ANALYSIS OF THE INTERACTION BETWEEN MICROPLASTICS AND POPS IN FRESHWATER ENVIRONMENTS – AN EXPERIMENTAL STUDY UNDER LABORATORY CONDITIONS

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ABSTRACT

This study studies the interaction between persistent organic pollutants and microplastics in freshwater, aiming to identify potential correlations between their concentrations. The analysis is grounded in laboratory experiments examining the adsorption capacity of common plastic polymers (e.g., PET, PS, PP, PVC, AC, PE, and PA) for persistent organic pollutants. The research uniquely explores the synergistic behaviour of these pollutants, providing foundational knowledge for future studies focused on selective adsorption mechanisms and the fragmentation processes of contaminated plastics into microplastics.

RÉSUMÉ: Analyse de l'interaction entre les microplastiques et les polluants organiques persistants dans les environnements d'eau douce – une étude expérimentale en conditions de laboratoire.

Cette étude examine l'interaction entre les polluants organiques persistants et les microplastiques dans les d'eau douce, en visant à identifier d'éventuelles corrélations entre leurs concentrations. L'analyse elle repose sur des expérimentations en laboratoire portant sur la capacité d'adsorption de polymères plastiques courants (ex.: PET, PS, PP, PVC, AC, PE et PA) vis-à-vis des polluants organiques persistants. La recherche explore de manière inédite le comportement synergique de ces polluants et constitue une base pour des études futures sur les mécanismes d'adsorption sélective et la fragmentation des plastiques contaminés en microplastiques.

REZUMAT: Analiza interacțiunii dintre microplastice și poluanți organici persistenți în medii de apă dulce – un studiu experimental în condiții de laborator.

Studiul de față investighează interacțiunea dintre poluanți organici persistenți și microplastice în mediile dulcicole, urmărind identificarea posibilelor corelații între concentrațiile acestora. Analiza are la bază experimente de laborator privind capacitatea de adsorbție a unor polimeri plastici frecvent întâlniți (ex.: PET, PS, PP, PVC, AC, PE și PA) față de poluanți organici persistenți. Cercetarea explorează într-un mod inedit comportamentul sinergic al acestor poluanți și oferă o bază solidă pentru studii viitoare asupra mecanismelor de adsorbție selectivă și fragmentării materialelor plastice contaminate până la nivelul microplasticelor.

INTRODUCTION

The fast development of urban settlements, alongside intense industrialisation, the expansion of intensive agriculture, intensification of transports, etc. induced growing threats to freshwater ecosystems (Błońska et al., 2024, Adom, 2018; Khoshnood and Khooshnood 2015; Sandu et al., 2008; Olosutean and Ilie, 2010; Yldiz et al 2010). The harmful effects of human stressors on nature are becoming increasingly obvious, jeopardising both wildlife and human health (Cianfaglione et al., 2025; Bănăduc et al 2024, 2023, 2022; Amado et al., 2020; Meijide et al., 2018; Zhu et al., 2018). Also, climate change – accelerated by anthropogenic pressures – has caused dangerous environmental imbalances, disrupting vital reproductive and feeding processes in aquatic organisms (Schmeller et al., 2018).

In such vulnerable ecosystems, even minor external stressors can become fatal. Pollution originating from urban areas has long impacted both the flora and fauna of aquatic habitats (Schmeller et al., 2018). Identifying the sources, characterising the effects, and inventorying spatial distribution of pollutants is thus critical to protect freshwater species and maintain ecosystem stability (Liu et al., 2018; Zhao et al., 2018). These insights are essential for the development of sustainable conservation strategies (Sumon et al., 2018), as well as for advancing environmental policy and strategies through a better understanding of the oxidative degradation of pollutants (Schmeller et al., 2018).

Freshwater ecosystems are among the most ecologically valuable ecosystems on Earth (Ghermandi et al., 2008), providing many services vital to humans. Despite their adaptability, they are considered highly sensitive (Naiman and Turner, 2000). Ongoing contamination, particularly in small water bodies such as lakes, reservoirs, and marshes, but not only, poses severe environmental, economic, and public health risks. Historically, these ecosystems have fulfilled essential economic (e.g., fisheries, agriculture), social (e.g., drinking water supply), and ecological (e.g., nutrient cycling, biodiversity support, etc.) functions, making their protection a key element of sustainable development (Kumaraswamy et al., 2020).

Today, multiple sources of pollution affect freshwater environments, including industrial and household waste, sewage discharge, air-water-soil pollution, and unsuitable construction materials (Qadri and Faiq, 2020). Persistent pollutants resulting from poor waste management degrade habitat quality and pose long-term ecological threats. These compounds, especially heavy metals, persistent organic pollutants (POPs), and microplastics (MPs), are characterized by their long term resistance to natural degradation and their tendency to bioaccumulate (Curtean-Bănăduc et al., 2021, 2017, 2016a-d; Gomez-Ramírez et al., 2014).

While much care has been studied about marine MPs pollution, freshwaters remained underexplored despite similar concerns. Most studies have focused on single-species effects, neglecting broader ecological interactions and ecosystem-level processes (Ockenden et al., 2021). MPs are widely distributed across environments and can travel long distances via rivers and ocean currents (Li et al., 2020), yet their interactions with pollutants remain insufficiently understood.

POPs are of particular concern due to their toxicity, volatility, and chemical stability, enabling long-range transport through the atmosphere (UNECE, 2000). Substances such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), once used by humans, persist in the environment and accumulate in animal tissues, transferring through trophic circuits (Kean et al., 2021). Even when environmental concentrations are low, internal concentrations in organisms may reach hazardous levels due to bioaccumulation (Persistent Organic Pollutants, EPA 2024). Thus, understanding the global movement and regulation of these substances is essential for both environmental and human health.

This study aims to deepen our understanding of the interaction between POPs and MPs in freshwater environments. It investigates whether a correlation exists between environmental concentrations of POPs and the quantity of MPs. The project is grounded in laboratory experimentation, examining how various common plastic polymers (PET, PS, PP, PVC, AC, PE, and PA) adsorb persistent pollutants. Given that POPs are hydrophobic and tend to bind to non-polar surfaces, MPs may serve as efficient transport vectors in aquatic environments.

