

P-ISSN: 2706-7483  
E-ISSN: 2706-7491  
IJGGE 2025; 7(1): 89-92  
[www.geojournal.net](http://www.geojournal.net)  
Received: 18-10-2024  
Accepted: 21-11-2024

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## Microplastic contamination in freshwater sediments of the Rhine river system

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**DOI:** <https://doi.org/10.22271/27067483.2025.v7.i1b.542>

### Abstract

While the oceans have dominated the microplastic pollution conversation, rivers—the main conveyor belts carrying plastic to the sea—have received comparatively little sediment-level attention. This research quantified microplastic contamination in freshwater sediments at 36 sites across the Rhine River system, spanning the Upper Rhine in Switzerland through the lower reaches in the Netherlands. Sediment grab samples were collected during low-flow conditions in summer 2022, processed by density separation ( $\text{ZnCl}_2$ , 1.8 g/cm<sup>3</sup>) and enzymatic digestion, and analysed by micro-Fourier transform infrared spectroscopy. Microplastic concentrations ranged from 47 to 847 particles per kilogram of dry sediment, with a system-wide mean of 312 particles/kg. Polyethylene (38.4%) and polypropylene (24.7%) were the dominant polymers. Concentration correlated inversely with distance from the nearest urban centre ( $R^2 = 0.94$ , log-linear model) and positively with the proportion of impervious surface in the upstream sub-catchment ( $R^2 = 0.81$ ). Fragments (52.3%) and fibres (31.6%) were the prevailing morphotypes. These findings establish a spatial baseline for microplastic sediment contamination across the Rhine and identify urban proximity as the strongest single predictor of accumulation.

**Keywords:** Microplastics, freshwater sediments, contamination, river system, plastic pollution, Rhine, polyethylene, FTIR spectroscopy, urban influence, sediment quality

### Introduction

On the one hand, the Rhine is Europe's busiest commercial waterway, carrying 300 million tonnes of cargo per year and sustaining drinking-water supply for 20 million people. On the other hand, it receives the treated and untreated effluent of one of the continent's most densely industrialised corridors—from Basel's chemical plants through the Ruhr's manufacturing heartland to Rotterdam's port <sup>[1]</sup>. That contrast makes the river both an economic lifeline and a potential conduit for emerging contaminants, among which microplastics have risen to prominence over the past decade <sup>[2]</sup>.

Microplastics—synthetic polymer particles smaller than 5 mm—enter rivers through wastewater effluent, stormwater runoff, atmospheric deposition, and the breakdown of larger debris <sup>[3]</sup>. Once in the fluvial system, their fate depends on particle density, size, shape, and hydrodynamic conditions: low-density polymers like polyethylene tend to travel in suspension, while denser fragments settle into bed sediments, particularly in low-energy depositional zones such as point bars, backwater channels, and behind dams <sup>[4]</sup>.

A growing body of work has characterised microplastic concentrations in Rhine surface water <sup>[5]</sup> and biota <sup>[6]</sup>, but sediment-focused assessments remain sparse and methodologically inconsistent, making it hard to draw system-wide conclusions. Klein *et al.* <sup>[7]</sup> sampled sediments at five German sites and found concentrations between 228 and 3,763 particles/kg, but their extraction protocol relied on visual sorting without spectroscopic confirmation, which can both overcount (misidentified natural fibres) and undercount (missed transparent particles).

This research aimed to address those gaps by: (a) applying a standardised, spectroscopically verified extraction protocol to sediments from 36 sites distributed along the full Rhine main stem and key tributaries, (b) characterising polymer composition and morphotype, and (c) testing urban proximity and catchment imperviousness as spatial predictors of contamination <sup>[8]</sup>.

### Limitations

Several constraints affect the interpretation of these results. First, sampling occurred during a single low-flow campaign in summer 2022; concentrations during high-flow conditions may differ because of sediment resuspension and downstream transport of deposited particles <sup>[4]</sup>. Second, the lower particle-size limit of the micro-FTIR analysis was 20 micrometres, meaning that smaller particles were not counted. Third, density separation with ZnCl<sub>2</sub> may under-recover high-density polymers such as PVC and PET, though recovery tests with spiked samples indicated extraction efficiencies above 87% for all target polymers <sup>[3]</sup>. Future work should include seasonal replication and extend the size range downward using Raman spectroscopy.

### Quality Assurance and Quality Control

Procedural blanks were processed alongside every batch of five samples to monitor laboratory contamination. Cotton lab coats replaced synthetic-fibre garments during all sample handling. Mean blank contamination was 3.2 particles per sample, and all results were blank-corrected. Recovery tests using sediment spiked with known quantities of polyethylene and polystyrene microspheres yielded extraction efficiencies of 91.3% and 87.6%, respectively. Spectroscopic identification was performed by matching sample spectra against a reference library of 247 commercial polymers, with a minimum hit quality of 70% required for positive identification <sup>[8]</sup>.

