Spatial distribution of microplastics in sediments and surface waters of the southern North Sea

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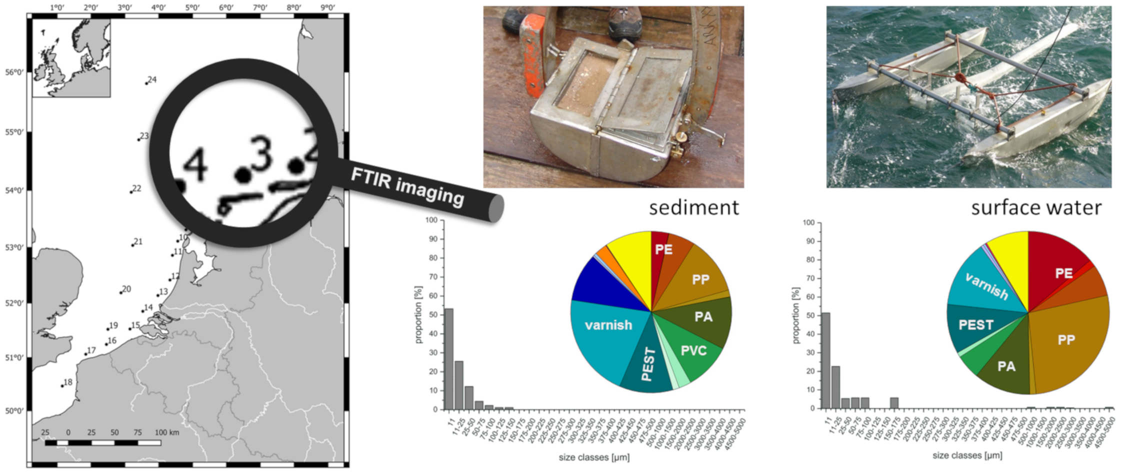
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sediment
surface water
proportion [%]
size classes [µm]
PE
PP
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PEST
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TITLE: Spatial distribution of microplastics in sediments and surface waters of the southern North Sea

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Abstract:

Microplastic pollution within the marine environment is of pressing concern globally. Accordingly, spatial monitoring of microplastic concentrations, composition and size distribution may help to identify sources and entry pathways, and hence allow initiating focused mitigation. Spatial distribution patterns of microplastics were investigated in two compartments of the southern North Sea by collecting sublittoral sediment and surface water samples from 24 stations. Large microplastics (500−5000 µm) were detected visually and identified using attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy. The remaining sample was digested enzymatically, concentrated onto filters and analyzed for small microplastics (11−500 µm) using Focal Plane Array (FPA) FTIR imaging. Microplastics were detected in all samples with concentrations ranging between 2.8–1188.8 particles kg^{-1} for sediments and 0.1–245.4 particles m^{-3} for surface waters. On average 98% of microplastics were <100 µm in sediments and 86% in surface waters. The most prevalent polymer types in both compartments were polypropylene, acrylates/polyurethane/varnish, and polyamide. However, polymer composition differed significantly between sediment and surface water samples as well as between the Frisian Islands and the English Channel sites. These results show that microplastics are not evenly distributed, in neither location nor size, which is illuminating regarding the development of monitoring protocols.

Keywords

FTIR imaging; microplastic; enzymatic sample treatment; polymer diversity; spatial distribution patterns

Capsule

Microplastic concentrations and compositions differ significantly between environmental compartments. Geographic distribution patterns are revealed by a statistical approach.

Microplastics <500 µm are more abundant and diverse than >500 µm ones, rendering the exclusive analysis of later ones insufficient for environmental risk assessment.

Introduction

Increasing plastics production and improper disposal have consequently led to an input of plastics into the marine environment which has been quantified to up to 12 million tons worldwide in 2010 (Jambeck et al., 2015). Once plastics reach the oceans, they are almost impossible to remove and merely disintegrate by chemical, physical and biological processes over time into smaller and more numerous microplastics (MP, <5 mm (Arthur et al., 2009)). Due to its ubiquity and longevity, plastic pollution in the marine environment has been recognized as a threat globally and is one of the "novel entities" referred to in the planetary boundaries concept (Rockström et al., 2009; Steffen et al., 2015; Villarrubia-Gómez et al., 2018). Moreover, marine pollution has been included in descriptor 10 (marine litter) in the European Marine Strategy Framework Directive (MSFD) 2008/56/EC (European Parliament Council, 2008; Galgani et al., 2010). More recently the issue of MP and the monitoring criteria of MP have been established by the EU Commission decision 2017/848 of 17 May 2017 (European Commission, 2017).

With decreasing particle size, the unambiguous identification of polymer type becomes more challenging. As of yet, no universally accepted standard operating procedure (SOP) exists, the harmonization of methods is urgently needed to allow for a comparison of data (Hidalgo-Ruz et al., 2012; Löder and Gerdts, 2015; Rochman et al., 2017).