Ultimately, this work forms a foundation for more advanced studies on selective adsorption mechanisms and plastic fragmentation models, while contributing to the refinement of POPs extraction protocols from plastic surfaces – an area with limited existing toxicological research. Freshwater habitats – including rivers, lakes, wetlands, groundwater, and glaciers – are vital for life and global biodiversity (Apostolaki et al., 2020), yet they represent only 2.5% of Earth's water, most of which is stored in glaciers (68.7%) and groundwater (30.1%) (Brown et al., 2014; Shikomanov, 1996). Protecting these limited ecosystems is essential, as they connect human settlements with natural landscapes and serve as critical resources for drinking water, agriculture, and ecological balance (Amoatey and Baawain, 2019).

The unbalanced development of chemical use and wastewater management has led to widespread contamination of hydrological systems (Daigger, 2007), involving a wide range of pollutants, including emerging contaminants, pesticides, endocrine disruptors, heavy metals, etc. (Amoatey and Baawain, 2019). This makes freshwater systems key battlegrounds for addressing modern major environmental challenges.

Water pollution degrades significantly water quality and disturbs aquatic habitats, food chains, nutrient cycles (Malik et al., 2020; Alrumman et al., 2016; Briggs, 2003) and also favours parasites, diseases, and invasive species (Öktener and Bănăduc, 2023). Acute contamination can cause mass mortality, while chronic exposure results in bioaccumulation across trophic levels, especially in fish – top predators in many aquatic systems (Curtean-Bănăduc et al., 2023, 2020; Mehboob et al., 2019; Khoshnood, 2017; Arthington et al., 2016; Sabra and Mehana, 2015).

Bioaccumulation leads to the internal concentration of pollutants beyond safe thresholds (Langenbach, 2013; Ashauer et al., 2010), with early research confirming the relevance of internal concentration (Meador et al., 2008; Escher and Hermens, 2004; McCarty and Mackay, 1993). This is particularly evident in small invertebrates, which easily absorb pollutants due to osmoregulation and thin epithelial layers (Monteiro-Riviere et al., 2008). When consumed, these pollutants move up trophic levels with magnified effects (Bailey and Duffy-Anderson, 2009; Poliakova et al., 2000).

Plastic waste, especially MPs, have recently emerged as a new vector for pollution. As synthetic particles < 5 mm, MPs can adsorb and transport POPs due to their lipophilic surfaces (Bakir et al., 2014, 2012; Dekiff et al., 2014). Their presence in cosmetic products and industrial processes (Wagner et al., 2014), and their ability to cross epithelial barriers (Yin et al., 2021; Teuten et al., 2009), make them especially harmful.

Studies suggest that MPs can induce metabolic dysfunctions and chronic toxicity in exposed organisms (Li et al., 2020; Fackelmann and Sommer, 2019; Qiao et al., 2019). Despite widespread concern (Depledge et al., 2013; United Nations Environment Programme, 2011; GESAMP, 2010; Sutherland et al., 2010), freshwater systems remain relatively underrepresented in scientific literature, despite their importance as initial sources of MPs discharged into oceans and watersheds.

Recent findings also highlight the combined risks of MPs-POPs interactions, particularly the sorption/desorption dynamics of hydrophobic pollutants on MPs (Karapanagioti and Kalavrouziotis, 2019; Lee et al., 2019; Wang et al., 2018; Teuten et al., 2007). MPs act as mobile versatile platforms, dispersing pollutants over large distances and even into water, sediments, and organisms where they form persistent deposits (Fu et al., 2021; Courtene-Jones et al., 2020). However, in freshwater systems such as shallow rivers, resuspension increases the risk of continuous pollutant exposure (Roos et al., 2011).

To conclude, this study underscores the urgent need for research into the interaction between POPs and MPs in freshwater environments, providing essential data for risk assessment, environmental monitoring, pollution control, and long-term ecological protection.

MATERIAL AND METHODS

The current study is based on a laboratory experiment designed to evaluate the interaction between MPs and POPs. The plastic samples were obtained from a variety of food packaging materials, sufficient to capture the heterogeneity of potential input sources. The experiment was conducted under simulated freshwater conditions. Particular attention was given to the adsorption behavior of persistent organic pollutants on the surfaces of different plastic polymers. Seven polymers commonly found in aquatic environments, with relevant physical-chemical propoperties (Tab. 1) were selected: Polyethylene Terephthalate (PET), Polystyrene (PS), Polypropylene (PP), Polyvinyl Chloride (PVC), Acrylic (AC), Polyethylene (PE), and Polyamide (PA). These materials were subjected to standardised laboratory protocols involving physical fragmentation, chemical contamination, and pollutant extraction, followed by gas chromatographic analysis.

To ensure replicability and comparability, the study followed a five-stage experimental design, illustrated in figure 1.

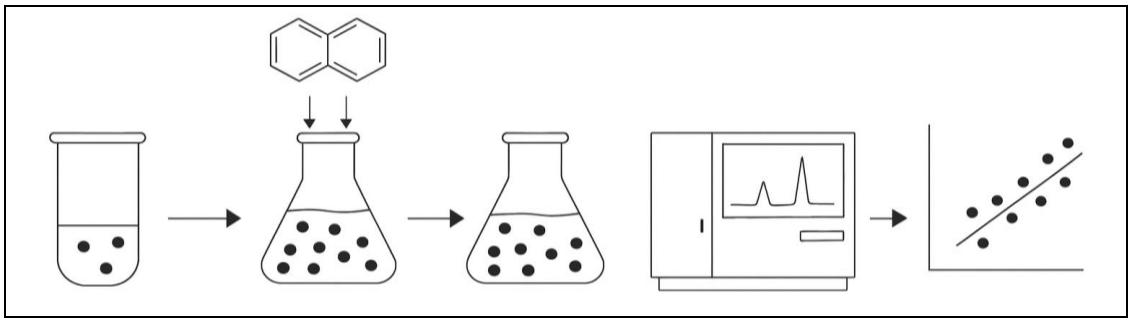

Figure 1: Schematic illustration of the experimental workflow: (1) polymer preparation, (2) POPs contamination, (3) pollutant extraction, (4) GC-MS analysis, (5) statistical analysis.

