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PFOS AND PFOA AS PFAS MICROPOLLUTANTS IN THE DAUGAVA RIVER: MONITORING AND REGULATORY PERSPECTIVES



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Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of highly persistent, bioaccumulative, and toxic chemicals that have been used for decades in industrial processes and consumer products. Among them, PFOS (perfluorooctane sulfonic acid, C₈HF₁₇O₃S) and PFOA (perfluorooctanoic acid, C₇HF₁₅CO₂H) are of particular concern due to their widespread occurrence, environmental persistence, and resistance to degradation.

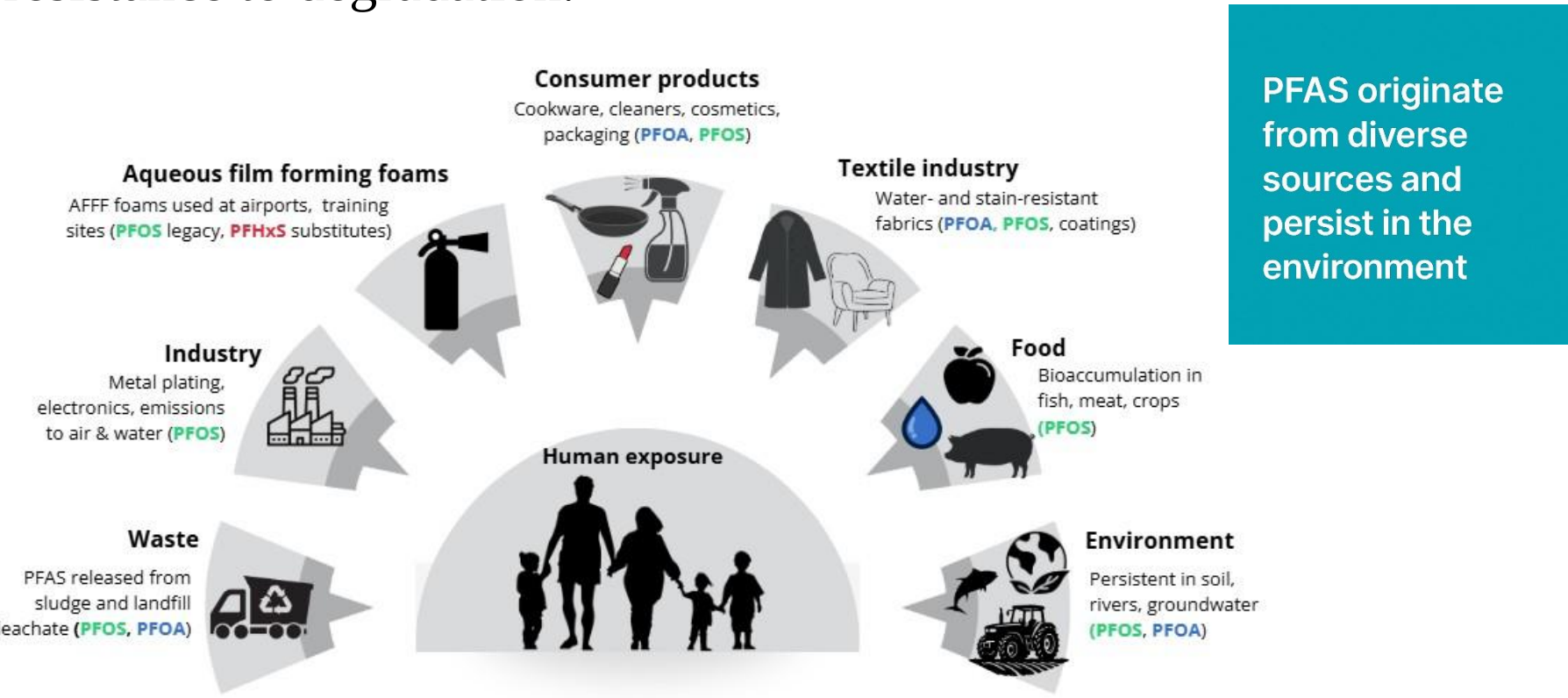


Figure1. Sources and Pathways of PFAS in the Environment

Although PFOS is regulated under the EU Environmental Quality Standards Directive, and PFOA was restricted in 2020 (Reg. (EU) 2017/1000), monitoring data in Latvian surface waters remain scarce. This study aims to assess PFOS and PFOA concentrations in surface waters of the Daugava River basin, compare them with EU Environmental Quality Standards (EQS), and identify potential sources and regulatory gaps.