According to Kroon et al. (2018) a merely visual identification of the potential MP particles is not sufficient. More than 60% of the particles might be misassigned (Hidalgo-Ruz et al., 2012; Kroon et al., 2018), if results are not validated by chemical identification. According to Rivers et al. (2019), a meaningful inter-study comparison requires not only data on particle number but also on particle size. As stated by Potthoff et al. (2017) it is very important to gain as much information as possible from MP particles, including number, polymer type, shape, size distribution and weathering status, to do a qualified risk assessment. This stresses the need to use spectroscopic methods, which can provide this information.

In this study, we aimed to gain a valuable insight into the spatial distribution of MP in the southern North Sea, in terms of the MP concentrations, polymer types and size classes. To achieve this, we sampled two marine compartments, sediments and surface waters, at 24 stations. We employed state-of-the-art techniques to extract MP and analyze samples based on attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy and focal plane array (FPA) based FTIR imaging. In the present study we also applied a novel approach based on uni- and multivariate statistics to investigate the questions: (1) Do MP metric parameters differ significantly between the two sampled compartments?; (2) Which polymer types and size classes contribute most to these differences?; (3) Do spatial patterns driven by polymer composition or size distribution exist within each compartment?

In this study we applied innovative analytical techniques to expand the field of environmental MP research and to generate assured and comparable data for the ongoing development of MP monitoring strategies.

Materials and Methods

Sampling

Sampling was conducted during a survey aboard the RV Heincke (He430) in the southern North Sea between the 30th of July and the 11th of August 2014. Sediment and water samples were taken at 24 stations (Figure 1, Supporting Information (SI) Table S1). Surface water was sampled using a Neuston Catamaran (HydroBios Apparatebau GmbH) towed alongside the vessel for up to 20 min. The attached net had an opening of 0.15 m × 0.30 m and a mesh size of 100 µm, capturing particles >100 µm but also smaller particles trapped in aggregates and due to clogging of the mesh during sampling. The sampled water volume and surface area were determined by a mechanical flowmeter (HydroBios Apparatebau GmbH) mounted at the opening of the net (SI Table S1). All materials collected in the cod end were rinsed into a 1-L Kautex-bottle (polyvinyl chloride with polyethylene containing lit, Kautex Textron GmbH & Co KG). Sediment samples were taken with a Van-Veen grab deployed at each station, with the upper 5 cm of the sediment transferred into 1-L Kautex-bottles with a metal spoon. All samples were immediately stored at -20 °C until further processing in the lab.

MP extraction from sediment and surface water samples

Multiple steps were taken to remove natural organic and inorganic matter to facilitate effective MP analysis. Measures for contamination prevention during sample processing are described in the SI Paragraph S1. Sediment samples of around 2 kg wet weight each were defrosted, transferred into glass jars, and then homogenized. Triplicates of approximately 5 cm³ each were taken to determine the dry weight of each sediment sample. Extraction of MP from the remaining sediments was performed using the MicroPlastics Sediment Separator (MPSS, HydroBios Apparatebau GmbH) with a high density zinc chloride solution ($ZnCl_2$, $\rho=1.7\ g\ cm^{-3}$) (Imhof et al., 2012). The general procedure of density separation followed the methodology of Bergmann et al. (2017) and Haave et al. (2019) and is shortly described in the SI Paragraph S2.

A size fractionation of each sample was conducted, as sample processing and analytical approaches varied for different MP size categories. The extracted sediment samples and the defrosted surface water samples were screened over a 500-µm stainless steel mesh (Haver & Boecker OHG). The material retained on the mesh was thoroughly rinsed with filtered water (Milli-Q, 0.2 µm), and Ethanol (30%) also to remove any residual $ZnCl_2$ in the case of the extracted sediment samples. This step divided the sample into two size fractions potentially containing particles of either >500 µm and <500 µm respectively.

All steps taken in the laboratory are displayed in a flow scheme (SI Figure S1), and are explained in the subsequent sections.

MP >500 µm

The >500 µm fraction was rinsed into a beaker and manually sorted in a Bogorov chamber under a stereo microscope (Olympus SZX16, Olympus) at a 100–320x magnification. All putative MP particles were transferred into glass petri dishes, photographed under the microscope (Olympus DP26 Digital Camera, Olympus) and measured (length at their longest dimension) using image analysis software (cellSens, Olympus).

MP <500 µm

The general approach to purify and extract MP from the <500 µm fraction followed the enzymatic-oxidative treatment published by Löder et al. (2017) which had proven effective for the degradation of a broad range of environmental matrices. This protocol was performed in newly developed Microplastic Reactors (Gerdts, 2017) (SI Figure S2). These semi-enclosed filtration units contain 20-µm stainless steel filters (Haver & Boecker OHG) and allow to add and remove solutions via vacuum and pressure filtration. Samples could be kept in the reactors and be exposed to the different chemical and enzyme treatment steps without requiring further sample transfers, by that reducing the risk of particle loss and sample contamination. The <500 µm sample fraction was transferred into the reactors before sodium dodecyl sulfate solution (SDS, 10%, Carl Roth) was added and the reactors were sealed and incubated at 50 ℃

for 24 hours. Following this, the technical enzyme purification steps with protease, cellulase and chitinase (ASA Spezialenzyme GmbH) as well as hydrogen peroxide (H_2O_2, 35%, Carl Roth) were performed sequentially. The samples were incubated at optimal pH and temperature conditions for each step. Between treatments the samples were flushed and rinsed several times using Milli-Q. A more detailed description of the full multi-step procedure can be found in the SI Paragraph S3.