Table 1: Physicochemical properties and common sources of selected plastic polymers.

Polymer code	Polymer name	Density (g/cm^3)	Hydrophobicity	Common sources
PET	Polyethylene Terephthalate	1.38	Moderate	Bottles, textiles
PS	Polystyrene	1.05	High	Packaging, insulation
PP	Polypropylene	0.90	High	Food containers, fibers
PVC	Polyvinyl Chloride	1.40	Moderate	Pipes, cables
AC	Acrylic	1.18	Variable	Paints, adhesives
PE	Polyethylene	0.94	High	Bags, films
PA	Polyamide (Nylon)	1.14	Moderate	Fishing lines, clothing

To accurately determine the full retention capacity of the contaminant under study for plastics commonly found in freshwater environments, it was necessary to use relatively small fragments (approx. five cm^2) of seven polymer types – polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), acrylic (AC), polyethylene (PE), and polyamide (PA) – were exposed to a controlled specific mixture of selected POPs. This specific mixture, prepared in the laboratory, contained equal volumes of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), yielding final concentrations of 25, 50, 100, and 200 ppb. These exposure levels were selected based on environmental relevance, with 25 ppb reflecting documented contamination in aquatic systems (Lotufo et al., 2001), and higher levels determined by a scalar progression model, reaching a theoretical maximum adsorption threshold at 200 ppb.

Plastic samples were standardised in shape and dimension (1.5 × 1.5 cm, < 1 mm thick) and submerged in POPs solutions for 24 hours under static conditions to simulate acute contamination events. Following this phase, POPs were extracted from the plastic surfaces using an adapted protocol tailored to the chemical reactivity of organic polymers with extraction solvents. Because conventional methods for sediments are not directly applicable to plastics, procedural modifications were necessary throughout the study to optimise purification and recovery.

Subsequent to extraction activity, compounds were completely separated and quantified based on their specific molecular characteristics. While various methods – liquid chromatography, gas chromatography (GC), and multidimensional GC – were considered in this research, gas chromatography was selected for its widespread use in POPs analysis (Salem et al., 2016; Kim et al., 2008) and its proven effectiveness in compound resolution. Despite requiring complete volatilisation of the samples (Megson et al., 2016), GC provided reliable detection and quantification. Each sample of the study required over 60 minutes for full analysis.

The total POPs load per polymer type was calculated post-identification, representing the surface-level adsorption capacity for each plastic type. This capacity was then extrapolated to the MPs scale using a theoretical fragmentation model based on binary division (2^n), where each MPs fragment was assumed to split into two equal parts, conserving density while halving volume and mass. Although this model does not reflect natural fragmentation dynamics, it allowed simulation of worst-case environmental scenarios regarding contaminant mobility.

To evaluate adsorption scaling for the selected particle size, the retention of POPs was quantified for MPs particles measuring 500 µm and 300 µm. These size classes are considered ecologically relevant in both freshwater and terrestrial environments. A spherical model was applied to standardize surface area calculations, enabling theoretical estimation of adsorption efficiency and pollutant transport potential. While real-world plastic debris rarely presents perfect geometry, this idealised model aimed to illustrate the minimum synergistic effect between MPs and POPs.

For practical reasons, manufacturing spherical plastic particles was not feasible. Instead, flat plastic strips of equivalent surface area were used. All materials originated from household food packaging, chosen for their high purity, declared food safety standards, and ecological relevance, as they represent primary contributors to plastic pollution in aquatic systems.

Laboratory protocol for contamination and analysis

To determine the maximum adsorption capacity of the analysed POPs on plastic surfaces, a total of five test concentrations (0, 25, 50, 100, and 200 ppb) were applied to each of the seven selected plastic types (PET, PS, PP, PVC, AC, PE, and PA). Each such plastic was cut into standard rectangular strips (~ 5 cm² surface area), judiciously prepared to minimize edge imperfections that could artificially increase surface contact and affect results. For each polymer, five nearly identical test strips were created to represent the negative control and four contamination levels. Table 2 illustrates the mass of the plastic strips for each material.

Table 2: Standardisation of the mass of plastic strips (± 2 mg), homologous to analysis samples. polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC), acrylic (AC), polyethylene (PE), and polyamide (PA).

Nr. Crt.	PET mg	PS mg	PA mg	AC mg	PE mg	PP mg	PVC mg
1.	74.1	49.7	43.5	498.8	162.4	113.4	400.9
2.	75.4	48.0	42.2	502.6	161.5	114.3	400.4
3.	74.1	51.4	44.0	501.1	160.0	115.2	400.1
4.	74.4	51.6	43.7	502.8	161.3	115.2	398.4
5.	73.0	51.5	41.8	501.1	161.8	114.5	400.6

Plastic strips were degreased, stripped of protective coatings, and submerged in ultra-pure water inside pre-cleaned test tubes. Specific volumes of POP mixtures – containing PCBs and OCPs – were pipetted into the tubes to reach the desired concentrations. To simulate environmental exposure, the tubes were vortexed to promote contaminant-surface interaction and sealed to prevent volatilisation. After 24 hours, the plastic strips were removed, rinsed of residual solution, and placed in extraction vessels.

The extraction of surface-bound POPs was conducted using a liquid-liquid extraction (LLE) method. Contaminated plastic strips were combined with sodium chloride solution, ultra-pure water, acetone, and cyclohexane, then subjected to vortexing, ultrasonication, and centrifugation. The resulting organic phase containing extracted POPs was transferred, concentrated, and further purified using 96% sulfuric acid to degrade interfering compounds. Special care was taken to prevent cross-contamination and loss of analytes through volatilisation, requiring thorough cleaning of labware, single-use pipettes, and careful sample handling under fume hoods.

