

# Occurrence and Spatial Distribution of Microplastics in River Shore Sediments of the Rhine-Main Area in Germany

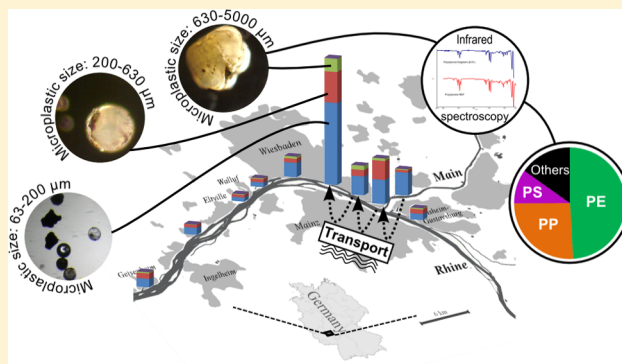
Sascha Klein,<sup>†,‡</sup> Eckhard Worch,<sup>‡</sup> and Thomas P. Knepper<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry and Biology, University of Applied Sciences Fresenius, D-65510 Idstein, Germany

<sup>‡</sup>Institute of Water Chemistry, Technische Universität Dresden, D-01069 Dresden, Germany

## S Supporting Information

**ABSTRACT:** Plastic debris is one of the most significant organic pollutants in the aquatic environment. Because of properties such as buoyancy and extreme durability, synthetic polymers are present in rivers, lakes, and oceans and accumulate in sediments all over the world. However, freshwater sediments have attracted less attention than the investigation of sediments in marine ecosystems. For this reason, river shore sediments of the rivers Rhine and Main in the Rhine-Main area in Germany were analyzed. The sample locations comprised shore sediment of a large European river (Rhine) and a river characterized by industrial influence (Main) in areas with varying population sizes as well as sites in proximity to nature reserves. All sediments analyzed contained microplastic particles (<5 mm) with mass fractions of up to 1 g kg<sup>-1</sup> or 4000 particles kg<sup>-1</sup>. Analysis of the plastics by infrared spectroscopy showed a large abundance of polyethylene, polypropylene, and polystyrene, which covered more than 75% of all polymer types identified in the sediment. Short distance transport of plastic particles from the tributary to the main stream could be confirmed by the identification of pellets, which were separated from shore sediment samples of both rivers. This systematic study shows the emerging pollution of inland river sediments with microplastics and, as a consequence thereof, underlines the importance of rivers as vectors of transport of microplastics into the ocean.



## INTRODUCTION

The production of synthetic polymers, so-called plastics, has increased >100-fold since the middle of the 20th Century to the current 260 Mt/year.<sup>1</sup> High production coupled with physical characteristics such as chemical inertness and very slow biodegradation of most plastics results in an accumulation of plastic debris in the environment.<sup>2</sup> There are many routes of discharge such as improper waste disposal, insufficient waste management, and urban runoffs.<sup>3</sup> Significant amounts of these plastics differing in shape and size, ranging from meters to micrometers, enter the aquatic environment.<sup>4,5</sup> Many studies reported the ubiquitous presence of plastic debris in marine habitats such as strandlines, coastal areas, and the open ocean itself.<sup>6–9</sup> These plastics are of considerable concern because for different economic and ecological reasons. Larger plastic debris, so-called macroplastics, such as nets, wraps, and bags pollutes shores and beaches and may therefore negatively affect the tourism industry. Floating debris can damage equipment or can entangle aquatic creatures, resulting in their death.<sup>10</sup>

More serious and widespread ecological impacts are expected for microplastics.<sup>11</sup> These small plastic particles <5 mm in size originate from various sources.<sup>12</sup> Microparticles made from synthetic polymers are used in cleansers and cosmetics to enhance the product properties.<sup>13</sup> Besides the steady breakdown of larger plastic debris, preproduction pellets used in

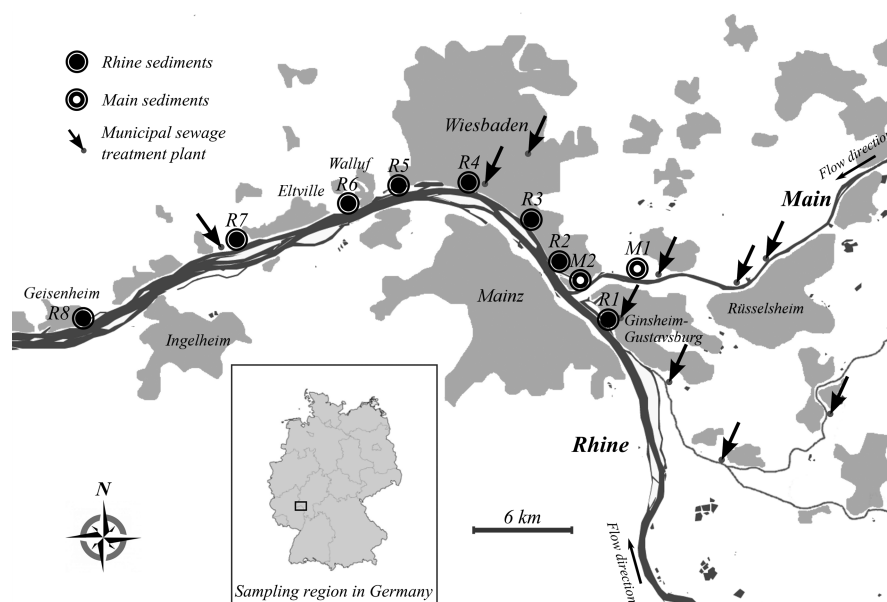
plastic production and emission from washing of synthetic textiles are known sources, among others. Thus, microplastics are most likely entering the aquatic environment by runoff from processing facilities or municipal sewage treatment plants.<sup>14–16</sup> Because different sources exist, microplastics occur in diverse shapes such as spheres, fibers, and fragments in environmental samples.<sup>17</sup> The small size of microplastics facilitates uptake of plastic particles by organisms as opposed to larger plastics.<sup>18</sup> Ingested plastic particles possibly act as stressors and cause damage to organ systems.<sup>19</sup> Furthermore, microplastics are potential carriers of organic contaminants. These contaminants can adsorb to the plastic particles from surrounding water or are already present in polymers in terms of additives or monomers used in plastic production.<sup>20</sup> Buoyant plastic particles can transport these adsorbed organic contaminants into surface-feeding organisms and less polluted aquatic systems where desorption processes can lead to increased concentrations of aqueous pollutants.<sup>21,22</sup> The emerging occurrence of plastics in marine environments has been intensively discussed in several studies. However, data