About two-thirds of the surface water samples (n=16), containing large amounts of biomass, were additionally treated with a Proteinase-K step after the second H_2O_2 treatment. The procedure was adapted from the protocol of Cole et al. (2014), using H_2O_2 instead of sodium perchlorate ($NaClO_4$).

Inorganic material (e.g. sand, calcium carbonate) was removed by a density separation performed in separation funnels containing $ZnCl_2$ (ρ=1.7 g cm^{-3}). Over a period of usually one to three days (n=30), but in some cases extended to seven days (n=16), the denser materials settled to the bottom and were removed.

The upper phase of the density separation treatment, containing the lighter material, was passed through 20-µm stainless steel filters to remove the $ZnCl_2$. The retained material was transferred into 100-mL glass bottles by rinsing the filter with Milli-Q and stored for analysis. For FTIR measurement the processed sample needed to be transferred onto aluminum oxide filters (Anodisc, 0.2 µm, Whatman GmbH) (Löder et al., 2015). Each sample was concentrated onto a 13 mm diameter filter area, using in-house fabricated glass filter funnels and a vacuum filtration unit. Prior to this a FlowCam (Fluid Imaging Technologies) was used to determine a suitable subsample volume that could be applied onto the filter area without overloading it (SI Paragraph S4) (Bergmann et al., 2017). Based on the FlowCam assessments, aliquots ranging from 1.2–73.2% (surface water samples) and 10.8–75.4% (sediment samples) of the total sample volumes were taken by mixing the sample thoroughly and pipetting the determined volume on an aluminum oxide filter each (SI Table S2). The loaded filters were transferred into covered glass petri dishes and dried for 48 hours at 30 ℃.

Identification and quantification of MP >500 µm using ATR-FTIR

All putative plastic particles were identified individually using an ATR-FTIR unit (Bruker Optik GmbH) with the exception of 30 particles which were analyzed within an accompanying study by Cabernard et al. (2018) using Raman spectroscopy. The IR spectra were collected in the spectral range of 400–4000 cm^{-1} and compared against our reference library (Primpke et al., 2018). Particles with a match of at least 700 (out of 1000) were counted as safely identified. If the match ranged between 600 and 700 the spectra were manually compared to database spectra and evaluated based on expert knowledge, as suggested by other studies (Hanke et al., 2013; Kroon et al., 2018; Lusher et al., 2013).

Spectral analysis of MP <500 µm using FTIR imaging

Particles of the smaller size fraction were analyzed using a FTIR-microscope (Hyperion 3000 coupled to a Tensor 27 spectrometer, Bruker Optik GmbH) equipped with a 15x objective and a focal plane array (FPA) detector. Settings for the measurements were similar to previous studies (Bergmann et al., 2017; Löder et al., 2015; Mintenig et al., 2017; Mintenig et al., 2019; Peeken et al., 2018; Primpke et al., 2017; Primpke et al., 2018) defining the lower detection limit of 11 µm. Technically, during processing of the samples the lower size limit is defined by the mesh size of the filters. However, also smaller particles will have been captured allowing a semi-quantitative analysis of particles between 11 µm and 20 µm.

By measuring a grid of 77×77 (surface waters) or 78×78 (sediments) FPA fields, corresponding to a filter area of 184 mm² and 188 mm², respectively, every particle was analyzed.

The FTIR imaging data were automatically analyzed following Primpke et al. (2017) with the adaptable database design (Primpke et al., 2018). Based on the identified spectra a subsequent image analysis provided particle numbers, polymer types and size classes of all identified particles. The threshold for this image analysis was set based on a manual spectra evaluation of a data-subset (SI Paragraph S5 and Table S3).

Data handling and statistical analysis

The MP counts of each analyzed filter were extrapolated to the respective sample based on the analyzed proportion (SI Table S2) and corrected for contamination recorded in procedural blank samples (n=6). The total amount of MP in both size fractions was combined and presented as MP per kg dry weight sediment (particles kg^{-1} (DW)) or water volume sampled (particles m^{-3}). Percentages of polymer types and size classes were arcsine square root (univariate statistics) or square root transformed (multivariate statistics) (Sokal and Rohlf, 1995). The multivariate analyses were carried out based on Hellinger distance transformation, a recommended measure for ordination and clustering of (polymer) species abundance data, which does not put high weights on rare (polymer) species (Legendre and Gallagher, 2001; Rao, 1995). To assess the polymer diversity, species richness and Shannon-Wiener-index H' (log base e) was calculated. To test if samples from the two compartments (sediment, surface water) differed significantly in their polymer composition or size class distribution, permutational multivariate analysis (PERMANOVA) (Anderson and Walsh, 2013) with 999 permutations at a significance level of $p<0.001$ was applied. To visualize these differences cluster analysis and canonical analysis on the principal coordinates (CAP) (Anderson and Willis, 2003) were performed with PRIMER plus the add-on PERMANOVA+ (PRIMER-E version 7.013) (Clarke and Gorley, 2015).