Following acid-phase purification, samples were concentrated to a final volume of 0.5 mL. Precise layering techniques and freezing-centrifugation cycles were applied to separate and isolate the purified extract. The supernatant was then filtered and transferred into sterile GC vials for chromatographic analysis.

Quantification of POPs was performed using a GC-MS/MS system (Agilent Technologies, triple quadrupole), which enabled the simultaneous detection of both PCB and OCP compounds. Prior to analysis, the instrument was calibrated with a 7-point standard curve (ranging from 3.125 to 200 ppb). Each plastic sample was analyzed individually, with a runtime of approximately 60 minutes per sample. Final pollutant concentrations were determined by retention time and peak integration, providing both qualitative and quantitative data for all treatment levels.

Statistical Analysis of Laboratory Data

Due to the large volume of data generated during the experiment, the variables were categorized according to their nature – numeric, categorical, factorial, or logical. Structuring the data into an organised and searchable database enabled both efficient handling and a clearer observation of relationships between key variables. The statistical analysis focused primarily on the interaction between contaminant adsorption capacity, plastic type, and contamination treatment concentration.

To perform this analysis, RStudio was selected for its versatility in data processing. This statistical software environment, built on the R programming language, supports advanced data importing, manipulation, visualisation, and modeling (RStudio Team, 2020). The analysis was conducted using the April 2024 release, RStudio 2024.04.0+735 – "Chocolate Cosmos", which includes enhanced features for intuitive exploration and prediction of complex datasets (Posit Team, 2024).

The first step involved computing pairwise correlation coefficients across all variables to examine their interdependencies. The correlation coefficient, which ranges from – 1 to 1, was used to quantify the strength and direction of these relationships. A value of – 1 indicates a perfect negative correlation, suggesting an inverse relationship, while + 1 indicates a perfect positive correlation. A coefficient of 0 implies no linear association between the variables (Fernando, 2024).

Subsequently, regression analysis was applied to assess the strength and statistical significance of associations between variables. The primary method used was linear regression, which estimates the best-fitting linear model based on statistical criteria, a method well-established in data modeling (Lindley, 1987).

Finally, the results were visualised using gradient-colored correlation matrices, which provided an intuitive and comparative view of variable fluctuation and associations across the dataset

RESULTS AND DISCUSSION

To ensure a more coherent interpretation of the pollutant concentrations quantified via gas chromatography – mass spectrometry (GC/MS/MS), persistent organic pollutants (POPs) were grouped according to their chemical families. The functional groups included:

- PCBs: PCB18, PCB20, PCB28, PCB31, PCB44, PCB52, PCB77, PCB81, PCB101, PCB105, PCB114, PCB118, PCB123, PCB126, PCB138, PCB149, PCB153, PCB156, PCB157, PCB167, PCB169, PCB170, PCB180, PCB189, and PCB194;
- HCHs: α-HCH, β-HCH, δ-HCH, and γ-HCH;
- DD compounds: o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDD, p,p'-DDE, and p,p'-DDT;
- Chlordanes: oxychlordane, trans-chlordane, and cis-chlordane;
- Hexachlorobenzene (HCB): treated as a single compound within its own category.

It is important to note that two analytical samples – PE 0 ppb (polyethylene, negative control) and PS 100 ppb (polystyrene, 100 ppb contamination treatment) – were excluded from the research. This was due to procedural errors during the POPs extraction phase, specifically the absence or incorrect addition of internal standards, which rendered POPs quantification invalid for these samples.

A synthesis of the quantified POPs values for each functional group is presented in table 3. This table reflects the mean contaminant concentrations detected on the surfaces of macroplastic samples, categorised by contamination treatment levels (0 ppb, 25 ppb, 50 ppb, 100 ppb, and 200 ppb).

Initial data analysis revealed the presence of baseline POPs concentrations even in the untreated plastic samples (0 ppb), which served as negative controls for our research. Despite prior decontamination of all plastic strips before testing, these low values suggest either intrinsic retention of contaminants within the plastic matrix or residual contamination from the material source. However, since these concentrations were negligible (ranging from 0 to 0.4 ppb), they were deemed not to affect the interpretation of adsorption capacity.

Further specific analysis, based on the known concentrations of contamination treatments, allowed for the identification of outlier samples – those presenting anomalously high pollutant levels. In rare cases, excessive concentrations of POPs can result from the use of recycled plastic materials, as contaminants may be trapped within the polymer matrix during reprocessing and later released under natural degradation processes (Eriksen et al., 2018).

Although this research primarily employed food-grade plastics derived from common commercial packaging – ensuring toxicological safety for human consumers – an exception was noted for the PA 100 ppb sample, which showed significantly elevated POPs concentrations, well beyond the expected treatment threshold. This suggested accidental laboratory contamination, and the sample was therefore excluded from statistical analysis to avoid bias.

Table 3 presents the average concentrations of the five POPs groups – PCB, DD, Chlordanes, and Hexachlorobenzene – across different polymer types and contamination treatments. Two control samples, PE 0 ppb and PS 100 ppb, were previously excluded due to extraction errors, as noted earlier.

Notably, detectable quantities of contaminants were recorded on several untreated samples (0 ppb), including PA, PS, PP, AC, PVC, and PET. These low values ($\leq$ 0.4 ppb) likely result from trace contamination or background absorption and were not considered to impact adsorption analysis.

The results of this research confirmed the fact that PCBs, DD compounds, Chlordanes, and HCB readily adhered to studied plastic surfaces. However, the HCH class (α-HCH, β-HCH, δ-HCH, and γ-HCH) consistently showed zero values across all used polymers, indicating in this context their lack of affinity for adsorption on plastic substrates. Additionally, several organochlorine pesticides (e.g., aldrin, heptachlor, endosulfan, dieldrin, endrin, and methoxychlor) were found to degrade under sulfuric acid purification and were also excluded from final analysis.

