


# Microplastics in sediments of the river Rhine—A workflow for preparation and analysis of sediment samples from aquatic river systems for monitoring purposes

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## Abstract

Microplastics (MP) can be detected in all environmental systems. Marine and terrestrial aquatic systems, especially the transported suspended solids, have often been the focus of scientific investigations in the past. Sediments of aquatic river systems, on the other hand, were often ignored due to the time-consuming sample preparation and analysis procedures. Spectroscopic measurement methods counting particle numbers are hardly suitable as detection methods, because there are plenty of natural particles next to a small number of MP particles. Integral methods, such as thermoanalytical methods are determining the particle mass independently of the inorganic components.

In this study, a workflow for sample preparation via density separation and subsequent analysis by thermal extraction desorption-gas chromatography/mass spectrometry is presented, which leads to representative and homogeneous samples and allows fast and robust MP mass content measurements suitable for routine analysis. Polymers were identified and quantified in all samples. Polyethylene and styrene-butadiene rubber are the dominant polymers, besides polypropylene and polystyrene. Overall, total polymer masses between 1.18 and 337.0 µg/g could be determined. Highest MP concentrations in riverbed sediment are found in sites characterized by low flow velocities in harbors and reservoirs, while MP concentrations in sandy/gravelly bed sediments with higher flow velocities are small.

## KEYWORDS

aquatic sediments, microplastics, monitoring workflow, Rhine river, river sediments, sample preparation, TED-GC/MS

## INTRODUCTION

Microplastics (MP) have been detected in every ecosystem and environmental matrix since they were first discovered in 1972 by K.L. Smith [1–4]. Detection methods are becoming more precise and

diverse over the years, whereas representative sampling and sample preparation have not yet been sufficiently studied for all environmental compartments. Studies of aquatic media from sampling to MP quantification have been increasingly carried out in recent years [5, 6], aiming to determine the load of MP, tracing of sources, sinks

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and transport pathways and to establish monitoring concepts [7] for scientific understanding and regulatory efforts. However, results of these studies indicate incomparability issues due to a broad range of sampling strategies, sample preparation and detection of suspended matter in freshwater systems [8].

While there are numbers of MP studies of aquatic sediments, they are less common than those of the water column [9]. Harmonized procedures do not yet exist in this field in terms of field sampling, laboratory sample preparation and detection methods [10, 11].

Sediments contains plenty of inorganic compounds. Hence, routinely used density separation [12–14] seems to be a suitable method for MP investigations to increase the concentration of MP particles with simultaneous removal of natural inorganic particles. Typically, this is accomplished through the use of high-density aqueous salt solutions, utilizing sodium iodide (NaI), zinc chloride ( $ZnCl_2$ ) or sodium polytungstate solutions [15]. Densities above  $1.8\text{ g/cm}^3$  and high recoveries for the most common polymers are achieved via NaI solutions, which has been studied on marine sediments with a focus on monitoring purposes [16].  $ZnCl_2$  was also excluded due to its higher toxicity compared to NaI [17, 18].

Some detection methods have been shown to be better than others at producing rapid results for a larger number of samples, which is desirable in monitoring processes [19]. These differed not only in the time required for measurements, but also in the properties of the measurement results such as mass, concentration, particle number, size or shape. In general, two different measurement principles can be distinguished: thermoanalytical and spectroscopic methods and for some polymers there are also chemical extraction methods [20, 21]. Spectroscopic methods, such as  $\mu$ -Raman and  $\mu$ -IR, are the most widely used methods to identify individual MP particles by means of specific spectra [22]. In addition to the number of MP particles, properties such as grain shape and grain size are recorded. Since each particle is controlled and measured separately, a reduction of particles that are not plastic is necessary, inorganic as well as organic ones. Compared to relatively rapid density separation to remove inorganic material such as minerals, organic material reduction is more time consuming. This is done, among other things, by enzymatic treatment of the sample to remove components such as proteins, fats or lignocellulosic biomass [23]. These are non-destructive measurement methods that allow repeated measurement of the same sample. In return, it is not possible to generate a mass content via these methods.

Thermoanalytical methods with the focus on thermal extraction desorption-gas chromatography/mass spectrometry (TED-GC/MS) and pyrolysis gas chromatography-mass spectrometry (Pyr-GC-MS), are not able to record particle information such as grain shape, size or number, but result in mass concentration of MP, which is typically used for limit values [24]. Both measurement methods, Pyr-GC-MS and TED-GC/MS, could show in interlaboratory test that MP quantification in freshwater suspended solids lead to good results [25]. Further investigations of MP mass contents in suspended solids of fluvial systems were performed by TED-GC/MS, showing an

application for fluvial systems [26, 27], whereby in general a special sample preparation is not necessary for the measurement by TED-GC/MS.

