EVALUATING SONOCHEMICAL POTENTIAL FOR PFAS MITIGATION IN DIFFUSE AGRICULTURAL SYSTEMS

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Abstract. Diffuse pollution from multiple anthropogenic sources, including agricultural and industrial activities, represents a significant challenge for water management systems due to the presence of persistent micropollutants such as per- and polyfluoroalkyl substances (PFAS). These compounds are widely detected in surface waters and are characterized by high environmental persistence and mobility. Conventional treatment technologies are often insufficient for effective PFAS removal or degradation, particularly in decentralized rural environments. This study evaluates the sonochemical treatment potential for PFAS mitigation in diffuse agricultural systems using a data-driven approach. Monitoring data from Latvian river basins (Daugava and Lielupe) were analysed, with PFOS and PFOA used as representative indicator compounds of PFAS occurrence. PFOS and PFOA were detected at low but measurable concentrations, with PFOS ranging from 0.039-11.106 $ng \cdot L^{-1}$ and PFOA from 0.039-13.221 $ng \cdot L^{-1}$. Spatial variability and distribution patterns were assessed to identify areas influenced by diffuse pollution pathways. Based on the observed concentration patterns and transport processes, potential application points for sonochemical treatment were identified within rural water management systems, particularly in drainage flows and surface runoff pathways. The results highlight the relevance of diffuse pollution processes in PFAS transport and demonstrate the applicability of sonochemical treatment as a targeted and complementary approach for decentralized water treatment solutions.

Keywords: PFOA, PFOS, sonochemistry, agricultural runoff, surface water.

Introduction

Among emerging environmental contaminants, per- and polyfluoroalkyl substances (PFAS) represent a group of compounds widely used in industrial and consumer applications due to their unique physicochemical properties, including thermal stability and hydrophobic–lipophobic behavior [1]. Their resistance to degradation leads to long-term environmental persistence and widespread occurrence in aquatic systems [2]. PFAS contamination has been reported globally in rivers, groundwater, and marine environments, making them contaminants of increasing concern due to their ecological and human health impacts [3]. Rivers play a crucial role in the transport of PFAS, linking terrestrial emission sources with aquatic ecosystems and ultimately coastal and marine environments [4]. While point sources such as wastewater treatment plants are well documented, increasing attention is being given to diffuse pollution pathways, particularly in agricultural landscapes, where contamination sources are spatially distributed and more difficult to control [3].

The application of biosolids, organic fertilizers, and manure has been identified as a significant pathway for PFAS entry into agricultural soils [5]. Once present in soils, PFAS may be mobilized through runoff, drainage flow, and soil–water interactions, contributing to their transport into surface waters [6]. In addition, plant uptake and bioaccumulation processes may further influence PFAS cycling within agricultural systems and their potential transfer into the food chain [7]. These processes are strongly influenced by hydrological conditions, soil properties, and land-use practices. Within environmental monitoring, individual compounds such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are commonly used as representative indicators of PFAS occurrence due to their frequent detection and well-documented environmental behavior [3]. In the Baltic region, including Latvia, available monitoring data indicate the presence of PFAS in surface waters at low concentrations, with patterns reflecting both diffuse agricultural inputs and mixed anthropogenic pressures. The treatment of PFAS remains a major challenge due to their strong carbon–fluorine bonds and resistance to conventional degradation processes. Conventional treatment methods, such as adsorption and filtration, are often ineffective in achieving complete degradation and may result in the transfer of PFAS between environmental compartments rather than their destruction [2]. Consequently, there is an increasing need for advanced treatment technologies capable of degrading PFAS.

Sonochemical treatment, based on acoustic cavitation, has emerged as a promising advanced oxidation process of generating highly reactive radical species and capable of degrading persistent

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organic pollutants [8]. PFAS degradation in sonochemical systems is understood to occur primarily at the cavitation interface, where hydrophobic compounds accumulate and are exposed to extreme localized conditions [9]. Recent studies have demonstrated the potential of sonochemical processes for PFAS degradation and defluorination, particularly under optimized or hybrid conditions, particularly when combined with oxidants such as persulfate [10]. However, their applicability in complex environmental matrices and diffuse pollution systems remains insufficiently explored and may be limited by operational conditions [11; 12]. Therefore, integrated and optimized approaches are considered necessary for practical implementation [13]. The conceptual framework presented in Fig. 1 illustrates the main PFAS transport pathways in agricultural systems and highlights potential integration points for sonochemical treatment within rural water management systems.