To accuratelly demonstrate the progressive adsorption capacity of plastics for POPs, this research explored in detail correlations between contamination treatments (0, 25, 50, 100, and 200 ppb) and average selected pollutant concentrations. Statistically significant positive correlations were observed between POPs levels and contamination treatments for the studied materials PA, PE, PS, PP, and PET, suggesting increasing adsorption with rising pollutant availability.

Table 3: Summary of data obtained from laboratory analyses: average contamination value of macroplastics with PCBs (ppb).

Sample name	Functional groups of pollutants				
	HCH	HEXA	DD	PCB	Clordan
PA 0 ppb	0	0	0.14141	0.39649	0.22527
PS 0 ppb	0	0	0.29912	0.66759	0.24627
PP 0 ppb	0	0	0.06983	0.39235	0.232
AC 0ppb	0	0	0.0873	0.38333	0.2262
PVC 0ppb	0	0	0.06591	0.43383	0.23187
PET 0ppb	0	0	0.07367	0.43576	0.23646
PA 0ppb	0	25.9461	4.50533	7.21322	10.134
PE 0ppb	0	9.18102	5.45325	7.37738	13.4608
PS 25ppb	0	36.9837	16.9381	11.8369	20.9069
PP 25ppb	0	4.89334	6.61687	7.41998	14.5071
AC 25ppb	0	12.2168	3.09514	4.16868	6.3804
PVC 25ppb	0	14.5423	5.73641	7.70209	11.9761
PET 25ppb	0	2.13489	4.28281	5.31021	6.48923
PA 50ppb	0	53.3729	27.7959	38.4444	47.2867
PE 50ppb	0	15.1303	17.1808	23.4193	32.3212
PS 50ppb	0	77.2541	16.8855	22.889	21.147
PP 50ppb	0	10.2218	22.2414	32.0026	43.5993
AC 50ppb	0	23.3889	6.9582	10.9856	11.362
PVC 50ppb	0	30.7659	24.3796	33.6127	36.0621
PET 50ppb	0	3.23342	13.7902	20.5145	14.2846
PA 100ppb	0	334.373	344.298	499.763	572.643
PE 100ppb	0	23.6509	21.5871	30.6937	39.6482
PP 100ppb	0	26.5597	38.561	60.6729	74.1542
AC 100ppb	0	54.2315	36.6385	54.3524	54.9953
PVC 100ppb	0	41.0978	22.955	34.7266	38.8551
PET 100ppb	0	3.71169	25.3002	40.7287	25.6671
PA 200ppb	0	107.09	50.8444	81.0792	83.9836
PE 200ppb	0	40.2709	46.1588	70.4481	88.7695
PS 200ppb	0	244.081	58.2249	78.3183	98.7392
PP 200ppb	0	35.9476	44.8763	63.1186	83.8504
AC 200ppb	0	46.6581	20.8951	30.0958	33.5007
PVC 200ppb	0	52.7477	25.8238	39.9656	47.1422
PET 200ppb	0	175.216	136.123	211.825	223.597

Conversely, the materials AC and PVC exhibited relatively stable adsorption values across treatments, indicating non-significant correlations ($p > 0.05$). All significant relationships identified in this study analysis were positively linear and are detailed in tables 4-10.

Table 4: Matrix for analszing correlations between contamination treatments and average values of pollutants adsorbed by Polyamide (PA).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexaclorbenzen	0.964746	1			
DD	0.942241	0.98293	1		
PCB	0.965516	0.98743	0.99688	1	
Clordan	0.939894	0.98623	0.99951	0.99564	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.035254	1			
DD	0.057759	0.01707	1		
PCB	0.034484	0.01257	0.00312	1	
Clordan	0.060106	0.01377	0.00049	0.00436	1

Table 5: Matrix of analysis of correlations between contamination treatments and average values of pollutants adsorbed by Polyethylene (PE).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.998509	1			
DD	0.984286	0.98784	1		
PCB	0.987304	0.98865	0.99918	1	
Clordan	0.984825	0.98537	0.9983	0.9997	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.001491	1			
DD	0.015714	0.01216	1		
PCB	0.012696	0.01135	0.00082	1	
Clordan	0.015175	0.01463	0.0017	0.0003	1

Table 6: Matrix of analysis of correlations between contamination treatments and average values of pollutants adsorbed by Polystyrene (PS).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.9976666	1			
DD	0.9858878	0.98594	1		
PCB	0.9993119	0.99949	0.98725	1	
Clordan	0.9933883	0.98823	0.99547	0.99168	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.0023334	1			
DD	0.0141122	0.01406	1		
PCB	0.0006881	0.00051	0.01275	1	
Clordan	0.0066117	0.01177	0.00453	0.00832	1

Table 7: Matrix of analysis of correlations between contamination treatments and average values of pollutants adsorbed by Polypropylene (PP).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.9705574	1			
DD	0.9234446	0.97609	1		
PCB	0.8912469	0.96415	0.99574	1	
Clordan	0.9140933	0.9712	0.99952	0.99625	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.0060377	1			
DD	0.0251331	0.00442	1		
PCB	0.042343	0.0081	0.00033	1	
Clordan	0.029833	0.00584	1.2E-05	0.00028	1

Table 8: Matrix of correlation analysis between contamination treatments and average values of pollutants adsorbed by Acryl (AC).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.829389	1			
DD	0.665329	0.94822	1		
PCB	0.652015	0.94481	0.99966	1	
Clordan	0.690441	0.95845	0.99913	0.99794	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.082396	1			
DD	0.220372	0.01403	1		
PCB	0.233128	0.01544	7.5E-06	1	
Clordan	0.196868	0.0101	3.1E-05	0.00011	1

Table 9: Matrix of analysis of correlations between contamination treatments and average values of pollutants adsorbed by Polyvinyl Chloride (PVC).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.924214	1			
DD	0.765627	0.93751	1		
PCB	0.813957	0.96054	0.99594	1	
Clordan	0.853239	0.98159	0.9866	0.99487	1
The indicator of statistical significance (“p-value”) of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.024758	1			
DD	0.131312	0.01857	1		
PCB	0.093594	0.00935	0.00031	1	
Clordan	0.065986	0.00299	0.00186	0.00044	1

Table 10: Matrix of analysis of correlations between contamination treatments and average values of pollutants adsorbed by Polyvinyl Chloride (PVC).