In general, a homogeneous laboratory sample is necessary for each method to obtain a robust result. Second, the representativeness of the subsample being analyzed must be ensured.

The main objective in this study is the identification of MP and their mass quantification within river sediments from the Rhine and the Lahn with TED-GC/MS measurements, but not the development of a sampling strategy. For this purpose, a workflow for sample preparation was developed, which includes that expected MP concentrations are low and presumably inhomogeneous distributed over the samples. In addition, a sample- and matrix-specific validation of the measurement method (TED-GC/MS) was carried out for the sediment samples.

The workflow for the preparation of sediment samples, which is presented in this study, is based on findings from the project "Plastic in Soils" (Ressortforschungsplan VH 3717 72 232 0), since the expected composition in terms of low MP mass and accompanying complex matrix is similar in soils and sediments. It includes possible steps of freeze-drying, sieving and density separation with subsequent detection by TED-GC/MS. In our study, we show that this sample preparation is required, on the one hand, to obtain an increased MP concentration in the sample. On the other hand, this is especially necessary to obtain a homogeneous laboratory sample for a representative analytical sample to analyze via TED-GC/MS.

## MATERIALS

To prove if the workflow of sample preparation and detection developed for soils can be transferred to aquatic riverine sediments, we took eight sediment samples with variable depositional environments from the river Rhine and the river Lahn near Koblenz (Germany) (for a summary of samples see Table 1). The river Rhine is the largest river in Germany (contributing catchment area of  $185,000\text{ km}^2$ ), draining large parts the European Alps into the North Sea. Being the most important water way in Europe, the river Rhine is strongly regulated. Along most of its flow path, the channel bed is formed by sand and gravel, especially in the free-flowing sections between Iffezheim (the most downstream barrage in the Upper Rhine) and the Dutch/German border. Sampling in the river Rhine was conducted during low flow when the channel bed was freely accessible. Sampling of the sandy/gravelly bed sediments conducted upstream (Braubach) and downstream (Lahnstein, Horchheim) of the confluence of the river Lahn. Furthermore, we sampled fine grained sediments in the Rhine harbor of Ehrenbreitstein, which is characterized by the deposition of fine-grained sediment.

The river Lahn is a tributary of the river Rhine, with a contributing catchment size of  $5925\text{ km}^2$ . The river Lahn is strongly impounded by numerous reservoirs to secure navigation. Riverbed sediments in the reservoirs are mainly fine grained, dominated by silts and clays and smaller fractions of sand. Sampling in the river Lahn was conducted 200 m upstream of the Nievern barrage.

**TABLE 1** Sample locations of this study.

Sample ID	Location	River	River km	Sample weight	Comment
1a	Ehrenbreitstein 1	Rhine, harbor	591	270.1 g	Fine fraction dominant
1b	Ehrenbreitstein 1	Rhine, harbor	591	166.0 g	Fine fraction dominant
2b	Ehrenbreitstein 2	Rhine, harbor	591	177.6 g	Fine fraction dominant
3a	Horchheim	Rhine	587.9	940.4 g	Dominantly sand & gravels
4a	Lahnstein	Rhine	586.5	757.1 g	Dominantly sand & gravels
5a	Braubach	Rhine	581.9	844.5 g	Dominantly sand & gravels
7a	Nievern	Lahn	128	300.3 g	Fine fraction dominant
7b	Nievern	Lahn	128	90.7 g	Fine fraction dominant

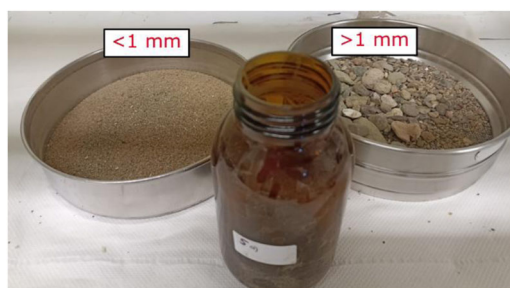
Fine grained samples were taken using a Van Veen sampler either from ponton (harbor of Ehrenbreitstein) or from bridges (Nievern) and sandy/gravelly samples were taken using a stainless-steel shovel.