Received: July 30, 2014

Revised: April 17, 2015

Accepted: April 22, 2015

Published: April 22, 2015



**Figure 1.** Sampling region in the Rhine-Main area. Sample locations along the river Rhine and the river Main are marked with circles: (R1) Ginsheim-Gustavsburg, (M1) MZ-Kostheim 1, (M2) MZ-Kostheim 2, (R2) MZ-Kastel 1, (R3) MZ-Kastel 2, (R4) WI-Biebrich, (R5) WI-Schierstein, (R6) Walluf, (R7) Erbach, and (R8) Geisenheim. Gray shading indicates settled areas; the arrows show municipal sewage treatment plant locations.

concerning freshwater systems are still very rare, even though a great impact of rivers on the microplastic pollution of marine habitats is very likely. As rivers can act as vectors for the transport of litter into oceans, a riverine transport of microplastics seems highly probable.<sup>23</sup> Furthermore, other studies revealed large amounts of microplastics in inland water systems. A study of the Great Lakes showed large amounts of microplastics on the water surface with an elevated abundance of particles in the proximity of cities, an effect that was observed for estuarine tributaries in the Chesapeake Bay, as well.<sup>24,25</sup> An investigation of a subalpine lake revealed high concentrations of microplastics in shore sediments with a large abundance of buoyant particles such as PE and PP.<sup>26</sup> In addition, microplastics in the Danube River indicate the exceptional urgency of systematic studies of the microplastic burden of freshwater systems.<sup>27</sup>

To overcome the lack of data, we conducted this study to gather information about the occurrence of microplastics, the abundance of different particle shapes, and polymer types present in river shore sediments. Monitoring shore sediments appears to be advantageous, as sampling of sediments is facilitated compared to that of the water column. Moreover, nonbuoyant particles can be analyzed in sediment samples rather than in water surface samples. We tested the following hypotheses. Microplastic concentrations are increased in the proximity of industrial areas, cities, and sewage treatment plants. Buoyant microplastics predominate over nonbuoyant microplastics, and polymers with a large production volume are present primarily in river shore sediments.

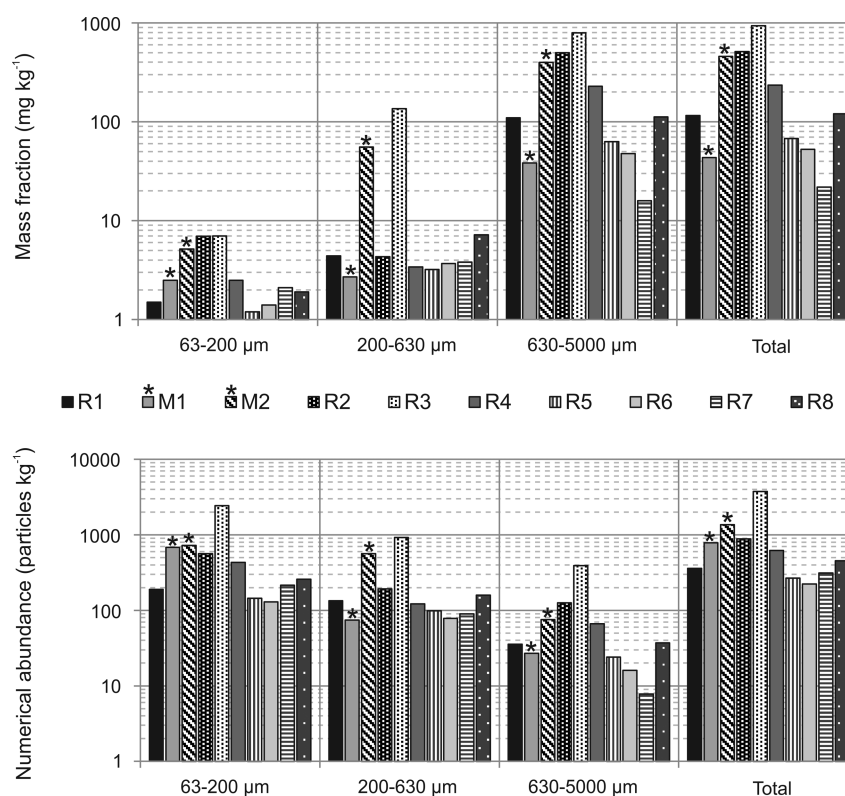
This investigation focused on the spatial distribution of microplastics in freshwater sediments collected along the shores of the river Rhine and the Main mouth located in Germany. The sampling sites were chosen to assess the discharges in settled areas of varying population density, in the proximity of nature reserves, and by direct sources (e.g., sewage treatment plants and waste disposal) and diffuse sources (transport by river). The influence of the transport of plastic debris from

tributaries to main streams was monitored by sampling at the confluence of the rivers Rhine and Main. Further, the analysis of shape and plastic type done in this study should show whether the microplastic portion of freshwater sediments is comparable to that of marine sediments and if the extent of pollution of river systems has reached that of marine ecosystems.