	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.89145705	1			
DD	0.9502173	0.98794	1		
PCB	0.95197778	0.98682	0.99993	1	
Clordan	0.9259983	0.99653	0.99737	0.9968	1
The indicator of statistical significance ("p-value") of the obtained correlations					
	Treatment	Hexa	DD	PCB	Clordan
Treatment	1				
Hexa	0.04222172	1			
DD	0.01323371	0.00159	1		
PCB	0.01254134	0.00181	7.2E-07	1	
Clordan	0.02389549	0.00025	0.00016	0.00022	1

Legend:

– 1 (negative correlation)	0 (no correlation)	+ 1 (positive correlation)
$p \geq 0.05$ (insignificant correlation)	$p \leq 0.05$ (significant correlation)	$p \leq 0.001$ ("overpowered trial")

The findings of this study support the initial hypothesis: as contamination levels increase in freshwater environments, plastic materials – including MPs – exhibit a corresponding rise in pollutants adsorption. Correlation matrices also revealed significant positive interrelationships among various classes of POPs. This observation is particularly noteworthy, as certain POPs display stronger surface-binding affinities than others.

However, the phenomenon of competitive adsorption among POPs in natural environments remains poorly understood. The current study acknowledges this as a potential avenue for further research, given that POPs interactions may influence adsorption dynamics on plastic surfaces.

Having confirmed the ability of plastic materials to retain POPs, the next objective was to assess their saturation potential. By comparing the contaminant retention values at the two highest treatment levels (100 ppb and 200 ppb), the study determined the maximum adsorption capacity of each selected plastic type. The outcomes of this analysis are presented in table 11.

Acrylic (AC) adsorbed a higher amount of POPs at the 100 ppb treatment level compared to the saturation level of 200 ppb. This anomaly was confirmed by analyzing average values, suggesting that AC reaches its saturation threshold at lower contamination levels. The subsequent decrease in POPs concentration for the 200 ppb AC sample may be attributed to the material's atypical chemical structure, which appears more resistant to POPs adsorption. Consequently, the highest recorded values for AC were used to calculate its saturation level, resulting in an average of 51.367 ppb. To explore the transport potential of POPs via selected MPs surfaces, the study applied a theoretical binary fragmentation model (2^n). This type of model assumes ideal spherical particles as transport vectors in aquatic environments. The analytical spheres were dimensionally equivalent to the test strips (5 cm^2 surface area), allowing a direct extrapolation of POPs retention to MPs surfaces.

Table 11: Saturation values recorded for all POPs according to plastic types (treatment 200 ppb; exposure surface – 5 cm^2)

	Contamination treatment 200 ppb							
		PA	PE	PS	PP	AC	PVC	PET
HEXA	hexaclorbenzen	107.09	40.27	244.08	35.95	46.66	52.75	175.2162
DD	o p DDD	71.92	69.05	77.51	67.16	34.13	41.19	188.8989
	o p DDT	60.59	51.92	92.56	57.60	32.52	33.06	182.3179
	o p DDE	81.22	78.25	108.71	73.41	23.50	37.41	187.73
	p p DDD	0.04	0.06	0.90	0.06	0.04	0.07	0.065016
	p p DDE	0.00	0.00	1.01	0.00	0.00	0.00	0.211092
	p p DDT	91.29	77.67	68.66	71.03	35.17	43.22	257.5166
CLORDAN	oxiclordan	90.52	95.22	116.53	87.68	30.50	46.26	233.7118
	trans clordan	64.86	70.60	69.75	69.90	30.57	40.22	186.3978
	cis clordan	96.57	100.49	109.94	93.97	39.43	54.94	250.6801
PCB	PCB18	97.14	49.86	214.59	43.12	34.99	49.42	191.9532
	PCB20	79.37	50.21	105.14	50.71	14.14	32.15	163.0871
	PCB28	59.50	72.97	71.79	68.59	14.88	26.61	189.6748
	PCB31	57.67	68.11	80.95	58.57	5.34	16.19	143.8739
	PCB101	47.86	71.82	47.61	60.67	10.23	17.74	142.9857
	PCB44	65.10	65.75	49.26	55.98	31.54	33.71	177.1183
	PCB52	63.34	61.43	62.64	58.18	26.73	34.45	166.3932
	PCB105	81.34	80.48	70.96	71.89	41.42	56.50	205.1235
	PCB114	67.52	59.49	61.06	58.51	25.60	45.30	196.3485
	PCB118	85.36	71.95	75.43	75.25	44.21	55.57	254.2309
	PCB123	71.14	62.95	54.83	60.22	29.66	38.15	181.9334
	PCB149	77.75	70.36	71.14	62.39	28.65	38.79	199.5625
	PCB153	97.92	84.58	73.43	77.10	37.31	47.71	274.7441
	PCB77	113.52	85.64	83.34	80.01	44.48	52.57	304.2463
	PCB81	87.01	76.34	69.82	71.26	35.20	44.18	232.9883
	PCB126	112.77	99.21	97.03	87.77	44.10	54.58	271.3223
	PCB138	118.22	96.34	98.98	86.38	48.89	54.04	265.1292
	PCB156	2.43	2.69	17.33	2.40	2.50	2.54	2.59986
	PCB157	70.01	57.96	56.87	65.04	29.49	48.74	197.0088
	PCB167	102.83	86.98	83.37	69.45	36.95	44.86	271.1868
	PCB180	93.13	79.61	92.12	62.55	33.63	39.00	249.7511
	PCB169	97.83	79.81	89.20	65.10	35.01	43.85	261.9738
	PCB170	95.26	78.63	89.28	64.96	33.69	42.38	261.5151
	PCB189	90.17	75.42	66.23	63.03	32.55	41.18	246.4093
	PCB194	92.78	72.62	75.56	58.84	31.20	38.94	244.4538
Average:		76.89	66.99	81.36	60.99	29.28	38.52	198.81
Total:		2691.09	2344.73	2847.61	2134.72	1024.93	1348.26	6958.36

Table 12 outlines the fragmentation scheme, presenting the dimensional parameters of resulting MPs particles. It also includes the number of fragmentations required to reach approximate particle diameters of 500 µm and 300 µm, values chosen based on previous studies addressing MPs distribution in freshwater habitats. Specifically, 500 µm marks the transition from macroplastics to microplastics, while 300 µm represents the most prevalent MPs size class in lotic systems, such as rivers and streams (Semmouri et al., 2023; Mendoza and Balcer, 2019) (Fig. 2).