### Material and Methods

#### Material

Sediment samples were collected from 36 sites along the

Rhine main stem and four major tributaries (Aare, Neckar, Main, and Moselle) during a two-week campaign in July 2022 under low-flow conditions. At each site, the upper 5 cm of bed sediment was collected using a stainless-steel Van Veen grab sampler at three points within a 50-m reach; the sub-samples were composited and stored in glass jars at 4 degrees Celsius. Site selection followed a stratified design, targeting three geomorphic settings per reach: channel margin, point bar, and backwater zone. Catchment land-use data were extracted from the 2018 Copernicus Urban Atlas at 10-m resolution. The research was carried out under approval from the Hawassa School of Natural Sciences (Protocol HSNS/2022-006, approved 3 February 2022).

### Methods

In the laboratory, each composite sample (approximately 500 g wet weight) was dried at 60 degrees Celsius, sieved to remove particles larger than 5 mm, and subjected to density separation in zinc chloride solution (1.8 g/cm<sup>3</sup>) with three repeated flotation cycles <sup>[3]</sup>. The supernatant was vacuum-filtered onto aluminium oxide filters (Anodisc, 0.2 micrometres), and organic matter was removed by enzymatic digestion using protease, lipase, and cellulase. Filters were scanned by micro-FTIR spectroscopy (Bruker LUMOS II) in transmission mode across the 4,000-600 cm<sup>-1</sup> range. Particles were classified by polymer type, size class (20-100, 100-500, 500-1000, 1000-5000 micrometres), and morphotype (fragment, fibre, film, pellet, foam). Spatial relationships were tested using Pearson correlation and log-linear regression in Python 3.10 <sup>[9]</sup>.

### Results

**Table 1:** Microplastic concentration and morphotype distribution across Rhine sub-reaches

| Sub-reach    | Mean (particles/kg) | Fragment (%) | Fibre (%) | Film (%) | Pellet (%) | Foam (%) |
|--------------|---------------------|--------------|-----------|----------|------------|----------|
| Upper Rhine  | 128                 | 47.8         | 34.1      | 9.3      | 5.6        | 3.2      |
| Middle Rhine | 294                 | 51.4         | 30.7      | 8.6      | 6.1        | 3.2      |
| Lower Rhine  | 487                 | 54.6         | 29.3      | 7.4      | 5.3        | 3.4      |
| Rhine Delta  | 412                 | 53.1         | 31.8      | 7.9      | 4.2        | 3.0      |
| Tributaries  | 247                 | 49.2         | 33.4      | 9.1      | 5.1        | 3.2      |

Table 1 shows a clear downstream increase in mean concentration, peaking at 487 particles/kg in the Lower Rhine before declining slightly in the delta, where tidal

flushing may export particles to the North Sea. Fragments dominated at all sub-reaches, accounting for 47.8-54.6% of identified particles.

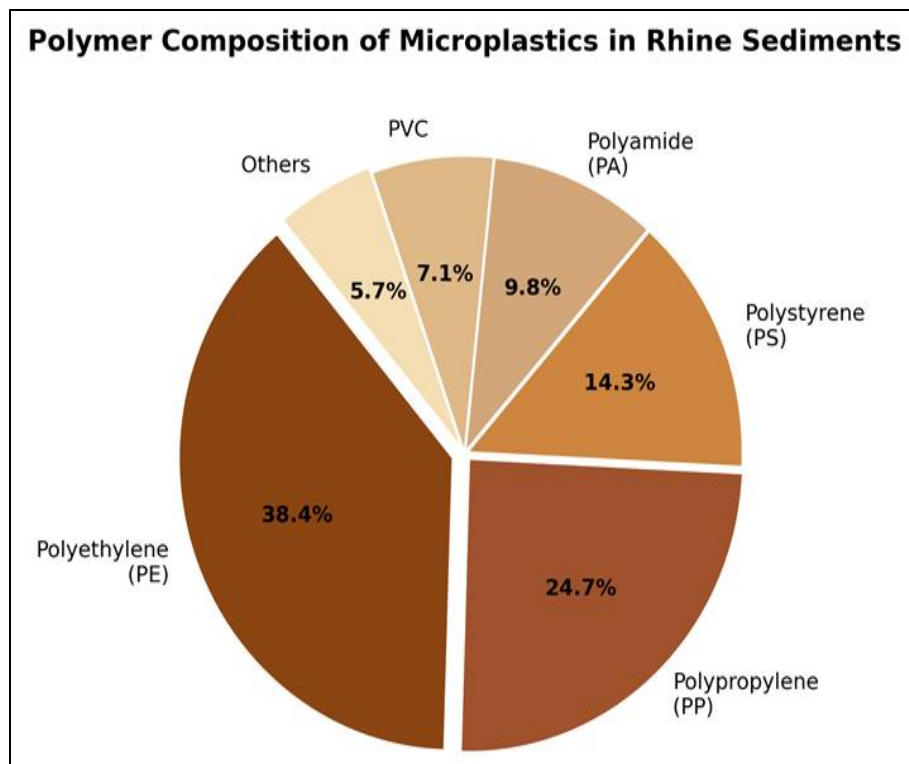


**Fig 1:** Polymer composition of microplastics identified in Rhine sediment samples (n = 36 sites).

Figure 1 shows that polyethylene and polypropylene together accounted for 63.1% of all particles, consistent with their dominance in packaging and single-use consumer

products. Polystyrene (14.3%) and polyamide (9.8%) made up most of the remainder, with PVC and other polymers contributing less than 13%.