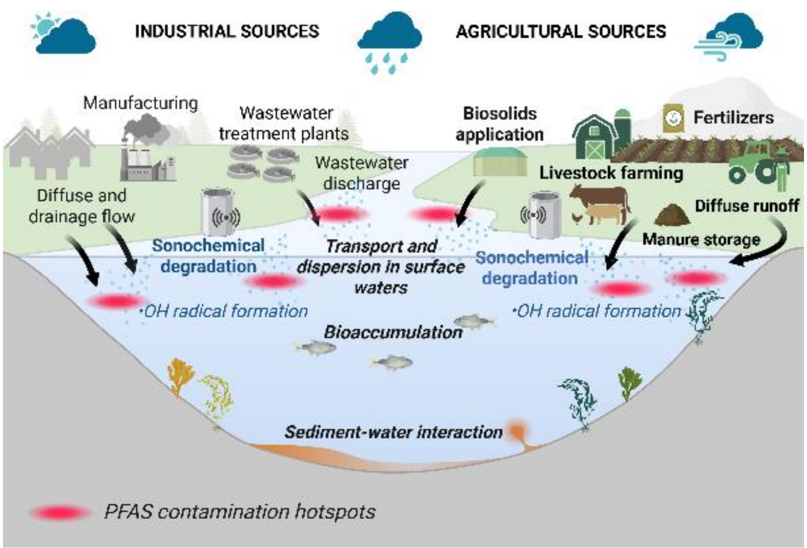

Fig. 1. **Conceptual framework of PFAS transport and sonochemical mitigation in diffuse agricultural systems (created with BioRender.com)**

This study applies a data-driven approach to evaluate the potential of sonochemical treatment for PFAS mitigation in diffuse agricultural systems. Using monitoring data from the Daugava and Lielupe river basins, it assesses PFOS and PFOA occurrence and spatial variability, and identifies priority locations for treatment implementation, addressing a gap in region-specific integrated assessments.

Materials and methods

The study was conducted in two major river basins in Latvia: the Daugava River Basin (further – DRB) and the Lielupe River Basin (further – LRB), representing catchments with contrasting land-use characteristics. The DRB is characterised by a mixed urban–rural environment, while the LRB is predominantly influenced by agricultural activities. These differences provide a basis for evaluating PFAS occurrence under varying anthropogenic pressures. PFAS occurrence using PFOA and PFOS as indicators was assessed using surface water monitoring data obtained from the Latvian Environment, Geology and Meteorology Centre (LVĢMC) publicly available database [14]. Monitoring stations included in the analysis represent official surface water monitoring sites distributed across both river basins (Fig. 2), covering a total of 43 monitoring locations (24 in the DRB covered the period 2017-2025 and 19 in the LRB covered the period 2018-2024). The dataset consists of a total of 892 observations, including 504 measurements from the DRB and 388 measurements from the LRB. Concentrations were originally reported in micrograms and subsequently converted to nanograms per litre ($ng \cdot L^{-1}$) to ensure comparability with other studies and regulatory thresholds.

The analysis focused on two commonly monitored indicator compounds, PFOS and PFOA, which were used to represent PFAS occurrence in surface waters. Descriptive statistical analysis was applied to evaluate concentration ranges, median values, and variability across monitoring stations and river basins. Spatial patterns were analysed using station-based aggregation of concentration data. To support spatial interpretation, monitoring stations were classified into four groups based on median PFAS concentrations (quartile-based classification), allowing the identification of relative concentration gradients and potential hotspot areas (Fig. 4). Concentration data were evaluated using descriptive statistical analysis and graphical visualization techniques. Spatial patterns were interpreted based on differences between monitoring stations. The results were further interpreted in the context of reported PFAS levels in Baltic and Scandinavian surface waters in order to provide a regional perspective on contamination levels and environmental relevance.

To support the transition from environmental monitoring data to engineering application, an interpretation-based evaluation approach was applied to assess the potential applicability of sonochemical treatment in diffuse agricultural systems. The evaluation was based on observed PFOA and PFOS concentration levels and their spatial distribution patterns across monitoring stations. These data were used to identify areas with relatively elevated concentrations and potential accumulation zones within the river basins. In addition, the interpretation considered general knowledge of diffuse pollution processes in agricultural catchments, including runoff and hydrological transport pathways, as described in the literature [3-6]. Based on these observations, potential locations where localized treatment could be applicable were conceptually identified, particularly in relation to surface water inflows, small tributaries, and areas influenced by diffuse inputs. The applicability of sonochemical treatment was evaluated in the context of decentralized and small-scale water management systems. This study represents a data-informed, conceptual assessment of potential application scenarios rather than a direct performance evaluation or modelling of treatment systems. A qualitative comparison with conventional PFAS treatment methods (e.g. adsorption and ion exchange) was included to position sonochemical processes within the broader context of available treatment technologies (Table 2).