## MATERIALS AND METHODS

**Sampling Sites.** The rivers monitored in this study included the rivers Rhine and Main in Germany. Both rivers flow through areas of high and low population density, as well as industrial areas and nature reserves. Sampling of the sediments was conducted at eight different locations along the river Rhine and at two locations along the river Main (Figure 1). The sample locations in Ginsheim-Gustavsburg (R1), Mainz-Kastel (R2 and R3), and Wiesbaden-Biebrich (R4) reflect the highly populated areas of the cities of Wiesbaden and Mainz. Sampling sites in the proximity of nature reserves are located in Wiesbaden-Schierstein (R5) and Erbach (R7). Walluf (R6) and Geisenheim (R8) represent rural populated areas along the river Rhine. The Main tributary was examined to evaluate the effect of river to river transport of plastic debris. Both sample locations in Mainz-Kostheim (M1 and M2) are located at the river Main near the confluence of both rivers.

**Sediment Sampling and Sample Treatment.** The samples were collected from the shoreline of the rivers Rhine and Main. At each sampling site, the sediment was collected at 35–40 randomly chosen spots that were distributed over a distance of 10–15 m, parallel to the shoreline. Each spot was located between the water line and the lowest flotsam line. The distance between the water and the flotsam line was in the range of 5–25 cm, depending on the sampling site. The sediment at each spot were taken with a stainless steel spoon in an area of approximately 30 cm<sup>2</sup> to a depth of 2–3 cm, resulting in one bulk sample of 3–4 kg of wet sediment. Stones and objects >10 mm in size were removed before each sample



**Figure 2.** Mass fraction and numerical abundance of plastic particles in river sediments analyzed. Marked samples (asterisks) were taken from the river Main. Bars represent the total plastic as well as the contributing amount of each size fraction in milligrams per kilogram and number of particles per kilogram. Data are shown on a logarithmic scale.

was taken. At sampling sites R4 and R8, three independent replicates were taken to estimate the within-site variability. For each replicate, the described sampling technique was used and spots that were already sampled were not sampled again to avoid false negative results (see Figure S1 of the Supporting Information).

The wet sediment was dried at 50 °C for 3 days, subsequently weighed, and sieved using sieves with mesh sizes of 63, 200, and 630  $\mu\text{m}$ . The fraction containing  $>630 \mu\text{m}$  particles was examined again with the naked eye. Larger particles were measured, and  $>5 \text{ mm}$  particles were removed with tweezers. Finally, microplastics were investigated in the following fractions: 630–5000, 200–630, and 63–200  $\mu\text{m}$ . The  $<63 \mu\text{m}$  particles were discarded. The synthetic polymers were separated from each fraction by a modified density separation described by Thompson et al.<sup>4</sup> To improve the separation of smaller plastic particles, density separation was conducted in filter flasks (Figure S4 of the Supporting Information). Depending on the total weight, the sediment fractions were mixed with up to 300 mL of a saturated sodium chloride solution (365 g  $\text{L}^{-1}$ ) in filter flasks and stirred for 15 min. The sediment particles were subsequently allowed to settle overnight. Floating particles were transferred through the glass hose of the filter flasks to glass fiber filters (Whatman GF/A 47 mm, GE Healthcare Europe GmbH) by applying a vacuum with a water-jet pump. To maintain the level of the solution, the saturated sodium chloride solution was continuously added to the separation flask. All tubing was subsequently rinsed intensively several times with ultrapure water to transfer adherent plastic particles to the glass fiber filter. The modified density separation was validated and compared to the original method (Figure S3 of the Supporting

Information). For further information about the density separation method, see the Supporting Information.

To destroy natural debris, all size fractions were treated with a mixture (1:3, v:v) of a hydrogen peroxide solution (30%) and concentrated sulfuric acid. The reaction was conducted overnight. The mixture was poured into 300 mL of distilled water, vacuum-filtrated through glass fiber filters, rinsed again several times with ultrapure water, and dried in a desiccator for 3 days. Glass fiber filters were weighed prior to vacuum filtration for the accurate determination of the total plastic weight. During all steps of sample treatment, openings were covered with aluminum foil to prevent contamination with other particles or fibers.

**Analysis.** The  $>630 \mu\text{m}$  particles were counted with the naked eye, and 63–200  $\mu\text{m}$  plastic particles and 200–630  $\mu\text{m}$  plastic particles were visually identified and counted using a binocular microscope with a magnification range of 40–100 $\times$  (BA310E with Moticam X, Motic). All particles were classified by their shape into categories “pellet”, “sphere”, “fragment”, and “fiber”. Defined particles of all size fractions were measured to check proper size fractionation. The measurement was taken with Motic images plus (version 2.0). The calibration was performed with 0.1 and 0.6 mm dots of a calibration slide for microscopes (Motic). Pictures for size analysis were taken with Moticam X.

