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Land-Use Controls on PFAS Distribution and Source Apportionment in Surface Waters of the Nakdong River Basin, South Korea

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Per- and polyfluoroalkyl substances (PFAS) contamination in mixed land-use river systems is influenced by multiple co-occurring sources, making watershed-scale source attribution challenging. This study investigated the occurrence of PFAS and their source contributions in surface waters of the Nakdong River Basin near the Gumi industrial complex, South Korea, with emphasis on land-use-driven variability among tributaries and watershed-scale source apportionment using positive matrix factorization (PMF). Surface water samples were collected from 23 sites, including three sites along the mainstream and twenty sites located within four tributaries. Seventeen PFAS compounds were quantified using liquid chromatography–tandem mass spectrometry (LC-MS/MS). The tributary sites were further classified by land use into agricultural (n = 10), urban (n = 5), and industrial and wastewater treatment plant (WWTP)-influenced groups (n = 5) to compare detection frequency, concentrations, and compositional characteristics. PFAS occurrence showed clear land-use dependence. Agricultural catchments showed limited detection and relatively low concentrations, dominated by short-chain perfluoroalkyl carboxylic acids (PFCA). Urban tributaries exhibited mixed PFCA and perfluoroalkyl sulfonic acid (PFSA) signatures. The highest detection frequencies and concentrations were observed in industrial and WWTP-influenced streams, reaching 171.4 ng/L. PMF was applied to resolve mixed PFAS sources and quantify their relative contributions. Industrial activities and aqueous film-forming foam (AFFF) inputs emerged as the dominant source, followed by municipal wastewater and WWTP discharge. Source contributions varied by river type, with industrial signals prevailing in the mainstream and mixed industrial and wastewater influences observed in impacted tributaries. Agricultural tributaries were characterized primarily by secondary or indirect inputs, reflecting the high environmental mobility of PFAS. These findings identify PFAS-vulnerable tributaries and provide a quantitative basis for watershed-scale management of PFAS contamination in surface water systems.