Table 12: Fragmentation scheme of test spheres, using the equational model (2n) and their dimensional values.

Number of fragmenta -tions (type 2n)	Number of test spheres	Volume of spheres (μm^3)	Radius (µm)	Diametre (µm)	Surface (μm^2)	Total surface of the spheres (μm^2)	Total contact surface (cm^2)
1	1	1.05E+12	6301.906	12603.8123	498808105	498808105	~ 5
2	2	5.25E+11	5001.942	10003.8836	314243936	628487873	~ 6.23
3	4	2.63E+11	3970.136	7940.27112	197970423	791881692	~ 7.92
4	8	1.31E+11	3151.171	6302.34298	124719315	997754518	~ 9.98
5	16	6.57E+10	2501.144	5002.28851	78571875.7	1257150011	~ 12.57
6	32	3.28E+10	1985.205	3970.41076	49499467.4	1583982956	~ 15.84
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
~ 14	16033	65525349	250	500	785001.778	1.2586E+10	~ 125.86
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
~ 16	74238	14151350	150	300	282601.221	2.098E+10	~ 209.79
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
~21	~ 2E+6	523949	50	100	31400	6.296E+10	~ 629.6

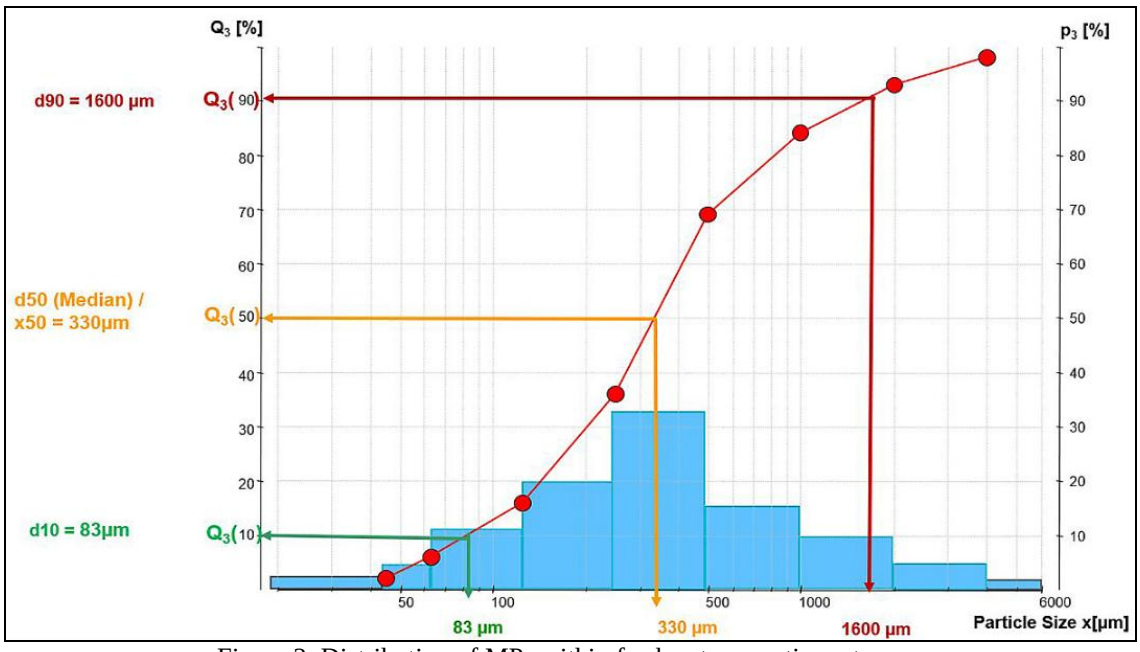

Figure 2: Distribution of MPs within freshwater aquatic systems, with an average value of approximately ~300 µm (Mendoza and Balcer, 2019).

The results presented in table 13 demonstrate that after approximately 14 cycles of binary fragmentation (2^n), the initial analytical sphere (with a surface area of 5 cm^2) was divided into roughly 16,000 microspheres with a diameter of 500 µm and a combined surface area of 125.86 cm^2. This represents a 25-fold increase in total surface area, significantly enhancing the material's potential for POPs adsorption. For microspheres of 300 µm, the calculated total surface area reached approximately 209 cm^2, derived from 74,238 individual particles.

Table 13: Estimated values of POPs concentrations that can be adsorbed on the surface of MPs; transport potential.

Surface of exposure cm^2	Concentration of pollutants adsorbed on plastics (ppb)						
	PA	PE	PS	PP	AC	PVC	PET
5	76.88	66.99	81.36	60.99	51.367	38.5216	198.81
125.86	1935.22	1686.27	2047.99	1535.24	1293.01	969.666	5004.45
209.79	3225.73	2810.77	3413.7	2559.02	2155.26	1616.29	8341.68

Further theoretical fragmentation down to 100 µm diameter revealed a logarithmic increase in cumulative surface area, approaching a plateau around 630 cm^2. It is important to note that this surface area corresponds to over two million microspheres, a figure difficult to achieve under natural environmental conditions. Fragmentation capacity is ultimately constrained by the mechanical properties of each plastic type. Given the lack of data in the scientific literature regarding the maximum fragmentation limit of various plastics, the 300 µm diameter threshold was selected as the final reference point for estimating POPs adsorption potential on MPs.