All size fractions were examined carefully for remaining natural debris during the microscopic analysis. Obvious residual natural objects were removed with microforceps or a dental explorer. Suspected natural debris was separated with the tip of a dental explorer and tested for hardness.

The total plastic weight of each size fraction was determined by difference weighing of the preweighed filters and the dried



filter residues before the microscopic analysis. If residual natural debris was identified, the weighing of the filter was repeated.

Fourier transform infrared spectroscopy (FTIR) measurements of the polymers were performed by using a PerkinElmer Spectrum BX FTIR instrument (PerkinElmer). The FTIR instrument was equipped with a high attenuated transverse reflection (ATR) unit using a ZrSe crystal. The 630–5000  $\mu\text{m}$  particles were placed on the ATR crystal with tweezers or a dental explorer. The polymers were identified by means of an automatic comparison of the resulting spectra with a spectral database (Spectrum Search Plus, version 3.00.05, Synthetic polymers ATR-library). For accurate identification of the polymer, the match factor threshold was calculated as 0.70 (Figure S5 of the Supporting Information). The weight and numerical abundance of the plastic particles were determined again after polymer identification for each polymer type.

**Data.** As a consequence of the sampling method applied, all results refer to the weight of the sediments collected. All results regarding plastic concentrations are given as the dry weight of the polymer particles termed the mass of dry sediment (milligrams per kilogram) and as the number of plastic particles per dry mass of sediment (particles per kilogram). Particle numbers related to sediment weights were transformed to area-related values (particles per square meter) via the sampled volume (see the Supporting Information).

## ■ RESULTS AND DISCUSSION

**Mass Fraction and Particle Numbers of Microplastics in the River Shore Sediments.** Plastic particles were present in different shapes, sizes, and colors in all sediments that were analyzed in this study. The mass fraction of microplastics varied between 21.8 and 932  $\text{mg kg}^{-1}$ , and the number of particles identified as plastic accounted for 228–3763  $\text{particles kg}^{-1}$  along the river Rhine (Figure 2). The sediments from the river Main contained a plastic fraction between 43.5 and 459  $\text{mg kg}^{-1}$  or 786 and 1368  $\text{particles kg}^{-1}$ , respectively. The most abundant weight fractions over all samples in our study are microplastics with a size range of 630–5000  $\mu\text{m}$ . As expected, the smaller size fractions (63–200 and 200–600  $\mu\text{m}$ ) contribute least to the total plastic weight of the sediments investigated. In contrast, the most plastic particles in each sediment were determined in the smallest size fraction (63–200  $\mu\text{m}$ ) analyzed. The contribution of the largest size fraction to the total particle number is negligible (Figure 2).

The assessment of the within-site variability by replicate sampling at sites R4 and R8 revealed a good coverage of each sampling site by the sampling method described. The results showed only low relative standard deviations between the replicate samples (total particle weight of 14–18%, numerical abundance of 7–17%) at both sampling sites (Table S3 of the Supporting Information). This ensures a good comparability of the results obtained in this study to former studies on microplastic contamination in sediments. The modification of the density separation might result in larger values for the plastic particle numbers, because the modification especially seems to affect the recovery of smaller plastic particles [ $<630 \mu\text{m}$  (Figure S3 of the Supporting Information)].

Our results from the separation of microplastics from river shore sediments show that the extent of pollution of rivers with plastics is in the same concentration range that has recently been reported for sediments from marine habitats. Comparable amounts of plastic particles were identified in the Venetian lagoon, where 672–2175  $\text{particles kg}^{-1}$  were separated from

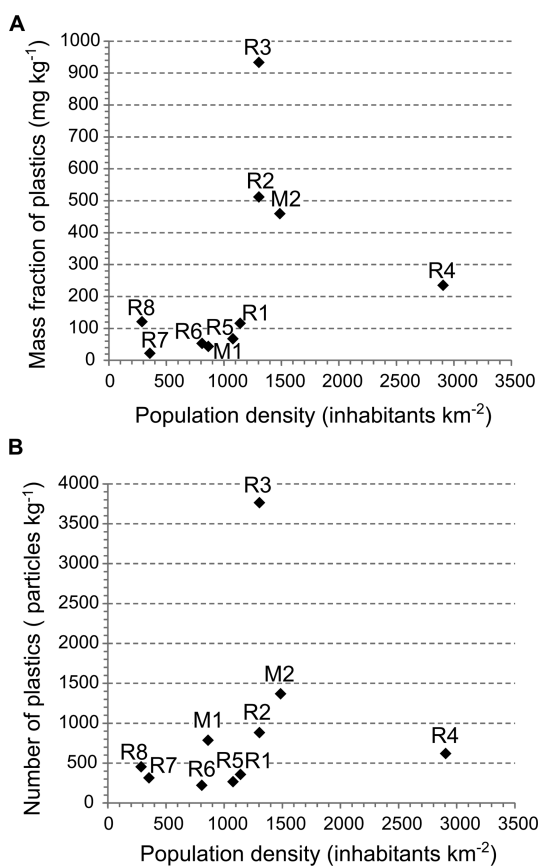
sediments.<sup>17</sup> Fewer microplastics were reported by Claessens et al. for the Belgian continental shelf and Belgian harbors.<sup>7</sup> All results of this study are significantly higher and exceed the number and mass of microplastics found in the Belgian study by up to 1 (68–390  $\text{particles kg}^{-1}$ ) or 2 orders of magnitude (0.9–7.2  $\text{mg kg}^{-1}$ ).<sup>7</sup> Possible explanations besides an increasing level of plastic pollution in the past several years are differences in the methodological approaches, as Claessens et al. included only  $<1 \text{ mm}$  particles in their study. However, this different definition used for microplastics does not explain the distinct differences in plastic particle numbers as larger particles do generally not contribute much to the total number of particles. Additionally, the estimation of the area-related results of this study (1800–30000  $\text{particles m}^{-2}$ ) is consistent with what has been reported for marine sediments (0.21–77000  $\text{particles m}^{-2}$ ) and shore sediments of Lake Garda (483–1108  $\text{particles kg}^{-1}$ ).<sup>26,28</sup>

