian et al., 2025) and landfill leachates (Feng et al., 2024). The occurrence of H-PFBS at T2—situated in the heavily populated Daejeon area (> 1 million)—points toward a dominant municipal wastewater footprint. In domestic WWTPs, prolonged anaerobic digestion and active microbial consortia provide ideal reducing environments that facilitate the biotransformation of polyfluorinated precursors and PFAAs into H-substituted byproducts (Lenka et al., 2021; Zhang et al., 2021; Yu et al., 2022; Wijayahena et al., 2025). Conversely, despite harboring the highest legacy PFBS levels, H-PFBS was entirely absent at T4. This divergence suggests that the emissions at T4 are characterized by fresh, untreated, or strictly point-source industrial effluents from the neighboring semiconductor and textile complexes. H-PFBS has been reported as an impurity generated during PFBS manufacturing and is generally present at only trace levels relative to PFBS (Newton et al., 2017; Guo et al., 2025). Therefore, the elevated H-PFBS abundance observed at T2 and its complete absence at T4 cannot be explained solely by direct inputs of manufacturing-related impurities, suggesting that additional transformation processes may have contributed to H-PFBS formation at T2. In such industrial streams, the lack of extensive biological wastewater treatment or sufficient environmental residence time restricts the microbial degradation pathways required to trigger H/F exchange (Zhang et al., 2022; Liu et al., 2024). It is important to note that because H-PFBS was semi-quantified without an authentic standard, a degree of uncertainty persists regarding its absolute quantification relative to PFBS. No other emerging PFAS candidates with Level 2 or Level 3 confidence were detected across the basin. Consequently, regular and broad-scope screening expanding to even low-confidence or currently undetected chemical entities is warranted to comprehensively capture the rapidly evolving footprint of novel fluorinated alternatives.

## 3.4. Temporal declines of legacy PFASs and regulatory benchmarking

Comparison with a previous study conducted in the downstream region of the Geum River near Gunsan in 2008 (Naile et al., 2010) revealed that most PFAS have remained at comparably low levels, with congeners such as PFBA, PFHxA, PFHpA, PFNA, PFDA, PFUdA, PFDoA, PFBS, PFHxS, and PFDS generally staying below 10 ng/L. In contrast, PFOA and PFOS concentrations exhibited approximately 7- and 16-fold decreases, respectively, compared to the 2008 baselines. This significant reduction aligns with the declining trends documented in the Geum River basin between 2008 and 2012 (Naile et al., 2010; Hong et al., 2015), effectively reflecting the success of global and domestic phase-out initiatives and stringent regulatory restrictions on legacy sulfonate and carboxylate variants.

While regulatory standards for PFAS in ambient surface waters remain unestablished, these findings hold critical public health implications for South Korea, where surface waters from rivers and reservoirs constitute over 95% of the nation's drinking water resources (Lee et al., 2016; MOE, 2023). Consequently, ambient PFAS occurrence translates into direct pathway for human dietary exposure. To contextualize these risks, measured concentrations were benchmarked against international drinking water guideline values (Table S7). Unlike individual compound thresholds, these group-based guidelines regulate cumulative totals, encompassing 20 PFAS in Europe (100 ng/L) (EU, 2020) and 25 PFAS in Canada (30 ng/L) (Health Canada, 2025). While the Geum River basin was largely compliant with the European standard, 58.3% of sampling sites exceeded the more conservative Canadian thresholds. Furthermore, although individual congener levels generally satisfied domestic and international action levels (e.g., Korea, Japan, Australia, and the US) (MOE, 2019; MOEJ, 2025; NHMRC, 2025; US EPA, 2025), PFOA and PFOS concentrations exceeded the stringent EPA drinking water guidelines at 75.0% and 16.7% of sampling sites, respectively (Fig. S3). These focal exceedances underscore the critical need for sustained environmental surveillance and the optimization of advanced water treatment infrastructure to mitigate human exposure risks.