The limited number of samples does not allow for a representative estimate of MP in riverbed sediments of the Rhine and Lahn. We mainly selected the sites to evaluate the effect of the sediment matrix and to check for consistency of MP estimates upstream and downstream of the confluence between the Rhine and Lahn river.

The collected samples were then freeze-dried and were available as laboratory samples (lab sample) for further sample preparation. The prepared lab samples for subsequent analysis are called test samples or flotate.

To clarify whether density separation of sediment samples is necessary, TED-GC/MS measurements of two processed lab samples from the Rhine from 2019 were used as model samples for method validation. These samples were only used for pretesting purposes and are not subject to the MP load of the Rhine sampling campaign in 2022.

Nal for analysis (Merck KGaA) was used for density separation. For sustainability and climate protection reasons as well as cost reduction, the possibility of Nal reuse was tested with additional TED-GC/MS measurements to exclude contamination from previous samples. Stainless steel filters (Gebr. Kufferath AG) with a mesh size of 6  $\mu\text{m}$  were used to collect the flotate produced during density separation. The polymers used for the standard addition came from plastics producers and were kindly provided by PlasticsEurope Germany. They are all related to starting materials for the production of various plastics (packaging materials, consumer products) and are characterized by a very low additive content. The sample measurement by TED-GC/MS was performed in 150  $\mu\text{L}$   $\text{AlO}_x$  crucibles and using an internal standard. Internal standard of poly(styrene-(phenyl- $^{13}\text{C}_6$ )) ( $^{13}\text{C}_6$ -PS) (Merck KGaA) was used, since it is also a polymer, and the pyrolytic behavior is included in this. The internal standard d5-PS, which was used more frequently in the past, is not used because of the hydrogen-deuterium exchange that occurs [28]. TED-GC/MS measurements were done like previously described in literature [29, 30]. Thermogravimetric measurements were conducted with a thermobalances thermogravimetric analysis (TGA)/DSC 3+ (Mettler Toledo) with a heating rate of 10  $\text{K min}^{-1}$  from 25°C to 600°C under a nitrogen atmosphere.

**FIGURE 1** Picture of the sieved fractions <1 and >1 mm

## METHOD

The sample preparation was carried out by sieving [31] and density separation of the two model samples. The aim was to obtain an overview of the total polymer masses contained in these lab samples. Based on the results, it is possible to assess whether sample preparation is necessary for stable analysis.

### Sieving

The two model samples were dry sieved by hand using a stainless-steel sieve from Retsch with a diameter of 20 cm and with a sieve mesh size of 1 mm. The fractions >1 and <1 mm were obtained (Figure 1). Further sample preparation and investigations were carried out on the <1 mm fraction, as MP are defined as particles <1 mm [ISO/TR 21960:2020].

### Density separation

An aliquot of 50 g (sample 1) and 80 g (sample 2) was taken from the fraction <1 mm of each of the two model samples, which was then processed using density separation. For this purpose, a saturated sodium iodide (Nal) solution with a density of 1.85  $\text{g/cm}^3$  was prepared in advance. This was purified using a glass fiber filter to

exclude contamination by plastic particles in the NaI salt and the Milli-Q® water used. The samples were each mixed with the NaI solution in an Erlenmeyer flask followed by mixing with a stainless-steel rod for 3 min and an ultrasonic treatment for another 3 min. The process of mixing and ultrasonic treatment was repeated three times each. The sample was left to rest for 12–24 h to ensure effective sedimentation of the inorganic components. Subsequently, the floating phase (flotate) was obtained. The flotate was transferred to a vacuum filtration system with the help of a peristaltic pump and transferred to a stainless-steel filter with a mesh size of 6 µm. After a complete transfer, the filter cake was rinsed with sufficient Milli-Q water to remove retained NaI. Second, the adjacent filter material was rinsed sufficiently to transport adhering analytes onto the filter cake. Figure 2 shows the set-up of the filtration system and the experimental procedure.

In the next step, the filter cake was transferred to a beaker with the help of a silicone spatula and water and treated with ultrasound for 3 min together with the stainless-steel filter. The filter was then removed from the beaker and rinsed to avoid losing adhering analytes. The water-filter cake suspension was stored at 50°C in a drying oven until the water was evaporated completely.

## TED-GC/MS

The flotate was now weighed and prepared for measurement by TED-GC/MS. An aliquot of approximately 13 mg each was transferred into a crucible, mixed with 4.4 µg of the internal standard and measured by TED-GC/MS.

For quantification purposes, another aliquot of approximately 13 mg each was taken, mixed with 4.4 µg of internal standard and with corresponding pure plastic particles of known mass (standard addition). This was done for each individual sample.