Furthermore, the size distribution of microplastics in river shore sediments is in concordance with the results for the abundance of different particle sizes of plastic debris in marine sediments. A study of sediments collected along the Portuguese coast showed that the size fraction of  $>5000 \mu\text{m}$  particles accounted for  $>90\%$  of the total plastic weight, but only 30% of the items were counted as macroplastics.<sup>8</sup> Additionally, Brown et al. described an increasing numerical abundance of microplastics with a decreasing particle size for estuarine shorelines.<sup>6</sup> This leads to the assumption that the tendencies of microplastic size distribution in shore sediments of freshwater systems and marine systems are very likely comparable. In contrast to findings for microplastics in sediment samples, the results of Eriksen et al. showed fewer particles in a smaller size fraction (0.3–1 mm) compared to larger microplastics (1–5 mm). This was related to possible removal processes of smaller plastic particles, i.e., sinking or beaching of the particles, and could possibly result in higher sediment concentrations of  $<630 \mu\text{m}$  particles.<sup>9</sup> Furthermore, the limiting mesh size could result in lower concentrations of smaller particles.<sup>28</sup>

The results of this study show that German rivers are already heavily polluted systems, as described by Lechner et al. with respect to the river Danube.<sup>27</sup> A detailed analysis of the spatial variation of microplastics is necessary to identify possible sources for the high level of pollution of the location investigated.

**Spatial Variations of Microplastic Concentrations in Rivers Rhine and Main.** The microplastic concentrations found in this study showed substantial differences along the river Rhine (Figure 2). The abundance of microplastics in the Rhine sediments in the vicinity of the confluence with the tributary Main (R2 and R3) increased strongly. The microplastic concentration of both rivers is on the same order of magnitude in the vicinity of the confluence with the river Main (samples M2 and R2). In contrast, the microplastic concentration before the confluence of the rivers Rhine and Main (R1) was considerably lower. The largest amount of plastic particles was separated from sediment collected at site R3. Very low mass fractions of microplastics were found in sediment samples close to nature reserves at R5 and R7 (67.4 and 21.8  $\text{mg kg}^{-1}$ , respectively). Despite the low mass fractions of these sediments, the numbers of microplastics found (268  $\text{particles kg}^{-1}$  at R5, 314  $\text{particles kg}^{-1}$  at R7) were in the range of Rhine sediment samples, which were collected in less populated areas (R1, R6, and R8) and confirm a diffuse ubiquitous distribution of small microplastic particles.

There are several possible reasons, which could explain the large to very large abundance of microplastics at sampling sites M2 and R2–R4. At a first glance, it is noticeable that all four sites are located in densely populated areas (1305–2907 inhabitants  $\text{km}^{-2}$ ). However, there is no significant correlation of the population density and the masses and numbers of microplastics separated at each sample location [microplastic weight  $n = 10$ ,  $R^2 = 0.09$ ,  $P \gg 0.05$ ; microplastic number  $n = 10$ ,  $R^2 = 0.03$ ,  $P \gg 0.05$  (Figure 3)]. The correlation coefficient



**Figure 3.** Correlation of the population density and (A) weight and (B) the number of plastic particles. Sampling sites are indicated.

increases if the sampling site with the highest population density (R4) is excluded from the correlation, though the less populated regions do not show any clear relation of the microplastic concentration of sediments to population density. This indicates that there is no direct or diffuse source of the microplastic concentration of the investigated river shore sediments that could be represented by the population density. This result is in concordance with the result of an earlier study of shore sediments,<sup>16</sup> though it is contrary to what has been recently reported for surface waters of the Laurentian Great Lakes or estuaries in the Chesapeake Bay.<sup>24,25</sup> These contradictory observations might be explained by the comparatively high resolution of sampling sites in a relatively small sampling area with highly diverse population densities considered in our study.

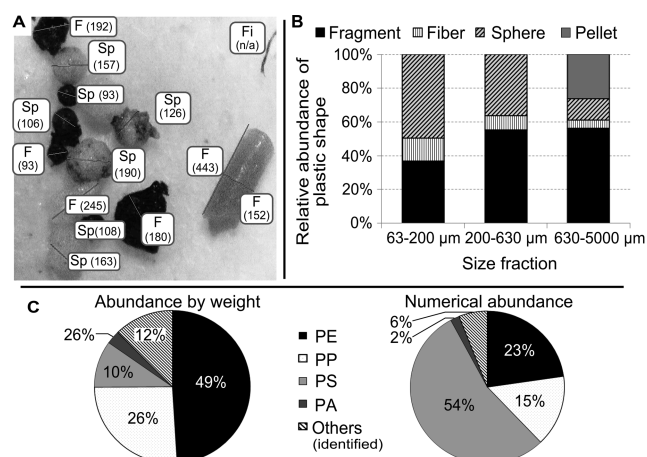
It is important to notice that the population density does not represent locations of other point sources like industrial activity or municipal sewage treatment plants. Sewage treatment plants, for example, are known sources of small plastic particles and fibers, which could explain the large abundance of particles in