Analyses of variances (ANOVA) was performed with Statistica 13 (Statsoft) to show which polymer types or size classes had the greatest influence on observed differences. To identify which stations of both compartments individually group in terms of polymer composition and size distribution a non-hierarchical clustering based on k-means and coupled to similarity profile test (SIMPROF, henceforth referred to as kR-clustering) was performed using PRIMER-7 on the basis of the Hellinger distance matrix with square root transformed data. The significance level for SIMPROF was set to 5% and performed with 999 permutations to define the optimal number of k-groups (between 2 and 10) to describe the clustering of the samples, which is based on maximizing R (Clarke and Gorley, 2015). An ANOVA followed by a Tukey HSD test was used to test the influence of each polymer type on the respective group.

Maps showing the geographical position of the samples along with the MP concentration, polymer composition and diversity as well as assigned groups were prepared using QGIS (version 3.2 ‘Bonn’). The displayed shoreline data was taken from the Global Self-consistent, Hierarchical, High-resolution Geography Database (GSHHS) https://www.ngdc.noaa.gov/mgg/shorelines/gshhs.html, hosted by the National Oceanic And Atmospheric Administration (NOAA) by Wessel and Smith (1996).

RESULTS

Comparison of two size fractions of MP in sediment and surface water samples

Microplastics from 23 sediment and 23 surface water samples, out of 24 sampled stations, could successfully be extracted and analyzed. For each sample two size fractions (MP >500 µm and MP <500 µm) were analyzed separately and their results later combined for statistical analyses. The two size fractions differed considerably concerning polymer composition and size distribution. Overall, for MP > 500 µm, only one polymer type (polyester) was identified in sediment samples and eight different polymer types were found in surface water samples. Concerning MP <500 µm, 21 different polymer types were found in the sediment samples and 19 different polymer types in surface water samples.

In sediment samples only 0.04% of all detected particles were >500 µm while 99.96% were MP <500 µm. For surface water samples 6.02% of all the detected particles were >500 µm while 93.98% accounted for MP <500 µm. A selection of MP >500 µm detected in five surface water samples can be found in the SI Figure S3. Two examples of filters with MP <500 µm and their respective false color plot of one station for sediments and surface waters each are shown in the SI Figure S4.

Comparison of MP occurrence in sediments and surface waters of the southern North Sea

Combining both size fractions, MP concentrations in sediments ranged from 2.8 (station 11) to 1188.8 particles kg^{-1} (DW) (station 23) and for surface waters from 0.1 (station 22) to 245.4 particles m^{-3} (station 20) (SI Table S4, Figure 1).

The two investigated compartments, sediments and surface waters, differed greatly regarding MP-concentration (Figure 1) and polymer composition (PERMANOVA, *p*-value=0.001, SI Table S5). This was also confirmed in the cluster analysis where samples from the same environmental compartment were grouped together (SI Figure S5). The separation of most of the samples into the two a priori defined groups, sediments and surface waters, was also supported by CAP, depicted in SI Figure S6, with a reasonably high correlation value of 0.89 and revealed six samples to be mismatched with a mis-classification error of 13.04%. Sediment samples from three stations (11, 18, and 21) were falsely allocated to surface waters and three surface water samples (stations 6, 22, and 23) were allocated to sediments. ANOVA was significant when comparing polymer richness and Shannon-Wiener index H' based on polymer types for both compartments (*p*-value=0.001) (SI Table S6). The spatial distribution of this polymer diversity is depicted in SI Figure S7. Figure 2 shows the relative polymer composition for sediments (Figure 2a) and surface waters (Figure 2b). The number of different polymer types in sediment samples was on average 11 and ranged between 3 (station 11) and 15 (station 1) with Shannon-Wiener index H' ranging between 0.89 (station 11) and 2.29 (station 5). For surface water samples on average 7 different polymer types were detected ranging from 1 (station 15) to 14 (stations 2, 6 and 17) with Shannon-Wiener index H' ranging from 0 (station 15) to 2.07 (station 17).

Polyethylene (PE), polypropylene (PP), and polyester/polyethylene terephthalate (PEST) were present in more than 75% of all samples from both compartments. In sediment samples acrylates/polyurethane/varnish (acrylates/PUR/varnish) were omnipresent. Additionally to the aforementioned polymers, PE chlorinated, polystyrene (PS), polyamide (PA), polyvinyl chloride (PVC), and rubber type 3 were frequent. Figure 3 shows that, in sediment samples, 13 different polymer types contributed on average between 1.3% (nitrile rubber) and 21.0% (acrylates/PUR/varnish) to the polymer composition while eight polymer types contributed less than 1% (in descending order): ethylene vinyl acetate (EVA), polycaprolactone, rubber type 1, PE oxidized, polyisoprene chlorinated, acrylonitrile butadiene, polycarbonate (PC), and polysulfone (PSU). In surface water samples nine different polymer types contributed on average between 1.3% (PS) and 26.7% (PP) to the polymer composition while ten polymer types contributed less than 1% (in descending order): chemically modified cellulose (CMC), polycaprolactone, EVA, rubber type 1, polyoxymethylene (POM), PE oxidized, PC, nitrile rubber,

rubber type 2, and polychloroprene (Figure 3). Furthermore, an ANOVA revealed the polymer types contributing most to the dissimilarity of surface water and sediment samples: PE (ANOVA, *p*-value=0.010), PP (ANOVA, *p*-value=0.042), PVC (ANOVA, *p*-value=0.007), nitrile rubber (ANOVA, *p*-value=0.001), polychloroprene (ANOVA, *p*-value=0.000), and POM (ANOVA, *p*-value=0.000) (SI Table S7).