## 3.5 Risk-based prioritization of legacy and emerging PFAS in the Geum River Basin

To prioritize legacy and emerging PFASs detected in the Geum River basin, an integrated assessment framework combining QSAR-derived PBT properties and environmental exposure metrics was applied (Table S7), following the methodology proposed by Hu et al. (2023). The QSAR-based PBT assessment revealed that, among PFCAs, log $K_{OW}$ values increased progressively from 2.14 for PFBA to 6.15 for PFDA alongside increasing carbon-chain length. PFNA and PFDA exhibited relatively high predicted bioconcentration factors (BCFs) of 10.0 and 56.2 L/kg, respectively. Furthermore, PFDA showed the lowest predicted Fish $LC_{50}$ (96 h) value (0.79 mg/L) among the target compounds, indicating the greatest ecotoxicological potential. Based on the BIOWIN persistence criteria (BIOWIN 1 < 0.5, BIOWIN 3 < 2.25, and BIOWIN 5 < 0.5) (Karamertzanis et al., 2026), ten PFAS, excluding PFBA, PFPeA, and PFHxA, were classified as relatively persistent. BIOWIN scores generally decreased with increasing carbon-chain length, suggesting lower predicted biodegradability and greater environmental persistence for longer-chain variants.

Among PFSAs, PFOS exhibited the highest lipophilicity (log $K_{OW}$ = 4.49) and substantial predicted toxicity, with Fish $LC_{50}$ (96 h) and Daphnid $LC_{50}$ (48 h) values of 24 and 17 mg/L, respectively. In contrast, the short-chain sulfonate PFBS showed lower predicted toxicity and bioaccumulation potential, with a log $K_{OW}$ of 1.82 and Fish $LC_{50}$ (96 h) of $3.6 \times 10^3$ mg/L. Similarly, the alternative compound 6:2 FTS exhibited moderate predicted toxicity, with a log $K_{OW}$ of 2.66, Fish $LC_{50}$ (96 h) of $4.4 \times 10^2$ mg/L, Daphnid $LC_{50}$ (48 h) of $2.8 \times 10^2$ mg/L, and Algae $EC_{50}$ (96 h) of $1.4 \times 10^2$ mg/L. These results closely align with previous literature demonstrating that extended PFAS carbon-chain length drives elevated bioaccumulation potential and ecotoxicity (Shi et al., 2018; Gomis et al., 2018). Notably, the transformation product H-

PFBS identified through suspect screening exhibited the lowest predicted hazard profile among all evaluated compounds, characterized by a predicted log $K_{OW}$ of 1.21, BCF of 3.16 L/kg, and Fish $LC_{50}$ (96 h) of $1.2 \times 10^4$ mg/L.

The ToxPi scores integrating these individual QSAR indicators (Fig. 4) ranked PFDA (0.82), PFNA (0.64), PFOS (0.60), and PFOA (0.49) as the highest-priority compounds, directly reflecting the intrinsic hazards associated with long-chain structural motifs (Table S8, Fig. S4). Conversely, short-chain alternatives such as PFBA, PFPeA, PFBS, and H-PFBS exhibited ToxPi scores below 0.25, indicating minor intrinsic hazards. Crucially, a distinct divergence emerged when incorporating environmental exposure metrics—such as ambient concentrations and detection frequencies—into a comprehensive RI (Fig. 4). Under this exposure-integrated framework, PFBS (0.23), PFOA (0.19), and PFHxA (0.15) were reclassified as the top-priority chemical management targets. Remarkably, PFBS commanded the highest RI despite its benign intrinsic toxicity, heavily skewed by its elevated concentrations and ubiquitous occurrence throughout the basin. This critical pivot demonstrates that certain alternative short-chain PFAS, particularly PFBS, can eclipse legacy compounds in watershed management priority due to sheer environmental loading. In absolute contrast, PFDA, despite yielding the highest intrinsic ToxPi score, presented a near-zero RI owing to its trace environmental concentrations and restricted detection frequency (41.7%).