2008-2013	2009	2020	2020	2020	2022	2023-2026
Water Framework Directive (2008/105/EC, amended by 2013/39/EU)	Stockholm Convention & EU POPs Regulation (Reg. (EC) No 850/2004 → Reg. (EU) 2019/1021)	POPs Regulation (EU) 2019/1021 – PFOA inclusion	Drinking Water Directive (EU) 2020/2184	Food Regulation (EU) 2022/1428 & 1431	Regulation (EU) 2023/1608 & Stockholm Convention (Annex A)	REACH “Universal PFAS Restriction” Proposal (ECHA, 2023)
Environmental Quality Standards (EQS) for PFOS: 0.65 ng/L (inland) and 0.13 ng/L (coastal)	PFOS listed under Annex B, later moved to Annex A — complete restriction on production and use in the EU	PFOA added to Annex I (Annex A of Stockholm Convention): full restriction on manufacture and use from 2020	New PFAS limits to be implemented by 13.01.2026: PFAS 20 (key PFAS substances) = 0.1 µg/L; Total PFAS = 0.5 µg/L	Sets maximum levels for PFOS, PFOA, PFNA, and PFHxS in food (products regulated from 2023)	PFHxS (PFOS/PFOA substitute) added to Annex A, resulting in a complete ban EU-wide and globally	Proposed broad ban on ~10 000 PFAS substances; evaluation under way; decision expected by 2026

Figure2. Timeline of Key EU PFAS Regulations

Materials and Methods

Water samples from six monitoring stations operated by the Latvian Environment, Geology and Meteorology Centre (LVĢMC) along the Daugava River were analyzed.

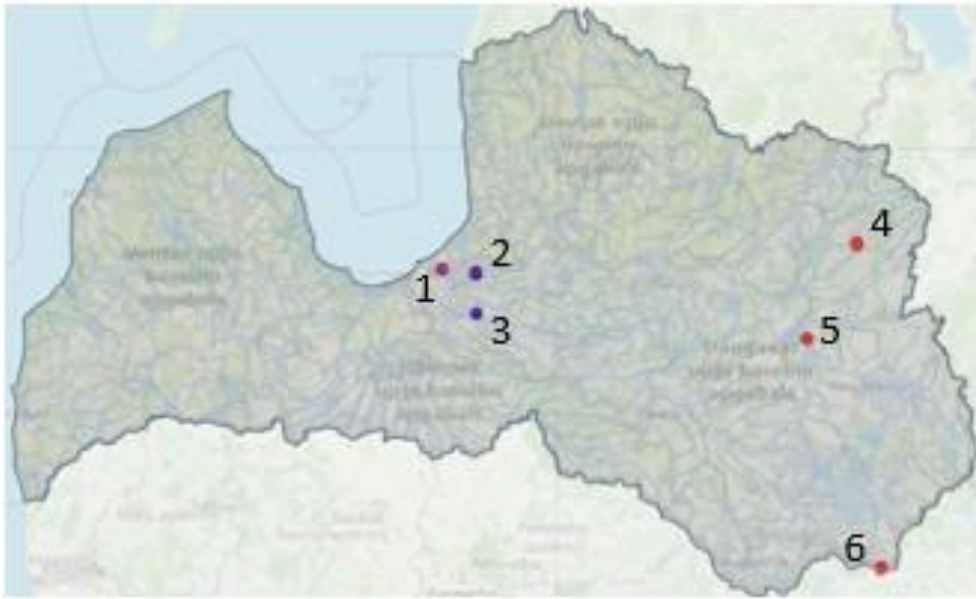


Figure3. LVĢMC Monitoring stations for PFOA and PFOS in the Daugava River basin (1- Ķīšezers, pretī Mīlgrāvja caurtekaiLielā; 2- Lielā Jugla, 0.2km augšpus Zaķiem;3- Rīgas ūdenskrātuve, 1.0 km leļpus Lipšiem; 4- Balvu ezers, vidusdaļā; 5- Rēzekne, grīva; 6- Daugava, Piedruja, Latvijas - Baltkrievijas robeža).