When comparing the size distribution (11–5000 µm) of polymers in sediment and surface water samples, they differed significantly (PERMANOVA, *p*-value=0.001) (SI Table S8). Cluster analysis revealed a higher variance in surface water than in sediment samples (SI Figure S8). This was highlighted by CAP which had a moderately large correlation value of 0.61 and revealed only surface water samples (n=8) to be mis-classified with a relatively low mis-classification error of 17.39% (SI Figure S9). Furthermore, in both compartments the size distribution of MP is clearly skewed towards the smallest size classes (Figure 4). The ANOVA for the individual size classes revealed that the average abundance of polymers in the size classes 25–50 µm (*p*-value=0.008) and 50–75 µm (*p*-value=0.007) was significantly higher for sediment than surface water samples. This was the opposite for size classes 500–1000 µm (*p*-value=0.031), 2000–2500 µm (*p*-value=0.038), and 2500–3000 µm (*p*-value=0.004) (SI Table S9).

Spatial distribution of MP occurrence in the southern North Sea

After confirming significant differences between the sediment and surface water compartments, intra-compartmental variations between sampling stations were investigated.

A kR-clustering with SIMPROF was applied to highlight stations that were more similar concerning their polymer composition. Figure 5 shows the spatial distribution of these identified kR groups. Five groups (A–E) were found to best represent the clustering of sediment samples (R=0.921) (SI Figure S10) with most samples belonging to group D (n=12) (Figure 5a). Furthermore, the result of CAP reinforces the significant differences between the samples of the five groups with high correlation values (0.931–0.996) with only two samples being mis-classified

(SI Figure S11). One sample from group C was mis-classified as belonging to group B (station 11) and one sample from group B was mis-classified as being part of group E (station 15) with a low mis-classification error of 8.70%. To discover which polymer types drive this clustering in sediment samples an ANOVA with a subsequent Tukey HSD was performed. This analysis revealed six polymer types that contributed significantly to the dissimilarity between the grouped stations (SI Table S10), which are PE chlorinated, PA, CMC, acrylates/PUR/varnish, polychloroprene and rubber type 3. Polychloroprene dominated samples belonging to group D (n=12, stations 1–3, 5–10, and 22–24). Polyamide was preeminent for group E (n=5, stations 4, 12, and 19–21). Sediment samples from the Rhine-Meuse-delta (station 14, 15) belonged to group B (n=2) and were dominated by rubber type 3. Group C (n=2) was characterized by a low polymer diversity (station 11, 16) and the prevalence of acrylates/PUR/varnish and CMC was distinct for group A (n=2, station 13, 18).

For surface water samples kR-clustering revealed four groups (A−D) that represented the best possible clustering (R=0.868), where most samples are clustering closely and belong to group C (n=13) (Figure 5b, SI Figure S12). The clustering was confirmed by CAP with relatively high correlation values (0.811–0.970) (Figure S13). Only two samples (stations 15 and 18) were mis-classified to group C instead of group D resulting in an overall low mis-classification error of 8.7%. Six polymers, (PE, PE chlorinated, PVC, PEST, acrylates/PUR/varnish and rubber type 3), were revealed by ANOVA, with a subsequent Tukey HSD, to show significant differences between the four identified groups (SI Table S11). The presence of rubber type 3 characterized group C (n=13, station 1–2, 4–8, 11, 17, 20–21, and 23–24). Group B had significantly relatively more abundant (*p*-value=0.000) PEST (station 4, 13, 16, and 22). The absence of PE, PVC, and rubber type 3, as well as the relatively high presence of PE chlorinated, characterized group A (n=3, station 9, 10, and 19). Group D (n=3) was defined by an absence of PE chlorinated, PEST, and rubber type 3, as well as a relatively high presence of PVC and acrylates/PUR/varnish (station 14, 15, and 18).

Discussion

Through the integration of effective sample preparation together with state-of-the-art FTIR imaging and an automated analysis technique, MP could be detected in all analyzed sediment and surface water samples in the southern North Sea. The investigated compartments differed significantly in their polymer composition and particle size distribution. Average MP concentrations were considerably higher in sediments (234.5±254.3 particles kg^{-1} (DW)) than in surface waters (27.2±52.5 particles m^{-3}). However, a direct comparison is difficult because of different units of reference. When comparing the abundance of MP in a certain surface area the difference is even more striking with numbers ranging from 9.5 to 4041.9 particles m^{-2} in sediments and 0.01 to 24.5 particles m^{-2} in surface waters (SI Table S4). Furthermore, both compartments were clearly dominated by MP <500 µm. Although the numbers of MP >500 µm in surface water samples were noticeable, they had hardly any influence on the sample comparison between stations.