## RESULTS AND DISCUSSION

### Validation of density separation process

A determination of the recovery rate was carried out using a model matrix for quality assurance of the density separation process (Table 2). As a matrix, a glass fiber filter was cryo-milled and mixed with five different polymer types of known masses. The glass fiber powder serves as a comparable silicate-rich sediment, whereby the low particle size after grinding can also be referred to more problematic matrix during sedimentation. The smaller the particle size of the inorganic components, the longer the residence time in the water column, respectively, the sedimentation time of these.

With polymer recovery rates between 72% and 119% and a matrix reduction of 92%, the process is an effective method of concentrating the polymers while reducing the silicate matrix. The recovery of 72% for polyethylene (PE) is due to the relatively high proportion of particles <6 µm (SI particle size distribution) that pass through the filter into the filtrate and thus leave the sample.

**TABLE 2** Recovery rate of different polymers in a model matrix.

Polymer	Recovery rate/%
PE	72
PP	93
PET	118
PA	119
SBR (tire)	91
GF-matrixreduction	92

Abbreviations: PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber.

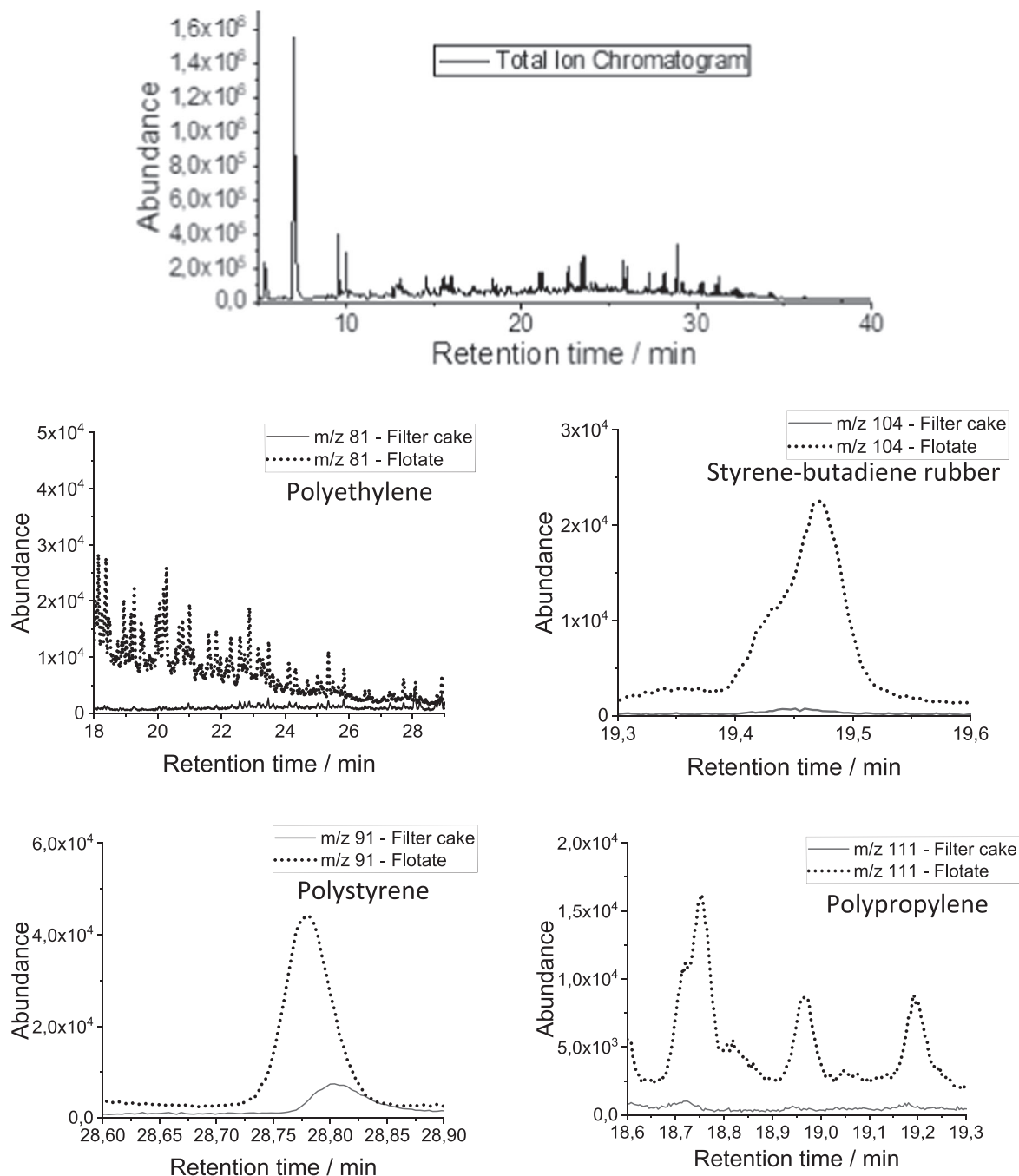


**FIGURE 2** Determination of the density of the NaI solution (left); sediment sample in NaI solution (center); vacuum filtration system with suction device (right)