Sampling campaigns were conducted between 2017 and 2023, during which PFOS and PFOA concentrations were measured in surface waters. PFOS and PFOA were quantified at µg/L levels, and descriptive statistics (minimum, maximum, mean, median, standard deviation, skewness, and kurtosis) were calculated using RStudio (package ggplot2). Data visualization included boxplots, a station location map, and a PFAS source and pathway schematic to illustrate potential origins and environmental transport routes.

Results and Discussions

PFOS and PFOA concentrations in surface waters of the Daugava River basin were non-normally distributed, with low median values and occasional high values observed at certain stations. Median values were used to represent the typical concentration levels, as they better describe non-normally distributed environmental data and are less influenced by outliers.

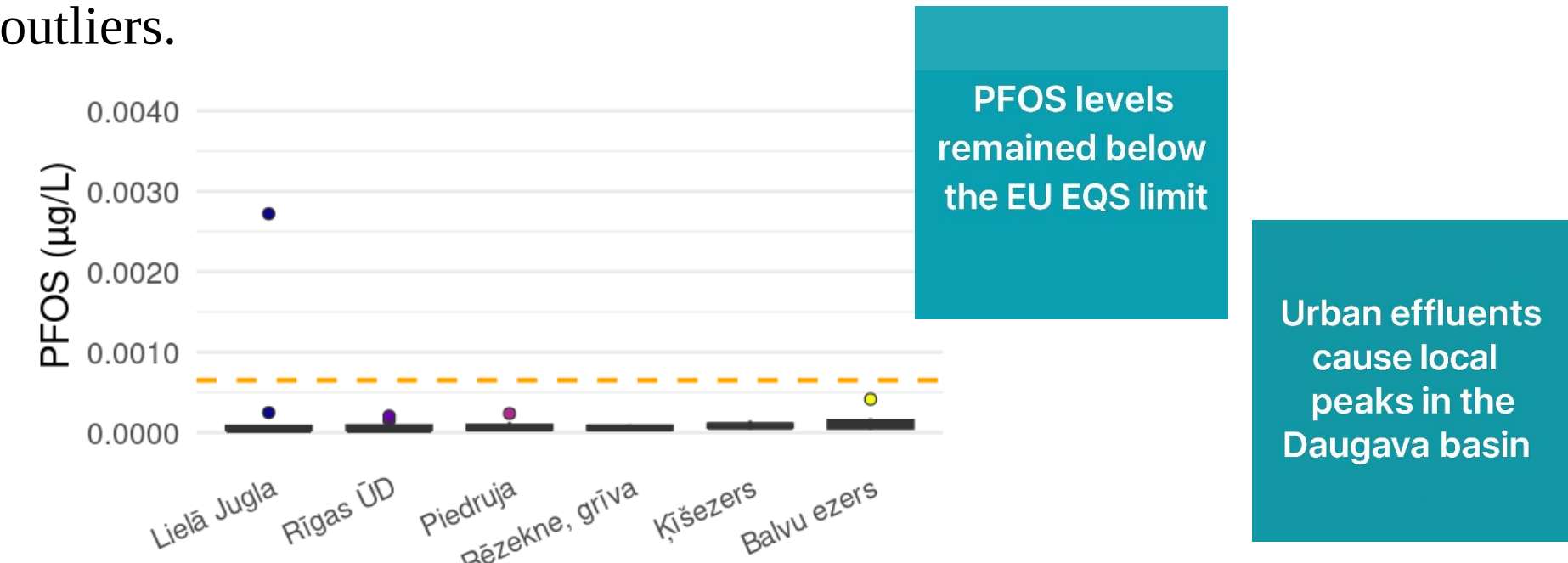


Figure4. PFOS concentrations by LVĢMC monitoring stations (µg/L)