Results and discussion

The spatial distribution of monitoring stations in DRB and LRB is presented in Fig. 2.

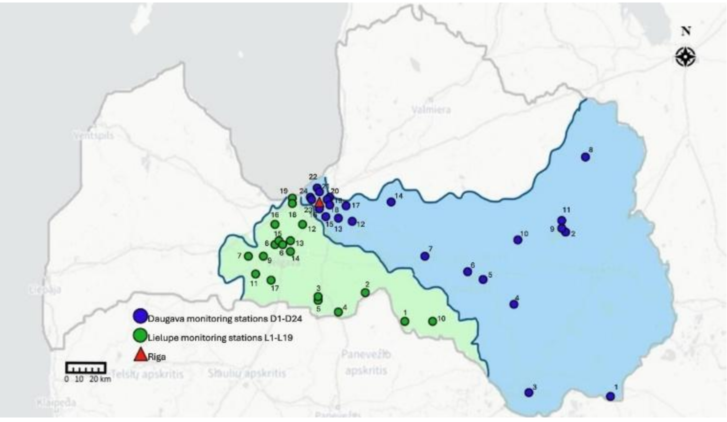

Fig. 2. **Spatial distribution of monitoring stations in the Daugava and Lielupe river basins**

PFOS and PFOA were detected in both river basins at low but measurable concentrations, indicating background contamination levels typical for European surface waters. Table 1 shows that PFOA concentrations in the DRB ranged from 0.039 to 13.221 ng·L^{-1}, while PFOS concentrations ranged from 0.039 to 11.106 ng·L^{-1}. In the LRB, PFOA concentrations ranged from 0.039 to 9.202 ng·L^{-1} and PFOS from 0.039 to 1.928 ng·L^{-1}.

Table 1

Descriptive statistics of PFOS and PFOA concentrations (ng·L^{-1}) in the Daugava and Lielupe river basins

Basin	Compound	N	Mean	Median	SD	Min	Max	Skewness	Kurtosis
Daugava	PFOA	252	0.5605	0.203	1.3290	0.039	13.221	7.15	61.32
Daugava	PFOS	252	0.1282	0.052	0.7162	0.039	11.106	14.48	216.71
Lielupe	PFOA	194	0.5366	0.194	0.9754	0.039	9.202	4.69	32.48
Lielupe	PFOS	194	0.0829	0.040	0.1494	0.039	1.928	10.01	117.65

The distribution of PFOS and PFOA concentrations is illustrated in Fig. 3.

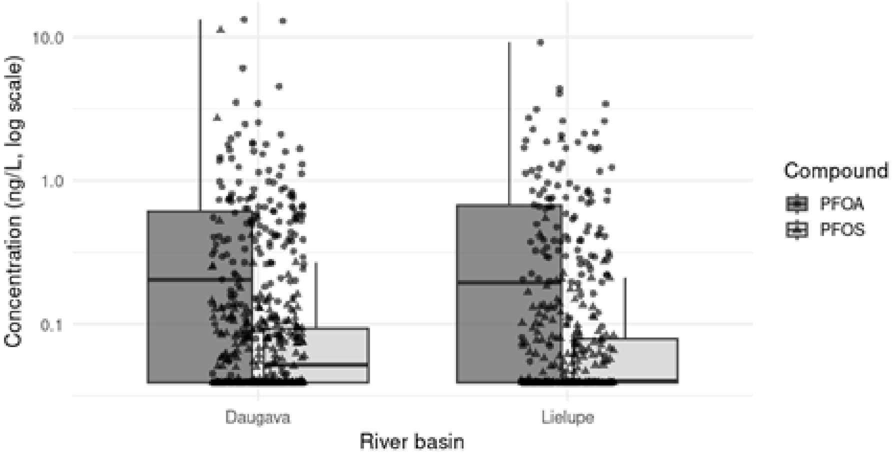

Fig. 3. **Distribution of PFOS and PFOA concentrations in the Daugava and Lielupe river basins (log 10 scale)**

The results indicate that PFOA concentrations are generally higher than PFOS in both river basins, which is consistent with previous studies and reflects differences in environmental behaviour and mobility. The boxplot distribution demonstrates a strongly skewed dataset, with mean values exceeding median values and high skewness and kurtosis, indicating the presence of extreme values and occasional elevated concentrations. Despite these variations, the overall concentration ranges are comparable between the two river basins, suggesting that PFAS occurrence is primarily influenced by diffuse sources rather than a single dominant emission point. These findings are consistent with reported PFAS levels in Baltic and Nordic surface waters, where low but persistent concentrations are commonly observed [15]. The observed low but persistent PFAS concentrations suggest that conventional treatment approaches may be insufficient, highlighting the need for destructive technologies such as sonochemical processes. To further analyse spatial variability, monitoring stations were classified into four groups based on median PFAS concentrations (combined PFOS and PFOA values). The resulting spatial distribution is presented in Fig. 4.