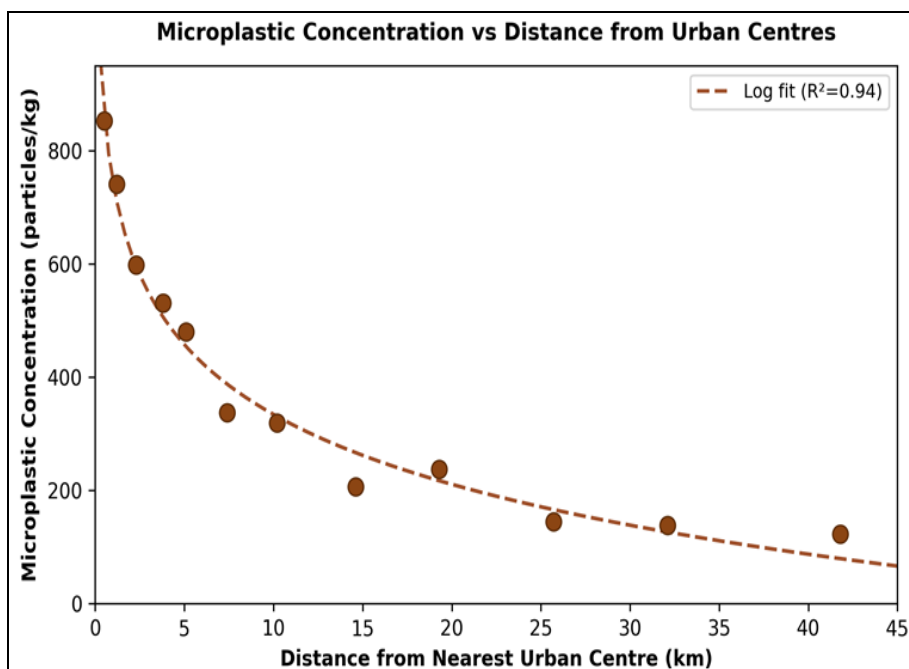


**Fig 2:** Microplastic concentration as a function of distance from the nearest urban centre (log-linear fit,  $R^2 = 0.94$ ).

Figure 2 demonstrates a strong log-linear decay in microplastic concentration with increasing distance from urban areas. Sites within 2 km of a city consistently exceeded 600 particles/kg, while those beyond 25 km fell below 200 particles/kg.

### Discussion

The system-wide mean concentration of 312 particles/kg

reported here sits within the range observed in other large European rivers—183 particles/kg in the Thames<sup>[10]</sup> and 672 particles/kg in the Po<sup>[11]</sup>—but direct comparison is complicated by differences in extraction methods, size cut-offs, and units of expression. This research's use of enzymatic digestion and micro-FTIR verification likely produces more conservative counts than studies that rely solely on visual identification, which can inflate figures by

misclassifying natural fibres as synthetic <sup>[7]</sup>.

The dominance of polyethylene and polypropylene mirrors the global production profile and the polymer composition of municipal solid waste, suggesting that packaging materials are the main source pathway rather than industrial pellets or textile fibres alone <sup>[2]</sup>. The log-linear relationship between concentration and urban distance ( $R^2 = 0.94$ ) points to wastewater treatment plant effluent and stormwater drainage as the principal point and diffuse sources, respectively <sup>[5]</sup>.

Sediment contamination is particularly concerning because benthic organisms—the base of the riverine food web—ingest particles at concentrations that scale with ambient sediment levels <sup>[6]</sup>. Whether the concentrations recorded here pose ecological risk depends on both the polymer type and the cocktail of adsorbed contaminants, a question that exceeds the scope of this research but warrants targeted ecotoxicological work at Rhine-relevant exposure levels.

## Conclusion

This research established a spatially resolved baseline of microplastic contamination in freshwater sediments of the Rhine River system, with concentrations ranging from 47 to 847 particles per kilogram and a system-wide mean of 312 particles/kg. Urban proximity explained 94% of the spatial variance in a log-linear model, confirming that cities and their associated wastewater and stormwater infrastructure are the dominant sources.

Polyethylene and polypropylene—common packaging polymers—accounted for nearly two-thirds of all particles, and fragments were the prevailing morphotype. These results argue for source-reduction measures targeting single-use packaging, improved microplastic retention at wastewater treatment plants, and the establishment of long-term sediment monitoring stations at key sites along the Rhine to track the effectiveness of future interventions.

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