The NaI solution was recycled for density separation of additional samples. To remove any residual MP particles in the solution, the solution was cleaned of solids by vacuum filtration through glass fiber filters after each sample processing. This is necessary to prevent contamination of further samples. The resulting filter cake was then transferred to an  $\text{AlO}_x$  crucible using a PTFE spatula and measured by TED-GC/MS. The aim of the measurement was to find out if MP enrichment could be detected

in the NaI solution, which could lead to a potential MP overdetection in the subsequent lab and test samples. No polymers could be detected in the measurements of the filter cake (Figure 3), which is why vacuum filtration via a glass fiber filter is sufficient to recycle the NaI solution.

In direct comparison with a sediment sample, it was also shown that the relevant mass traces for quantification do not have a significant portion.



**FIGURE 3** Total ion chromatogram of a filter cake (top) and the mass traces (m/z) of the specific pyrolysis products (m/z 81: PE; m/z 91: PS; m/z 104 SBR; m/z 111: PP) to the corresponding retention times compared to a measurement of a sediment sample. PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber

## Validation of density separation with model sample

Four different polymer types could be identified and quantified: PE, polypropylene (PP), polystyrene (PS), and styrene-butadiene rubber (SBR). It should be noted that the PS content is not representative, as the transport containers of the samples were made of PS. Polymer mass contents of 2.4–25.7  $\mu\text{g}/\text{mg}$  (model sample 1) and 0.14–3.4  $\mu\text{g}/\text{mg}$  (model sample 2) were detected in the flotates. Calculated back to the prepared initial mass, absolute polymer masses of 0.44–10.64 mg in 80 g initial sample (model sample 1) and 0.44–4.72 mg in 50 g initial mass (model sample 2) can be detected (Table 2). The different weights of 80 and 50 g were chosen because of the different starting material. Test sample 2 was visually characterized by a higher proportion of organic material, which is why a reduction in the initial weight was carried out. This was done to prevent a high proportion of flotates in the apparatus, which would lead to more difficult handling (Table 3).

The preliminary investigations with low  $\mu\text{g}/\text{g}$  masses (14,340–16,638  $\mu\text{g}/\text{g}$ ) showed that the samples of the river sediments require a concentration of the plastics (analytes) and thus a reduction of the inorganic sediments (matrix). The analytical masses after density separation tend to be at the lower limits of determination for MP particles in matrices [32], which means that it should be assumed that density preparation is indispensable. In addition, due to the low analyte absolute masses, it can be assumed that the analyte distribution in the subsample used for TED-GC/MS is not homogeneous without prior sample preparation. This confirms the visual observations of the flotates, which indicate that the polymer masses could also be concentrated on a few larger particles, among others (Figure 4).

## Validation of subsampling for detection (TGA-, TED-GC/MS measurements)

Before the riverbed samples can be measured, it must be demonstrated that the aliquots of the total samples are sufficiently homogeneous. For this purpose, the homogeneity of two different test samples are investigated on the one hand in thermogravimetric analyses and on the other hand in TED-GC/MS measurements.

**TABLE 3** Absolute polymer mass in the initial sample.

Sample	Polymer mass/mg				Initial sample mass/g
	PE	PP	SBR	PS	
Sample 1	10.64	–	0.44	2.23	80
Sample 2	4.72	0.44	0.70	1.31	50

Abbreviations: PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber.