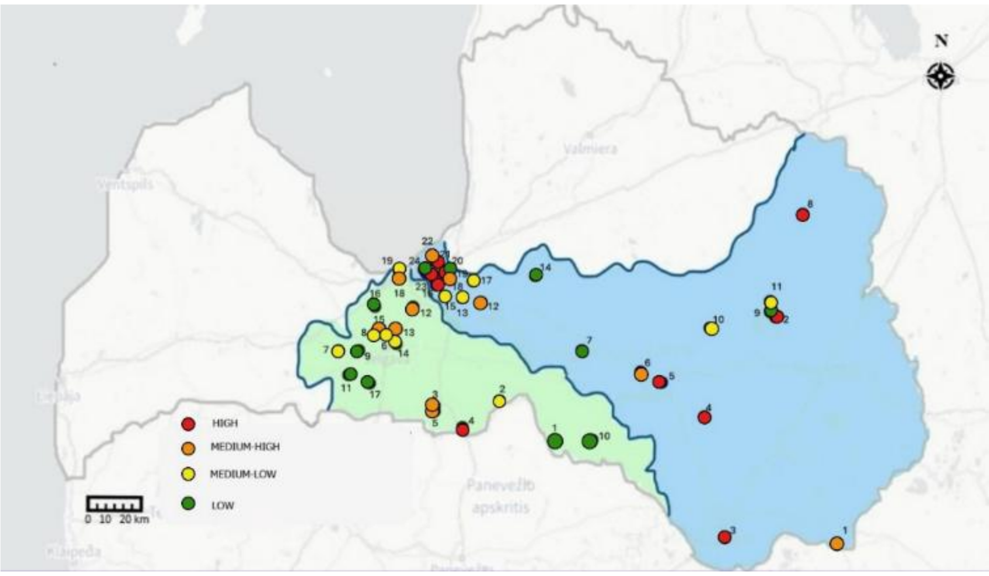

Fig. 4. **Spatial distribution of PFAS concentrations across monitoring stations based on median values**

The classification highlights clear spatial differences in PFAS concentrations, with certain monitoring stations forming localized hotspots likely influenced by land use, hydrological conditions, and mixed anthropogenic inputs such as agricultural runoff and urban activities. In contrast, lower concentration stations represent more uniform background conditions, confirming a heterogeneous distribution typical of diffuse pollution and emphasizing the need to consider local-scale variability when identifying priority areas for intervention.

The conceptual framework presented in Fig. 5 illustrates the main pathways of PFAS transport in agricultural systems and highlights potential points for the integration of sonochemical treatment within rural water management.

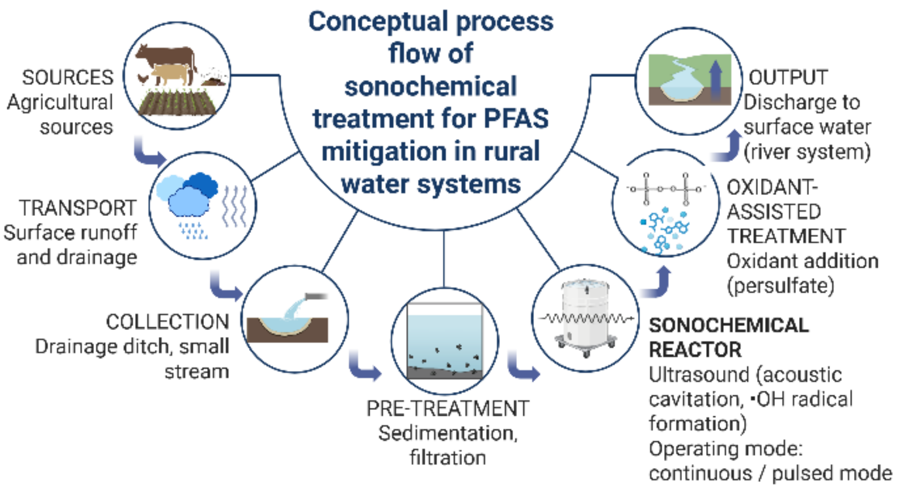

Fig. 5. **Conceptual process flow for sonochemical treatment of PFAS in rural water systems (created with BioRender.com)**