## 4. Conclusion

This study investigated the occurrence characteristics, spatial dynamics, and risk-based prioritization of legacy and emerging PFAS in the Geum River basin utilizing target analysis combined with suspect and non-target screening. Total PFAS concentrations ranged from 7.20 to 86.2 ng/L, with elevated levels observed in tributaries influenced by urban and industrial activities. Among the detected compounds, the short-chain alternative PFBS exhibited the highest concentration and detection frequency, while suspect and non-target screening identified H-PFBS, suggesting the presence of emerging transformation products. The QSAR-based PBT assessment identified long-chain structures—specifically PFDA, PFNA, PFOS, and PFOA—as the highest-hazards due to chain-length dependent toxicity and bioaccumulation. Conversely, the exposure integrated RI framework prioritized PFBS (0.23), PFOA (0.19), and PFHxA (0.15). Notably, PFBS commanded the top management priority under the RI framework despite its relatively low predicted PBT profile, driven by its elevated environmental loading and widespread distribution. These contrasting outcomes demonstrate that management priorities shift drastically depending on whether regulatory frameworks emphasize intrinsic structural hazards or actual environmental exposure. Despite these insights, certain limitations remain to be addressed. This study relied on water samples collected during a single sampling campaign, and the assessment of emerging suspect screening candidates was partly constrained by semi-quantitative determination, introducing a degree of uncertainty. Future investigations incorporating multi-seasonal monitoring and rigorous quantitative analysis of emerging alternatives will facilitate a more comprehensive evaluation of long-term PFAS occurrence dynamics and optimize risk-based management strategies in aquatic ecosystems.

## Declarations

# Author Contribution

Minsu Shin performed the investigation, conducted the formal analysis, developed the methodology, and wrote the original manuscript. Gyojin Choo supervised the study and contributed to manuscript review and editing.

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# Data Availability

The data supporting the findings of this study are available within the paper and its Supplementary Information.