**FIGURE 4** Larger MP particle from 80 g initial sample mass. MP, microplastic

## Validation: Homogeneous subsamples for measurements by TGA

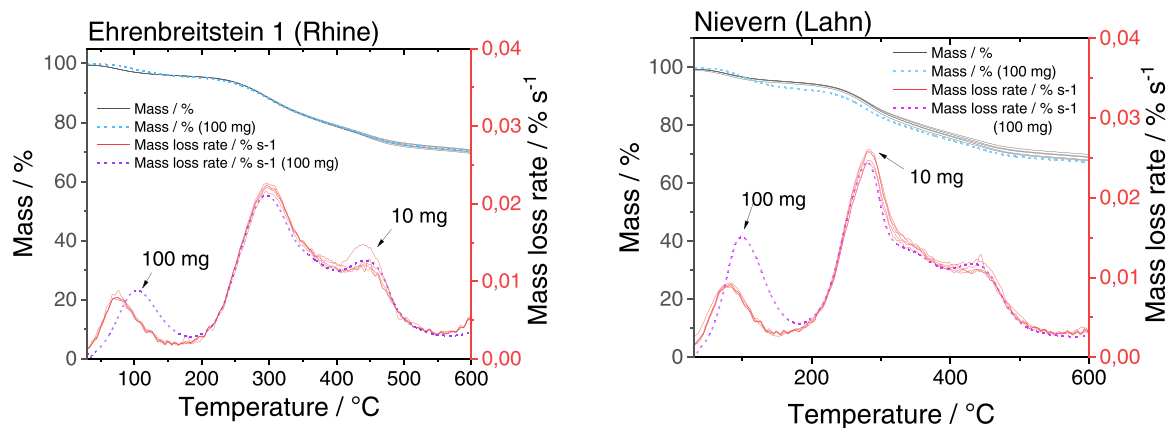
TGA measurements were carried out on two different test samples and weights. Selected samples were flotates from the Ehrenbreitstein 1 site on the Rhine and Nievern on the Lahn. For the TGA measurements, five measurements per sample á 10 mg (typical TED-GC/MS intake) and one measurement á 100 mg were carried out (Figure 5).

The five TGA measurements of the 10 mg sample are characterized by a high degree of homogeneity. The mass loss in the relevant temperature range for pyrolytic polymer degradation (350°C–600°C) is  $12.5 \pm 0.4\%$  for the samples Ehrenbreitstein 1 and  $11.3 \pm 0.3\%$  for Nievern. It should be noted that in the samples with the increased initial weight of 100 mg, the mass loss is 12.33% for Ehrenbreitstein and 10.9% for Nievern, both within the measurement accuracy and error tolerance of the initial weight of 10 mg (Table S1).

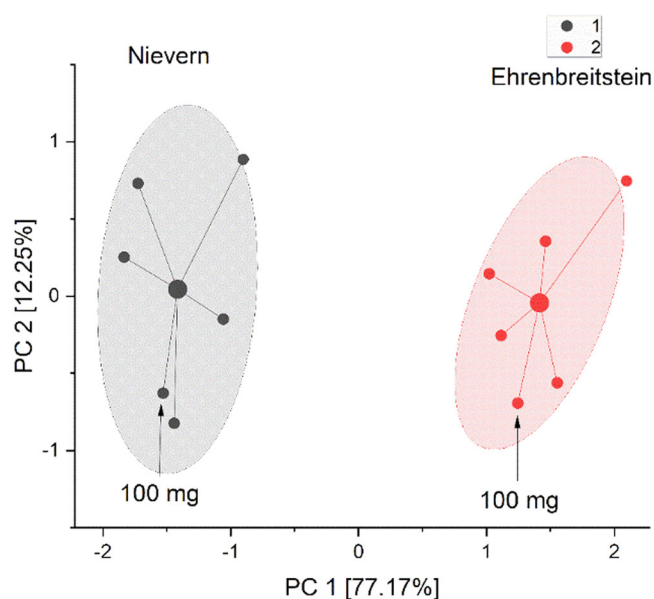
The homogeneity of a subsample of 10 mg thus corresponds to the homogeneity of the 100 mg subsample. To investigate this further, a cluster analysis of the data was performed and the measurements of 10 mg were directly compared to those of 100 mg. By means of a principal component analysis, the TGA data were checked with regard to cluster formation (Figure 6). The joint clustering of the 10 and 100 mg as well as the same sites also shows the homogeneity of the 10 mg weights for measurement by TED-GC/MS.

## Validation: Homogeneous subsamples for measurements by TED-GC/MS quantification

Next to the validation of the aliquot intake, validation of the measurement method TED-GC/MS according to the sediment matrix is necessary. Hence, a fivefold quantification of the flotates of the test sample Nievern was carried out under the same experimental



**FIGURE 5** TGA measurements of the samples Ehrenbreitstein 1 (Rhine, left) and Nievern (Lahn, right). TGA, thermogravimetric analysis



**FIGURE 6** Principal component analysis of the fivefold determination using TGA. TGA, thermogravimetric analysis

conditions as described before with density separation. The quantification is based on standard addition and via typical pyrolysis compounds listed in Table 4.