Diffuse pollution processes, including surface runoff, drainage flow, and soil–water interactions, play a key role in PFAS transport within agricultural systems. Hydrological connectivity facilitates the transfer of PFAS from terrestrial sources to surface waters, contributing to the observed spatial variability [3; 4]. Agricultural practices such as the application of biosolids and organic fertilizers represent important diffuse sources, enabling PFAS entry into soils and subsequent mobilisation to aquatic systems [5; 6]. In addition, plant uptake and bioaccumulation processes may influence PFAS cycling within agroecosystems [7]. Based on the identified concentration patterns, areas with elevated PFAS levels may represent suitable targets for localized or decentralized treatment approaches. In this context, sonochemical treatment can be considered as a potential technology for targeted application, particularly in smaller-scale systems where treatment volumes are manageable. Sonochemical processes are based on acoustic cavitation, generating extreme localized conditions that lead to the formation of reactive radical species capable of degrading persistent compounds [8]. PFAS degradation is understood to occur primarily at the bubble–liquid interface, where hydrophobic molecules accumulate and are exposed to high-energy conditions [9]. Experimental studies have demonstrated that sonochemical processes can promote PFAS degradation and defluorination, particularly when combined with oxidants such as persulfate [10; 16]. The applicability of sonochemical treatment in diffuse agricultural systems is supported by its potential to act as a destructive technology, in contrast to conventional methods such as adsorption and ion exchange, which primarily transfer PFAS between environmental compartments rather than degrading them (Table 2).

Table 2

Comparison of selected PFAS treatment technologies

Technology	Principle	Advantages	Limitations
Sonochemistry	Cavitation, •OH radicals	Degradation of PFAS	High energy demand [9-11]
Activated carbon	Adsorption	Widely used	No destruction [13]
Ion exchange	Sorption	Effective removal	Regeneration required [11; 13]

However, several limitations must be considered. Sonochemical treatment is energy-intensive and its efficiency is strongly influenced by operational parameters such as frequency, power intensity, and reaction time [9; 17]. In addition, complex environmental matrices containing dissolved organic matter or suspended solids may reduce treatment efficiency by affecting cavitation dynamics and radical availability [11]. Low-frequency ultrasound alone has been shown to be insufficient under certain conditions, highlighting the need for optimized or hybrid systems [12; 18]. Furthermore, scaling up sonochemical processes for large-volume water treatment remains a significant challenge [13; 19]. Overall, the integration of monitoring data with spatial analysis provides a basis for identifying potential implementation scenarios for sonochemical treatment in rural water systems. This data-informed approach supports the transition from environmental assessment to technology-oriented evaluation and contributes to the development of targeted and sustainable PFAS mitigation strategies in diffuse pollution contexts [1; 2].

Conclusions

1. PFAS are persistent and widely distributed contaminants in surface waters, including rural and agricultural catchments, confirming their relevance as emerging pollutants in water management systems.
2. Monitoring data from Latvian river basins (Daugava and Lielupe) showed low but detectable concentrations of PFOS and PFOA (PFOA: 0.039-13.22 ng·L^{-1}; PFOS: 0.039-11.11 ng·L^{-1}), consistent with background levels reported in Baltic and Nordic regions.
3. The observed variability, including differences between mean and median values, indicates a heterogeneous and skewed distribution of PFAS concentrations, with localized zones of elevated levels identified through spatial classification.
4. Diffuse pollution processes, including agricultural runoff, drainage flow, and soil–water interactions, play a significant role in PFAS transport, supporting the interpretation that PFAS occurrence is driven by distributed non-point sources rather than a single dominant emission source.
5. Sonochemical treatment shows potential as a destructive technology for PFAS degradation; however, its application is currently limited by energy demand, operational constraints, and scalability challenges.
6. The integration of monitoring data with spatial analysis provides a data-informed basis for identifying potential application areas, supporting the development of targeted and decentralized PFAS mitigation strategies.

Author contributions

Conceptualization, J.G., I.G., J.P.U.; methodology, J.G. and I.G.; formal analysis, J.G., J.P.U.; data curation, I.G., J.G.; writing – original draft preparation, J.G.; writing – review and editing, I.G. and J.P.U.; visualization, J.G. All authors have read and agreed to the published version of the manuscript.

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