the size range from 63 to 200  $\mu\text{m}$  in the sediment samples.<sup>16</sup> However, there are no municipal sewage treatment plants in the proximity of the most polluted sampling sites (R2 and R3). Moreover, sampling sites that are located near sewage treatment plants (R1, R4, and M1) do not show a distinctly larger abundance of 63–630  $\mu\text{m}$  particles. Additionally, the very high concentration of microplastics at sites R2 and R3 cannot be explained by a direct emission from industrial areas. A plastic processing industrial area is located between sampling sites R3 and R4, but neither a direct (site R4) nor an indirect (sites R5–R8) increase in microplastic concentration was shown downstream of this industrial area. For these reasons, our hypothesis is not confirmed, and neither the population density nor industrial activities or sewage treatment plant locations seem to be good indicators of microplastic pollution of the river shore sediments in the monitored area.

A possible reason for the missing correlations between the microplastic concentration on one side and expected indicators on the other might be that these factors are superimposed by hydrodynamic effects. These influences affect the mobilization or immobilization of sediments and riverine plastic transport, such as channel currents, channel geometry, stagnant water zones, and flood events. A comparison of sampling sites M2 and R1–R3 shows that microplastics of the river Main are likely introduced into the river Rhine (comparable microplastic concentrations at M2 and R2, but lower concentrations at R1), whereas the high concentration at R3 might indicate a local sink.<sup>29</sup> The fact that rivers are dynamic systems with fast changing water levels needs to be addressed. For this reason, all sinks are very likely temporal sinks that can be depleted during flood events and increase the amount of plastic litter in the river.<sup>23</sup> Nevertheless, further studies of plastic sink formations along rivers need to be conducted.

**Shape of Microplastic Particles.** The averaged numerical abundance of fragments, fibers, and spheres was different in each size fraction (Figure 4A,B). The percentage of spheres and fibers is highest in the smallest size fraction (50 and 13%, respectively) and lowest in the largest size fraction (13 and 5%, respectively), whereas fragments showed an opposite trend (51% for 630–5000  $\mu\text{m}$ , 37% for 63–200  $\mu\text{m}$ ). Because of their large size, preproduction pellets were detected in only the 630–5000  $\mu\text{m}$  size fraction. The larger proportion of spheres in the 63–200 and 200–630  $\mu\text{m}$  size fractions could be related to manufactured plastic microparticles that are produced in this size range and used in cleansers and cosmetics. This underlines the importance of these manufactured particles in river sediments, because they possibly represent a large portion of the spheres in the 63–200  $\mu\text{m}$  size fraction. The possibility that fragments, which were polished to a round form by physical forces, contribute to the number of spheres cannot be excluded. The small abundance of fibers, especially in the smallest size fraction, is very surprising, because many sewage treatment plants are located in the area investigated. A larger abundance of fibers was expected, because it is known that synthetic fibers can be emitted through washing processes and are not completely removed by sewage treatment.<sup>16</sup> The distribution of particle shapes of microplastics in the lagoon of Venice did not show any abundance of spheres or round particles, but the same percentage of fibers (11%) in relation to the total amount of particles was found.<sup>17</sup>

**Polymer Composition of the Separated Microplastics.** FTIR analysis of the 630–5000  $\mu\text{m}$  size fraction showed that >50% of the total plastic weight was contributed by



**Figure 4.** (A) Microscopic image of the 63–200  $\mu\text{m}$  size fraction. Particles were measured, and the size is displayed in micrometers in parentheses. The particles are classified as fragments (F), spheres (Sp), and fibers (Fi). (B) Composition of separated microplastics by shape. Results are displayed as the average abundance of each size fraction of randomly picked sediment samples. Numbers of particles ( $n$ ) classified for each size fraction were 382 (63–200  $\mu\text{m}$ ), 434 (200–630  $\mu\text{m}$ ), and 210 (630–5000  $\mu\text{m}$ ). (C) Average relative abundance of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide (PA), and other polymer types identified in sediments of all sampling sites. Data are plotted as the abundance of weight and as the abundance of particle numbers.

polyethylene (PE) and polypropylene (PP). The largest abundance in terms of particle number was represented by polystyrene (PS) particles. Almost all spherules found were polystyrene (PS), mainly in the form of expanded PS. Polymers PE, PP, and PS made up >75% of all microplastics identified in the sediments (Figure 4C). The remaining proportion of plastics consisted of various types of polymers. In addition to the plastics mentioned above, polyethylene terephthalate (PET), polyvinyl chloride (PVC), ethylene vinyl acetate, ethylene propylene diene rubber (EPDM), polyamide, and acrylic-based polymers were identified. This result is not very surprising for two reasons. On one hand, the high level of industrial relevance of PE, PP, and PS, as they cover 55.7% of the European plastic demand, is a reason for their large abundance.<sup>1</sup> On the other hand, the low specific densities of PE and PP and the floating ability of expanded PS allow the widespread distribution in aqueous systems. They can easily be transported by rainwater or rivers and accumulate in shore sediments. Consequently, these three polymers are also the most frequently identified polymers in studies of marine sediments.<sup>28</sup> The small abundance of the other polymers is possibly caused by their less frequent usage but could also be explained by different transport mechanisms in water systems. The transport of these mostly nonbuoyant particles needs to be compared to the transport of sediment. PVC and PET are also high-production volume polymers, but their high density (Table S2 of the Supporting Information) complicates the separation with sodium chloride. Thus, an underestimation of both PVC and PET loads in the river shore sediments is possible.