In all five subsamples, the polymers PE, PS, and SBR were identified and quantified. Table 5 lists the mass contents of the different polymers in the flotates and the initial sample, which were determined by a fivefold determination using TED-GC/MS. In addition, the relative standard deviation resulting from the five measurements is listed.

The initial weight is calculated by the following approach. The MP mass content of the flotate (MC) is determined directly with the TED-GC/MS measurement and is a direct measurement result. With the help of the mass content (flotate) (Equation 1), the polymer mass contained in the flotate ( $m_{\text{total}}(\text{polymer})$ ) is calculated by considering the total flotata mass ( $m_{\text{flotate}}$ ) (Equation 2). This polymer mass

**TABLE 4** Decomposition products used for quantification.

Polymer	Pyrolysis products
PE	Tetradecadiene
	Pentadecadiene
	Hexadecadiene
PS	2,4-Diphenyl-1-butene
SBR	Cyclohexenylbenzene

Abbreviations: PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber.

corresponds to the total polymer mass that was in the initial sample before density separation.

$$\frac{m_{\text{TED}}(\text{polymer})}{m_{\text{TED}}(\text{sample})} \times 1000 = \text{MC}, \quad (1)$$

whereby  $m_{\text{TED}}(\text{polymer})$  is the polymer mass determined by TED-GC/MS and  $m_{\text{TED}}(\text{sample})$  is the sample weight for the measurement.

$$\frac{\text{MC} \times m_{\text{flotate}}}{1000} = m_{\text{total}}(\text{polymer}). \quad (2)$$

This polymer mass corresponds to the total polymer mass that was in the initial sample mass before density separation ( $m$  (initial sample)) (Equation 3) and leads to the mass content of the initial sample ( $\text{MC}_{\text{initial}}$ ).

$$\frac{m_{\text{total}}(\text{polymer}) \times 1 \times 10^{-6}}{m(\text{initial sample})} = \text{MC}_{\text{initial}}. \quad (3)$$

The directly quantified polymer masses in approximately 10 mg sample mass are concentrated by density separation to such an extent that the factor above limit of quantification (LOQ) is reached many times over. The LOQ is twice the limit of detection (for PE 2.2  $\mu\text{g}$ , PS 0.08  $\mu\text{g}$ , SBR 0.06  $\mu\text{g}$ ). For PE, the measured polymer mass is by a factor of 15, for PS by a factor of 20 and for SBR by a factor of 118 higher than the LOQ (related to the LOQs for pure polymers), which allows a robust quantification.

**TABLE 5** The experimentally determined MP mass contents of the Nievern flotates (7a) and the MP masses calculated from them for the initial samples ( $n = 5$ ), where, in the case of PE, an average value of the three compounds was first taken for quantification for each individual sample.

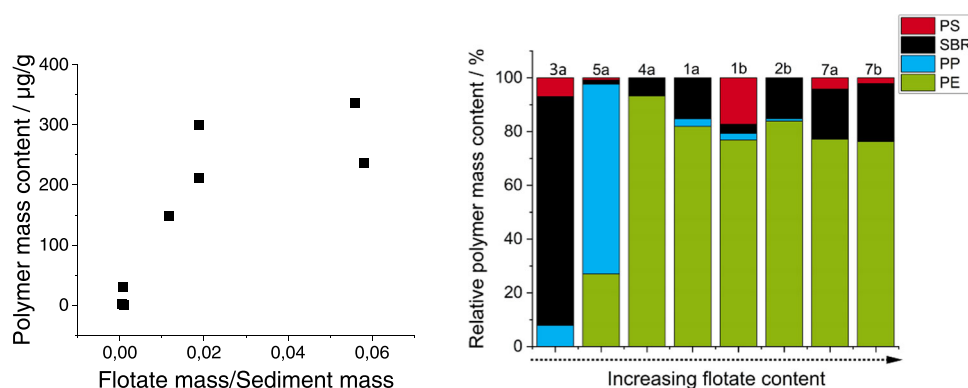
	Mass content (Flotate)/ $\mu\text{g}/\text{mg}$	Mass content (initial sample mass)/ $\mu\text{g}/\text{g}$	Standard deviation (initial sample mass)/ $\mu\text{g}/\text{g}$	Relative standard deviation (initial sample mass)/%
PE	4.71	260	60	23.1
PS	0.24	14	7	50.0
SBR	1.12	63	9	14.3

Abbreviations: MP, microplastic; PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber.