Along the West and East Frisian Islands (station 1−9) MP concentrations were of average extent in surface waters (3.5−58.6 particles m^{-3}) as well as sediments (38.7−318.4 particles kg^{-1} (DW)). Furthermore, sediment samples from this region were grouped together by cluster analysis since they showed similar polymer compositions with overall high polymer diversities. Both compartments in this region showed the lowest MP concentration at station 9, situated north of Texel, the most western Frisian Island, and the highest concentration at station 6, north of Ameland. It is very striking that samples from the mouth of the Scheldt and Rhine-Meuse-delta (station 14 and 15) differed greatly from all the others concerning their polymer composition, with surface water samples being dominated by acrylates/PUR/varnish and sediments additionally by rubber type 3, both indicating the influence of high marine traffic. In the English Channel region (station 16−19) polymer diversity and composition showed high variability, which was also true for the west coast of the Netherlands (station 10−13).

There is no clear gradient visible for surface waters, but those in the proximity to the English Channel, particularly station 20, which are influenced by riverine input from the Thames and the Rhine as well as channel water, exhibited the highest MP concentration (245.4 particles m^{-3}) with a decrease in the northern direction. These results agree with results from two studies where frequency of MP in fish and fulmars were highest in the Channel area (Foekema et al., 2013; van Franeker et al., 2011). For sediments MP concentration was highest at station 23 (1188.8 particles kg^{-1} (DW)), situated at the Dogger Bank and characterized by fine sediments. Further spatial patterns could be revealed by applying multivariate statistics, which has been attempted in previous studies as well (Hajbane and Pattiaratchi, 2017; Suaria et al., 2016). Hajbane and Pattiaratchi (2017) used multi-dimensional scaling (nMDS) to describe the differences in MP concentration and size classes between three distinct stations over time. Suaria et al. (2016) used principal component analysis (PCA) to compare a large number of surface water samples (n=74) regarding the relative frequencies of the seven most common polymer types. We used kR-clustering to reveal a spatial pattern regarding polymer composition followed by ANOVA to uncover the polymer types which drive this structure. The differences in polymer composition show a clear pattern with an imaginary line that can be drawn along 53° N. Stations below 53° N are more diverse in their polymer composition, which might be related to the influence coming from the English Channel as well as the high riverine input by the Thames, the Scheldt, the Rhine and the Meuse. On the contrary, stations located above 53° N exhibit a more similar polymer composition. ANOVA revealed that the sediment samples of these stations were characterized by the presence of polychloroprene and surface water samples by rubber type 3, represented by ethylene-propylene-diene monomer rubber (EPDM).

Interstudy comparison

In sediments sampled along the Belgian coast, Claessens et al. (2011) detected MP concentrations of up to 269 particles kg^{-1} (DW) on the shelf sea samples and 390 particles kg^{-1} (DW) in harbor areas, both in the size range of 38–1000 µm. They extracted MP by applying a density separation approach with sodium chloride (NaCl) and MP were visually preselected and identified using FTIR spectroscopy. In sediments of the Dutch North Sea coast Leslie et al. (2017) detected between 100–3600 particles kg^{-1} (DW). In their extensive study, they analyzed several compartments, among others sublittoral sediments close to the stations of this study. They analyzed only small aliquots of 20 g each which infers a large degree of extrapolation when referring to particles per kg and used NaCl for density separation which might have resulted in an underestimation of some denser polymer types. Furthermore, they mostly detected fibers of which only a small proportion (6%) was analyzed spectroscopically. Regardless of these potential limitations, concentrations were of the same order of magnitude as found in this study. Another study by Maes et al. (2017b) reported similar numbers for MP in sediments in the same area (0–3146 particles kg^{-1} (DW)). It is noteworthy to highlight that no MP fragments were counted in this study but mostly spheres and fibers contrary to our study. Maes et al. (2017b) also used small aliquots of 25 g for density separation with NaCl and identified plastics based on visual criteria only. When comparing results for surface water samples from the same study, MP concentrations were considerably higher in our study (0–1.5 vs. 0.1–245.4 particles m^{-3}). The most considerable differences between the two studies were in the mesh size of the sample net (333 µm vs. 100 µm) and the method for identification of MP (visual vs. ATR-FTIR and FTIR imaging). Relatively small aliquots of the samples were processed in these studies, especially regarding sediment samples. Our protocol enabled us to process the whole sample consisting of 1309−1770 g dry sediment and 15500−51300 L surface water concentrated by the net, respectively. It was however inevitable that we would only be able to analyze aliquots of the processed samples on the measuring filters, for practical reasons, i.e. to improve spectra quality and reduce time demand for analysis. However, for sediments the aliquots comprised on average 48.8% of the samples, being equivalent to a range of 141 to 1253 g sediment (DW), and for surface water samples the aliquots comprised on average 15.6% of the sample resulting in an equivalent volume of sea water ranging from 190 to 18236 L. To overcome the need for any extrapolation, multiple filters per sample could have been analyzed, but this would have increased the time demand by at least two days per filter. With new advances in reducing the analysis time, more filters could be analyzed more rapidly than has been possible until now. These developments in methodology are discussed further in the SI Paragraph S6.