Figure 3 illustrates the logarithmic surface increase of fragmented microspheres in relation to particle number. The chart extends down to the 100 µm diameter, beyond which the number of additional fragmentation events required to increase surface area by just 1 cm^2 exceeds 10,000 particles.

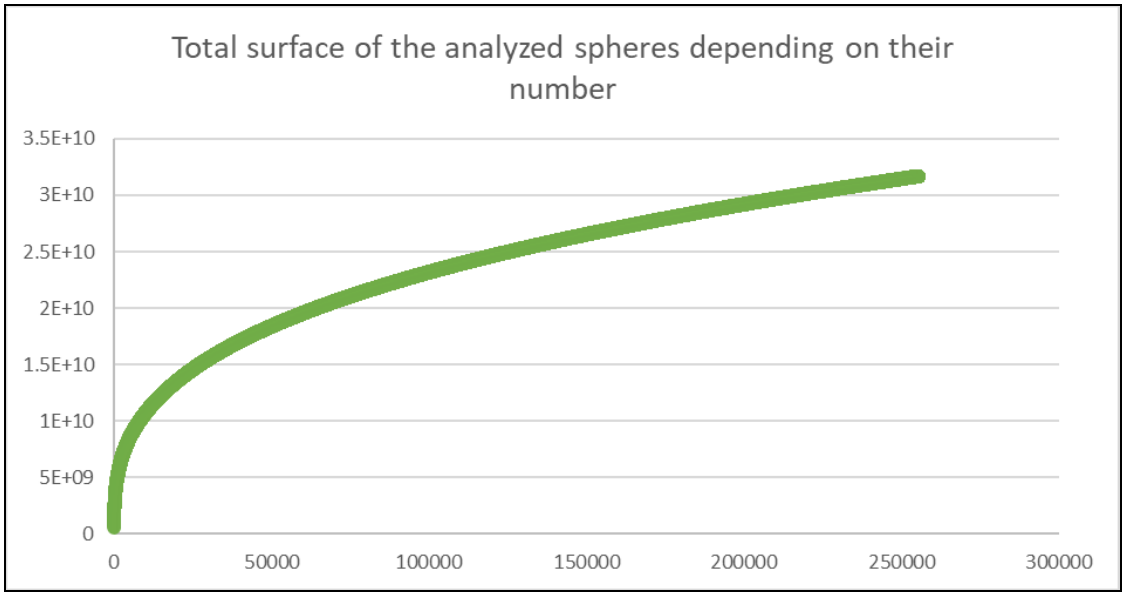

Figure 3: Graph of the function describing the increas in the contact/exposure surface area of plastics as a function of the number of analysis microspheres – logarithmic function.

Finally, using the data obtained in the laboratory analysis, which determined the adsorption of POPs on the surfaces of plastic materials and the data calculated in the fragmentation analysis, the value of pollutants that can be retained on the final MPs was estimated. Table 12 illustrates the new average values of pollutants that can be adsorbed by the microspheres created following the fragmentation process, depending on the type of plastic materials used (PA, PE, PS, PP, AC, PVC, and PET).

CONCLUSIONS

By addressing a transdisciplinary topic and employing novel analytical techniques, this study clearly demonstrates the substantial capacity of MPs to adsorb POPs on their surfaces. The 24-hour acute exposure of various macroplastic materials (Polyamide, Polyethylene, Polystyrene, Polypropylene, Acrylic, Polyvinyl Chloride, and Polyethylene Terephthalate) to a series of POPs contamination treatments (25 ppb, 50 ppb, 100 ppb, and 200 ppb) confirmed a progressive adhesion of pollutants, reaching a saturation threshold.

By analysing diverse polymers, the study revealed differential retention capacities depending on the plastic type. Polyamide, Polystyrene, and especially Polyethylene Terephthalate (PET) exhibited high adsorption potential for the chemical classes PCB, DD, Chlordane, and Hexachlorobenzene. Medium-level retention was observed for Polyethylene and Polypropylene, while Acrylic and PVC showed the lowest adsorption values.

With this information, the study proposed a theoretical fragmentation model to assess the potential for pollutant transport via MPs in freshwater ecosystems. As the number of fragmentations increased, the total exposed surface area also increased significantly. Starting from just 5 cm², repeated fragmentation yielded estimated exposure surfaces of approximately 125 cm² (500 µm) and 210 cm² (300 µm). These values were then used to estimate the total POPs transport potential of MPs. Alarmingly, PET-based MPs were capable of carrying over 8,000 ppb of pollutants, while PVC particles retained around 1,600 ppb.

Taking into account the documented contamination levels of freshwater systems with MPs, it is clear that the synergistic interaction between MPs and POPs poses a serious threat to ecological and human health. Literature confirms the ubiquity of plastic particles, even in remote environments such as Antarctica (Cunningham et al., 2020). POPs adsorption exacerbates contaminant management in nature and contributes to bioaccumulation processes. Additionally, the combined toxicity of MPs and POPs could potentially yield greater effects than individual exposures.

Freshwaters have long been connected to urban areas and are vulnerable to human pressures. Pollution of these systems leads to ecological imbalances and economic losses, affecting both food webs and ecosystem services. A thorough understanding of aquatic contamination processes is, therefore, essential for mitigation and prevention strategies.

Despite ongoing efforts to monitor ecological conditions in many watersheds, such assessments are often hindered by a lack of resources. New multiparametric methods may offer a solution, although their protocols remain under development. This study contributed to ecotoxicological knowledge by providing new insights into the adsorption behavior of POPs on MPs surfaces, potentially supporting the development of new identification and quantification techniques for pollutants in aquatic environments.

To conclude, the present study represents a preliminary investigation into a much broader research topic that will be revisited and deepened in the coming years. Among the potential future directions of this work are the exploration of competitive adsorption between different classes of POPs on plastic surfaces, as well as the analysis of desorption rates of POPs from experimentally contaminated MPs. This study encapsulates the essence of the current understanding regarding the interaction between POPs and MPs, offering a valuable foundation for future investigations and the development of new experimental methods in the field of environmental toxicology.

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