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## Figures

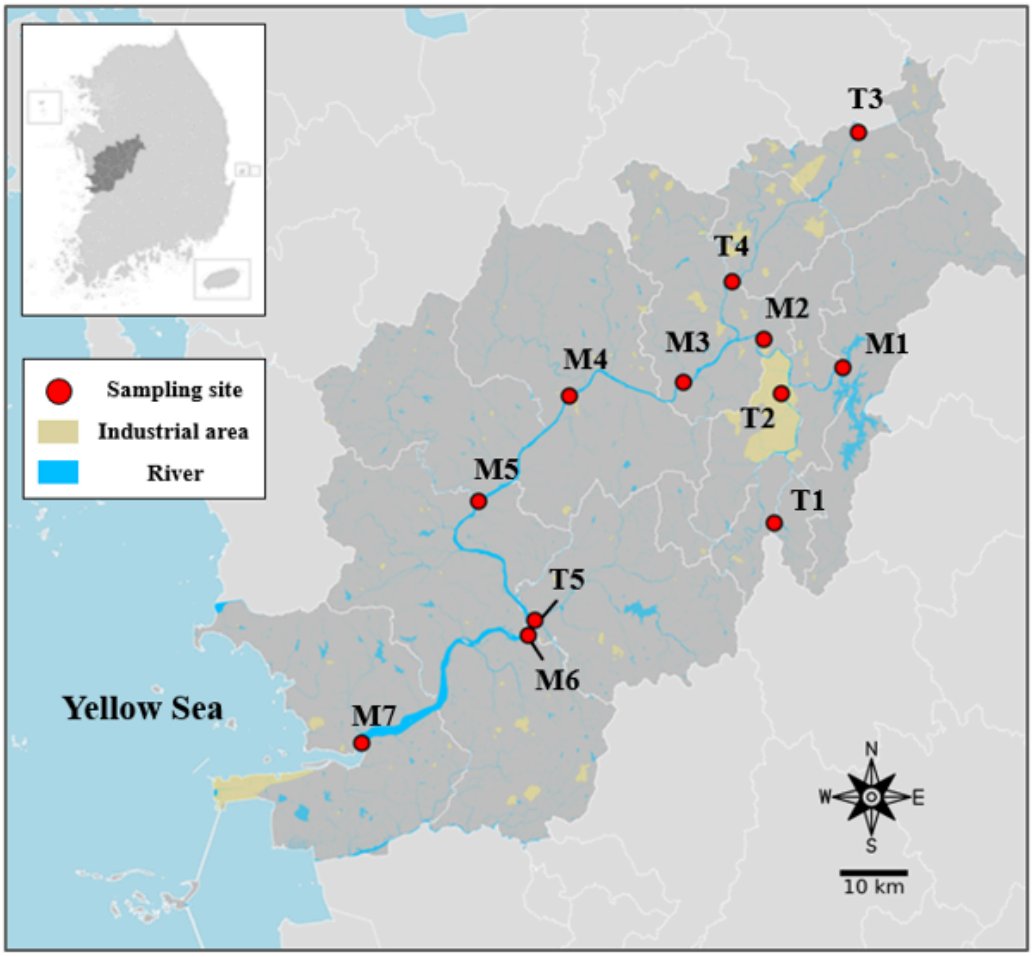



**Figure 1**

Location of sampling site in the Geum River basin

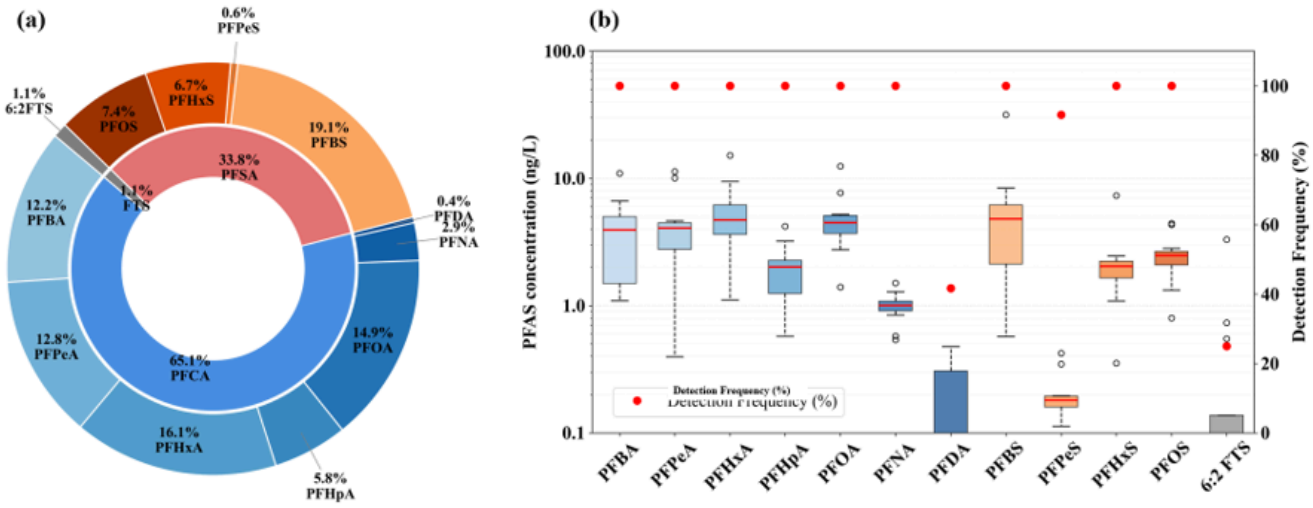



**Figure 2**

Distribution and concentrations of PFAS in the Geum River. (a) Distribution and (b) concentrations