We acknowledge that the lower limit of the filtration during sample processing was theoretically 20 µm. However, this limit can be considered lower when filters become clogged. For this reason, the number of particles between 11–20 µm should be considered as semi-quantitative, and therefore the total detected number is most likely an underestimation. Same applies to some extent also to the fraction 10−100 µm of the surface water samples due to the mesh size of the net. However, this emphasizes even more that very small MP are numerous and should be included in further research.

As in agreement with other studies (Filella, 2015; Hidalgo-Ruz et al., 2012; Ivleva et al., 2016), difficulties in interstudy comparisons due to variable sampling, sample preparation and analytical methods are well illustrated. Concerning possible analytical methods, the range includes simple visual identification only (Maes et al., 2017b), fluorescent tagging of synthetic polymers (Maes et al., 2017a), visual presorting followed by chemical identification of (a subset of) putative plastics (Enders et al., 2015; Leslie et al., 2017; Martin et al., 2017), spectroscopic imaging of whole sample filters using FTIR imaging (Bergmann et al., 2017; Haave et al., 2019; Mintenig et al., 2017; Mintenig et al., 2019; Peeken et al., 2018; Tagg et al., 2015; Vianello et al., 2013), µRaman spectroscopy (Cabernard et al., 2018), and thermoanalytical methods like Pyrolysis gas chromatography coupled to mass spectrometry (Py-GC-MS) (Fischer and Scholz-Böttcher, 2017) or thermal extraction-desorption (TED) GC-MS (Dümichen et al., 2017; Dümichen et al., 2019).

It has been shown that visual identification alone is insufficient (Kroon et al., 2018; Song et al., 2015) and the same can be said for methods relying on a visual preselection stage from which only a subset are verified by spectroscopic or thermoanalytical methods. When aiming for particle related data, the complementary spectroscopic methods of Raman microscopy and FTIR imaging are the most commonly used (Hanke et al., 2013; Käppler et al., 2016; Silva et al., 2018). Generally, there is a requirement within the research field to establish the usage of polymer characterization methods that omit the need for pre-sorting. If a pre-selection is unavoidable, it should follow certain criteria (Hidalgo-Ruz et al., 2012; Kroon et al., 2018; Norén, 2007) or be aided by dying with Nile red (Erni-Cassola et al., 2017; Maes et al., 2017a).

Implications

Beyond the harmonization of methods for reliable comparisons of MP data, another important issue in the field of marine environmental MP research is the need for clear identification of pathways, especially entry pathways. Previous research has shown that rivers are to be considered as one of the major sources (Lebreton et al., 2017; Schmidt et al., 2017). Studies focusing on rivers entering into the North Sea report relatively high numbers of MP (Leslie et al., 2017; Mani et al., 2019; Mani et al., 2015). Noteworthy, it has been shown in a recent study by Hurley et al. (2018) that MP from the river beds (approx. 70%) can be resuspended, flushed by flooding events and hence be introduced into the oceans. This implies that MP from riverine surface waters alongside those locked in bed sediments should both be considered as having the potential of entering the North Sea. In this regard, it is even more notable, considering that most of the polymer types reported in these riverine studies would be buoyant in seawater ($\rho \leq 1.025$ g cm^{-3}), that the concentrations detected in North Sea surface waters are surprisingly low. One explanation might be the very conservative approach of our study. The other, more significant, factor might be that the hydrodynamics of the North Sea have a generally anti-clockwise circulation in the center and a northeasterly export along the coast (Howarth, 2001; Thiel et al., 2011). This makes it less likely for MP to accumulate in North Sea surface waters. However, this horizontal transport facilitates the distribution of MP in the North Sea along with their chemical load and attached biofilm communities. In this regard it is noteworthy that Kirstein et al. (2016) confirmed the presence of potentially pathogenic bacteria in biofilms from MP collected in North Sea surface waters. Another aspect to acknowledge when considering distribution pathways is the vertical transport of MP. Möhlenkamp et al. (2018) showed that buoyant MP that become incorporated into aggregates can sink and eventually settle into the benthic boundary layer, providing an explanation to the presence of positively buoyant plastics in sublittoral sediments. This evidence was backed by another study by Porter et al. (2018) in which they showed the incorporation of different plastic types (PE, PP, PA, PS, and PVC), of different shapes (fibers, spheres, and fragments), and sizes (7–3000 µm) into marine snow. The incorporation of normally buoyant polymers in organic-rich aggregates increased the sinking velocity of all tested polymer types (Porter et al., 2018). The authors of both studies recorded that in case of a polymer buoyant in seawater, such as PE, as well as with a mixture of plastic microbeads (extracted from facial cleansers), sinking velocities increased to up to 818 and 831 m d^{-1} respectively (Möhlenkamp et al., 2018; Porter et al., 2018). This exceeds general sinking velocities of phytoplankton aggregates (53±22 m d^{-1}) (Möhlenkamp et al., 2018) and fecal pellets, which range, depending on the composition of the phytoplankton bloom, between 70–100 m d^{-1} (Frangoulis et al., 2001).