The compositions of the microplastics identified at the single sampling sites reveal several interesting patterns (Figure S7 of the Supporting Information). Particles of PE and PS were present in the sediments from all sites. PP was detected at all sites except the sediment sample from site R7. This could be

related to the general low level of plastic pollution at this sample location. Furthermore, the relative abundance of PE particles by weight is almost constant at sites R2–R8 (mean of 49.5%, standard deviation of 6.39%). In contrast, the composition of the polymer types by particle numbers changes strongly from sampling site R2 to R8. The relative numerical abundance of PE and PP particles of each site is proportional to the total level of plastic pollution in terms of weight and numbers of these sites. The differences in the patterns of abundance by weight and abundance by particle number can be explained by the different forms of appearance of PE, PP, and PS. PE and PP were present in the form of pellets, foils, and fragments, whereas PS was mainly observed in the form of expanded PS. Because of the low density of expanded PS, the contribution to the total weight is almost negligible. Thus, a change in the relative abundance of PS is illustrated more clearly by the composition of the particle number.

As already shown for the microplastic concentration, the river Main also likely has an observable influence on the polymer composition observed in the river Rhine. A difference is obviously visible behind the confluence of the river Main, where the variety of different polymer types greatly increases. Additionally, the tendency of particles of PE and PP to increase in number was clearly visible in the composition of the plastic.

An additional indicator of the influence of the river Main on plastic pollution of the river Rhine is the presence of equally colored EPDM pellets (blue) and PP pellets [silver (Figure S8 of the Supporting Information)]. These pellets were detected in the Main mouth (M2) as well as downstream of the confluence of the rivers Rhine and Main (R2 and R3). None of these pellets could be detected in the sediment from site R1, which was sampled at the river Rhine before the confluence of both rivers. IR spectra of both pellet species were identical. Generally, colored pellets are clearly found less frequently than noncolored or white pellets. The absence of silver pellets in other sediments and the rubberlike consistency of the blue EPDM pellets are further indicators of an identical origin for both pellet types along the river Main. The occurrence of these specific pellets shows the traceable influence of the Main plastic burden on the river Rhine. Consequently, it can be expected that transport of microplastics from tributaries to mainstreams is an important transport route for plastic microparticles, as sewage treatment plants and industrial areas are not always located on larger streams.

This study provides new insights into microplastic distribution in river sediments and transport in rivers. It shows that freshwater systems like rivers are severely influenced by microplastics. The results revealed high concentrations of microplastics that are in a range similar to that of polluted marine sediments. The spatial variation in the concentration of microplastics and polymer compositions over all sampling sites shows no relationship with the population density or proximity to industrial area and sewage treatment plants. Moreover, the transport of plastic particles from river to river underlines the importance of rivers as potential transport vectors. This study shows that the composition of microplastics does not differ significantly between freshwater sediments and marine sediments, in terms of size distributions or in terms of the abundance of polymer types. These findings emphasize the urgency to further monitor freshwater systems and identify point sources to mitigate the microplastic contamination of the aquatic environment in the near future.



## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Detailed coordinates of the sampling sites, a list of chemicals, design of the sediment sampling method, density of different polymers, details of density separation, including the scheme of the apparatus used for the density separation and recovery experiments, exemplary spectra of the FTIR analysis, tables of the triplicate analysis of sites R4 and R8, tables of the mass fraction and number of microplastics for all sampling sites, additional information about the relationship between numerical abundance and weight abundance, detailed diagram of polymer type composition, and microscopic images and IR spectra of river-transported pellets. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00492.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: knepper@hs-fresenius.de. Phone: +49 (0) 6126 9352 64. Fax: +49 (0) 6126 9352 173.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

S.K. gratefully acknowledges the funding of the Water Chemistry Society Germany.