PFOS concentrations remained below the EU Environmental Quality Standard (0.65 ng/L or 0.00065 µg/L), indicating diffuse background contamination rather than distinct point sources. For PFOA, no official EQS value has been established; however, the same reference level (0.65 ng/L) was provisionally applied for comparative purposes

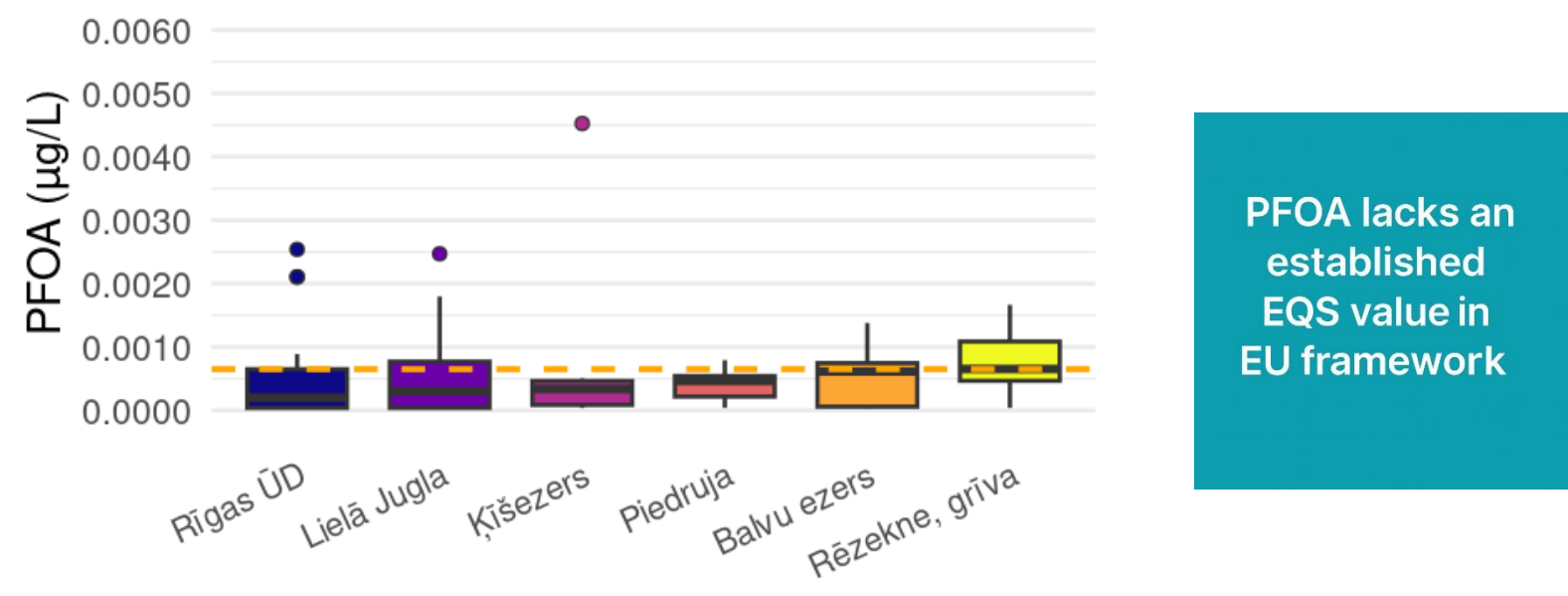


Figure5. PFOA concentrations by LVĢMC monitoring stations (µg/L)

Despite regulatory progress — including the 2020 PFOA prohibition (Reg. (EU) 2017/1000) and the proposed 2026 universal PFAS restriction under REACH — the presence of both compounds suggests persistent legacy pollution and diffuse inputs. These findings highlight the need for continued monitoring and stricter analytical standards within Latvian surface water assessments

Conclusion

PFOS and PFOA were consistently detected in surface waters of the Daugava River basin despite EU restrictions, confirming the persistence of legacy contamination and diffuse sources. PFOS concentrations remained below the EU EQS threshold, while no limit is yet established for PFOA. These findings highlight the need for continued PFAS monitoring, harmonized analysis, and improved source control within the forthcoming 2026 EU regulatory framework.