**TABLE 6** Polymer mass concentration in the sediment samples in the initial fraction  $<1$  mm ( $\mu\text{g}/\text{g}$ ).

Sample	Polymer mass content/ $\mu\text{g}/\text{g}$				Total (PE + PP + SBR + PS)
	PE	PP	SBR	PS	
Ehrenbreitstein 1 (1a)	121.36	4.16	22.62	–	148.14
Ehrenbreitstein 1 (1b)	162.7	5.3	7.25	36.52	211.77
Ehrenbreitstein 2 (2b)	251.42	2.64	45.53	–	299.59
Horchheim (3a)	–	0.17	1.84	0.15	2.16
Lahnstein (4a)	1.10	<LOQ	0.08	–	1.18
Braubach (5a)	8.02	20.98	0.46	0.24	29.7
Nievern (7a)	260.00	–	63.00	14.00	337.00
Nievern (7b)	180.00	–	51.00	5.00	236.00

Abbreviations: PE, polyethylene; PP, polypropylene; PS, polystyrene; SBR, styrene-butadiene rubber.



**FIGURE 7** Total polymer mass content against normalized flotata mass (left) and the relative polymer composition for the individual samples presenting with increasing flotata content (right)

Both validations, which were carried out on the sediment samples, examined different aspects of the subsamples: (1) homogeneity and (2) reproducibility of the MP quantification by TED-GC/MS. It has been shown that subsamples with 10 mg mass have sufficient homogeneity. Density separation leads to a significant concentration of the MP mass, whereby the limits of detection and quantification for the individual polymer types are clearly exceeded. Identification and quantification with TED-GC/MS is clearly possible.

### Measurement of river sediment samples

After conception and validation of the treatment and measurement procedure, the sediment samples from the river Rhine and Lahn were treated with the same procedure. The polymers identified in the sediment samples and the quantified masses are summarized in Table 6. The polymer masses are presented in  $\mu\text{g}/\text{g}$  of the initial fraction  $<1$  mm from the total samples.



The total polymer mass contents vary from 1.2 to 337.0  $\mu\text{g/g}$ . They are particularly small along the sandy/gravelly riverbanks of the river Rhine, which are characterized by a low fraction of fine sediments. Lowest concentrations are found in Lahnstein and Horchheim (1.2 and 2.2  $\mu\text{g/g}$ , respectively), downstream of the confluence of Rhine and Lahn. In Braubach, upstream of the confluence, the MP mass is 29.7  $\mu\text{g/g}$  and thus an order of magnitude higher than downstream. MP masses in the Rhine-harbor of Ehrenbreitstein are clearly elevated and range between 148.1 and 299.6  $\mu\text{g/g}$ . With 337.0  $\mu\text{g/g}$  the MP masses are highest in fine grained sediment deposits upstream of the Nievern barrage in the river Lahn. A large number of barrages along the river results in reduced flow velocity of the Lahn that increases the potential for fine sediment and plastic deposition.

In Figure 7, the total polymer content is plotted as a function of the flotite mass content, whereby the flotite mass was normalized to the respective initial sediment mass. It shows that higher polymer contents are accompanied by higher flotite contents, which results from higher organic contents (Figure 7 left).

With two exceptions, the PE is the dominant polymer (relative PE content is 76%–93%) of the total polymer mass. This is followed by SBR with an average of 21%. PP and PS are not present in all samples and, with two exceptions in each case, the values are in the single-digit percentage range (Figure 7 right). To exclude an influence of organics on the quantification of PE, further investigations should be performed.

## CONCLUSION

Overall, a robust workflow for sample preparation and measurement of river sediments could be developed and successfully applied for MP quantification of sediment samples. Density separation is necessary for all samples, not only to be above LOQ, but also to achieve homogenization. Measurements by TED-GC/MS are suitable for polymer type identification and mass quantification of MP particles in sediment samples. The determined masses show a polymer-dependent relative standard deviation of 15%–50%. It is assumed that even with density separation, the polymeric particles with a very low number are not uniformly distributed in the flotite, which leads to an increasing standard deviation.

Highest MP concentrations in riverbed sediment are found in site characterized by low flow velocities in harbors and reservoirs, while MP concentrations in sandy/gravelly bed sediments that deposit under higher flow velocities are small.

In summary, workflows developed for soil can be adapted for sediment samples. Freeze-drying the samples with subsequent sieving and density separation leads to a sufficient concentration of the analytes.

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## CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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