## ■ REFERENCES

- (1) *Plastics: The Facts 2013: An analysis of European latest plastics production, demand and waste data*; PlasticsEurope: Brussels, 2013; pp 1–36.
- (2) Eubeler, J. P.; Bernhard, M.; Knepper, T. P. Environmental biodegradation of synthetic polymers II. Biodegradation of different polymer groups. *TrAC, Trends Anal. Chem.* **2010**, 29 (1), 84–100.
- (3) Barnes, D. K. A.; Galgani, F.; Thompson, R. C.; Barlaz, M. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc., B* **2009**, 364 (1526), 1985–1998.
- (4) Thompson, R. C.; Olsen, Y.; Mitchell, R. P.; Davis, A.; Rowland, S. J.; John, A. W. G.; McGonigle, D.; Russell, A. E. Lost at sea: Where is all the plastic? *Science* **2004**, 304 (5672), 838.
- (5) Andrady, A. L. Microplastics in the marine environment. *Mar. Pollut. Bull.* **2011**, 62 (8), 1596–1605.
- (6) Browne, M. A.; Galloway, T. S.; Thompson, R. C. Spatial patterns of plastic debris along Estuarine shorelines. *Environ. Sci. Technol.* **2010**, 44 (9), 3404–3409.
- (7) Claessens, M.; Meester, S. D.; Landuyt, L. V.; Clerck, K. D.; Janssen, C. R. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* **2011**, 62 (10), 2199–2204.
- (8) Martins, J.; Sobral, P. Plastic marine debris on the Portuguese coastline: A matter of size? *Mar. Pollut. Bull.* **2011**, 62 (12), 2649–2653.
- (9) Eriksen, M.; Lebreton, L. C. M.; Carson, H. S.; Thiel, M.; Moore, C. J.; Borerro, J. C.; Galgani, F.; Ryan, P. G.; Reisser, J. Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. *PLoS One* **2014**, 9 (12), e111913.
- (10) Gregory, M. R. Environmental implications of plastic debris in marine settings-entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc., B* **2009**, 364 (1526), 2013–2025.
- (11) Rochman, C. M.; Browne, M. A.; Halpern, B. S.; Hentschel, B. T.; Hoh, E.; Karapanagioti, H. K.; Rios-Mendoza, L. M.; Takada, H.; Teh, S.; Thompson, R. C. Policy: Classify plastic waste as hazardous. *Nature* **2013**, 494 (7436), 169–171.
- (12) Ivar do Sul, J. A.; Costa, M. F. The present and future of microplastic pollution in the marine environment. *Environ. Pollut.* **2014**, 185, 352–364.
- (13) Fendall, L. S.; Sewell, M. A. Contributing to marine pollution by washing your face: Microplastics in facial cleansers. *Mar. Pollut. Bull.* **2009**, 58 (8), 1225–1228.
- (14) Cole, M.; Lindeque, P.; Halsband, C.; Galloway, T. S. Microplastics as contaminants in the marine environment: A review. *Mar. Pollut. Bull.* **2011**, 62 (12), 2588–2597.
- (15) Doyle, M. J.; Watson, W.; Bowlin, N. M.; Sheavly, S. B. Plastic particles in coastal pelagic ecosystems of the Northeast Pacific ocean. *Mar. Environ. Res.* **2011**, 71 (1), 41–52.
- (16) Browne, M. A.; Crump, P.; Niven, S. J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. Accumulation of Microplastic on Shorelines Worldwide: Sources and Sinks. *Environ. Sci. Technol.* **2011**, 45 (21), 9175–9179.
- (17) Vianello, A.; Boldrin, A.; Guerriero, P.; Moschino, V.; Rella, R.; Sturaro, A.; Da Ros, L. Microplastic particles in sediments of Lagoon of Venice, Italy: First observations on occurrence, spatial patterns and identification. *Estuarine, Coastal Shelf Sci.* **2013**, 130, 54–61.
- (18) Lusher, A. L.; McHugh, M.; Thompson, R. C. Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. *Mar. Pollut. Bull.* **2013**, 67 (1–2), 94–99.
- (19) Rochman, C. M.; Hoh, E.; Kurobe, T.; Teh, S. J. Ingested plastic transfers hazardous chemicals to fish and induces hepatic stress. *Sci. Rep.* **2013**, 3.
- (20) Rochman, C. M.; Hoh, E.; Hentschel, B. T.; Kaye, S. Long-Term Field Measurement of Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris. *Environ. Sci. Technol.* **2013**, 47 (3), 1646–1654.
- (21) Besseling, E.; Wegner, A.; Foekema, E. M.; van den Heuvel-Greve, M. J.; Koelmans, A. A. Effects of Microplastic on Fitness and PCB Bioaccumulation by the Lugworm *Arenicola marina* (L.). *Environ. Sci. Technol.* **2013**, 47 (1), 593–600.
- (22) Endo, S.; Yuyama, M.; Takada, H. Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. *Mar. Pollut. Bull.* **2013**, 74 (1), 125–131.
- (23) Rech, S.; Macaya-Caquilpán, V.; Pantoja, J. F.; Rivadeneira, M. M.; Jofre Madariaga, D.; Thiel, M. Rivers as a source of marine litter: A study from the SE Pacific. *Mar. Pollut. Bull.* **2014**, 82 (1–2), 66–75.
- (24) Eriksen, M.; Mason, S.; Wilson, S.; Box, C.; Zellers, A.; Edwards, W.; Farley, H.; Amato, S. Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Mar. Pollut. Bull.* **2013**, 77 (1–2), 177–182.
- (25) Yonkos, L. T.; Friedel, E. A.; Perez-Reyes, A. C.; Ghosal, S.; Arthur, C. D. Microplastics in Four Estuarine Rivers in the Chesapeake Bay, U.S.A. *Environ. Sci. Technol.* **2014**, 48, 14195–14202.
- (26) Imhof, H. K.; Ivleva, N. P.; Schmid, J.; Niessner, R.; Laforsch, C. Contamination of beach sediments of a subalpine lake with microplastic particles. *Curr. Biol.* **2013**, 23 (19), R867–R868.
- (27) Lechner, A.; Keckeis, H.; Lumesberger-Loisl, F.; Zens, B.; Krusch, R.; Tritthart, M.; Glas, M.; Schludermann, E. The Danube so colourful: A potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. *Environ. Pollut.* **2014**, 188, 177–181.
- (28) Hidalgo-Ruz, V.; Gutow, L.; Thompson, R. C.; Thiel, M. Microplastics in the marine environment: A review of the methods used for identification and quantification. *Environ. Sci. Technol.* **2012**, 46 (6), 3060–3075.
- (29) Best, J. L. Sediment transport and bed morphology at river channel confluences. *Sedimentology* **1988**, 35 (3), 481–498.