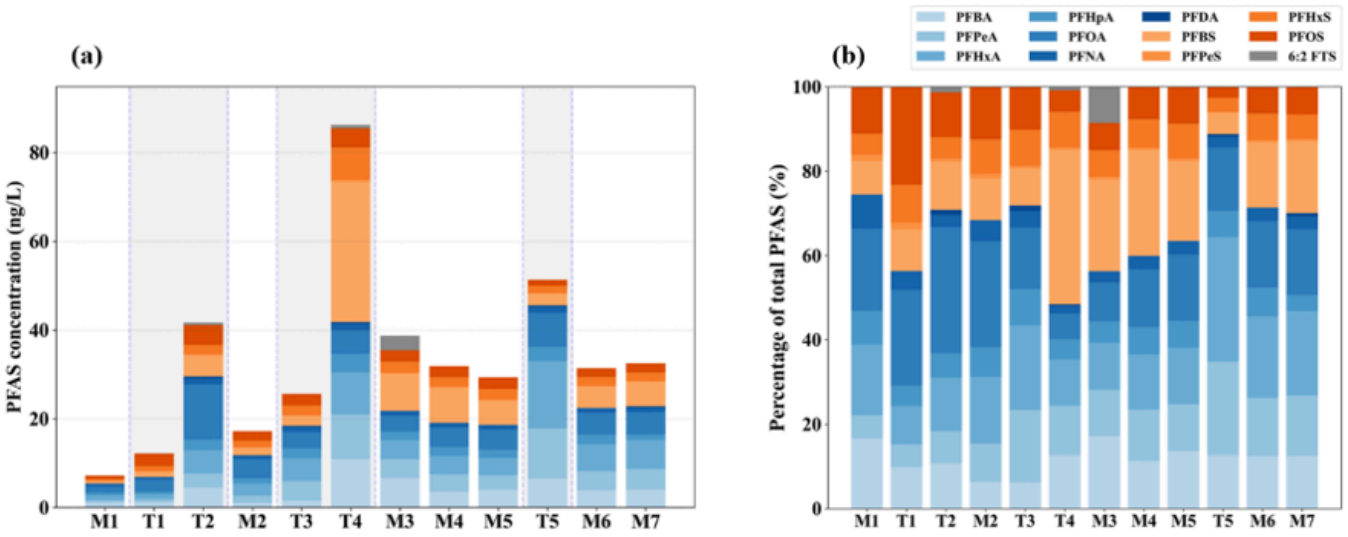



**Figure 3**

PFAS concentration and composition by sampling sites in Geum River. (a) concentration and (b) composition

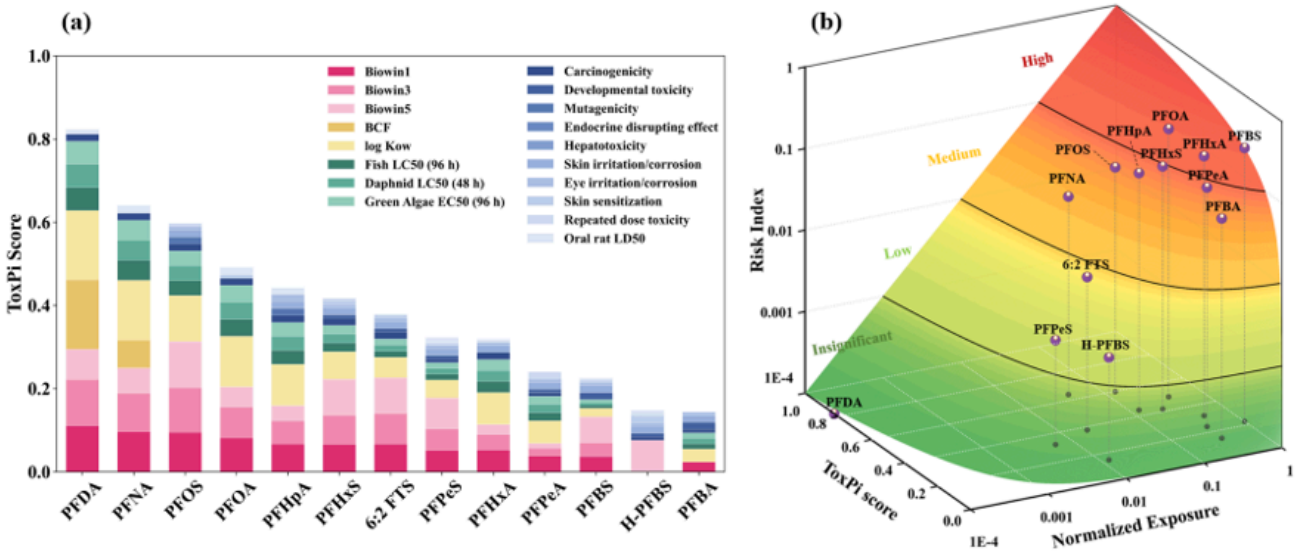



**Figure 4**

Risk-based prioritization of PFAS based on toxicity, persistence, bioaccumulation, and exposure criteria. (a) ToxPi scores and (b) 3D scatter plot of the Risk Index based on normalized exposure and ToxPi scores

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- papersupplementaryfile1.xlsx
- papersupplementaryfile2.pdf