A final consideration on the topic of vertical transport would be that the bioavailability of MP to filter and suspension feeders has been shown to be increased by their incorporation in aggregates (Porter et al., 2018; Ward and Kach, 2009). Recently, Katija et al. (2017) showed that MP are captured by larvaceans and that these can be contained in their fecal pellets or discarded houses, and may thus sink to the seafloor as part of these structures where they are available for benthic organisms.

Robust monitoring protocols are needed which should not only focus on large MP (>500 µm). In this study we demonstrated that it is not possible to extrapolate conclusions from analyzing MP >500 µm to ascertain data on MP <500 µm. For the development of risk management and assessment protocols, and to monitor trends in changes of polymer concentrations and composition, it is of importance that the focus should shift to be on the small or even very small size fraction (<100 µm). In agreement with previous studies (Leslie et al., 2017; Maes et al., 2017b) we found North Sea sediments to be considerably more contaminated than surface waters and that these may act as potential sinks. This clearly supports the statement of Leslie et al. (2017) to track changes in MP pollution in sediments in future monitoring approaches.

Supplementary Data. Paragraphs, figures and tables describing the sampling, sample processing and analysis in greater detail as well as presenting result for the statistical analysis

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Captions

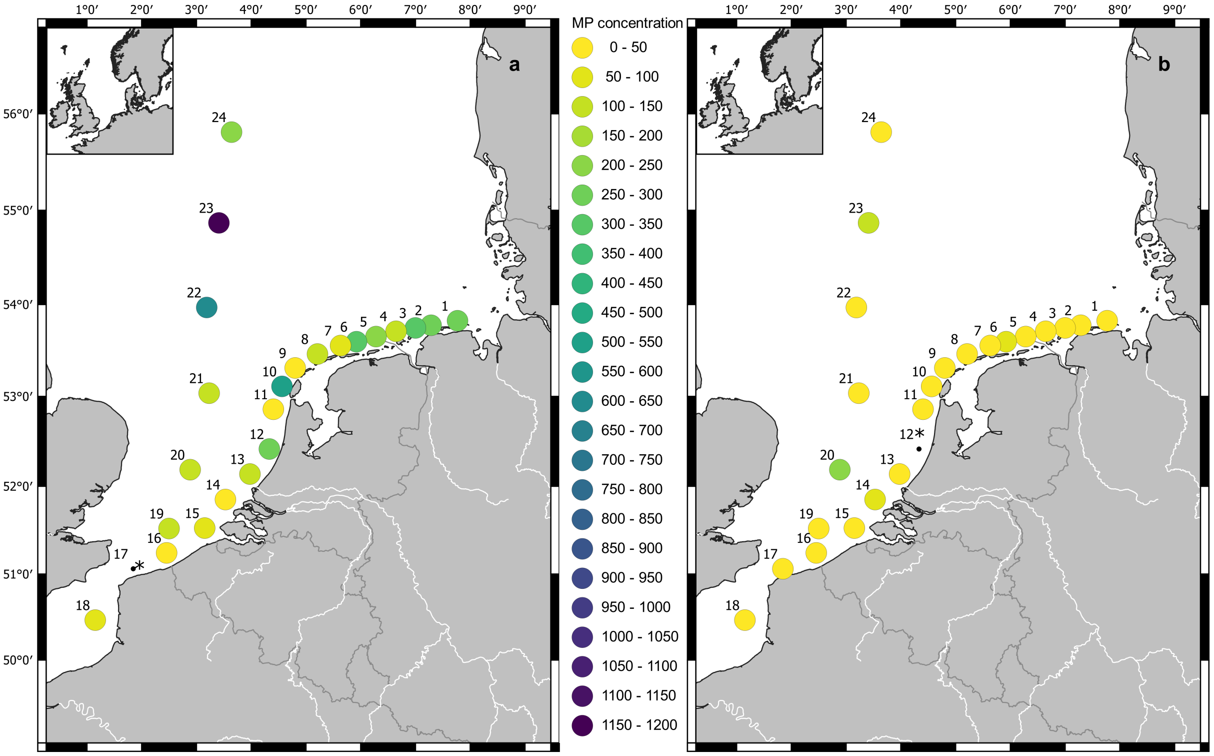
Figure 1 Geographic distribution of microplastic concentration in the southern North Sea. Microplastic concentration for sediment samples (a) reported in particles per kg and surface water samples (b) reported in particles per m³. Stations where no sample was analyzed are marked with *.

Figure 2 Spatial distribution of the relative polymer composition for sediment (a) and surface water samples (b). PE: polyethylene, PP: polypropylene, PS: polystyrene, PC: polycarbonate, PA: polyamide, PVC: polyvinyl chloride, CMC: chemically modified cellulose, PEST: polyester/polyethylene terephthalate, PUR: polyurethane, PSU: polysulfone, EVA: ethylene vinyl acetate, POM: polyoxymethylene. Stations where no sample was analyzed are marked with *.

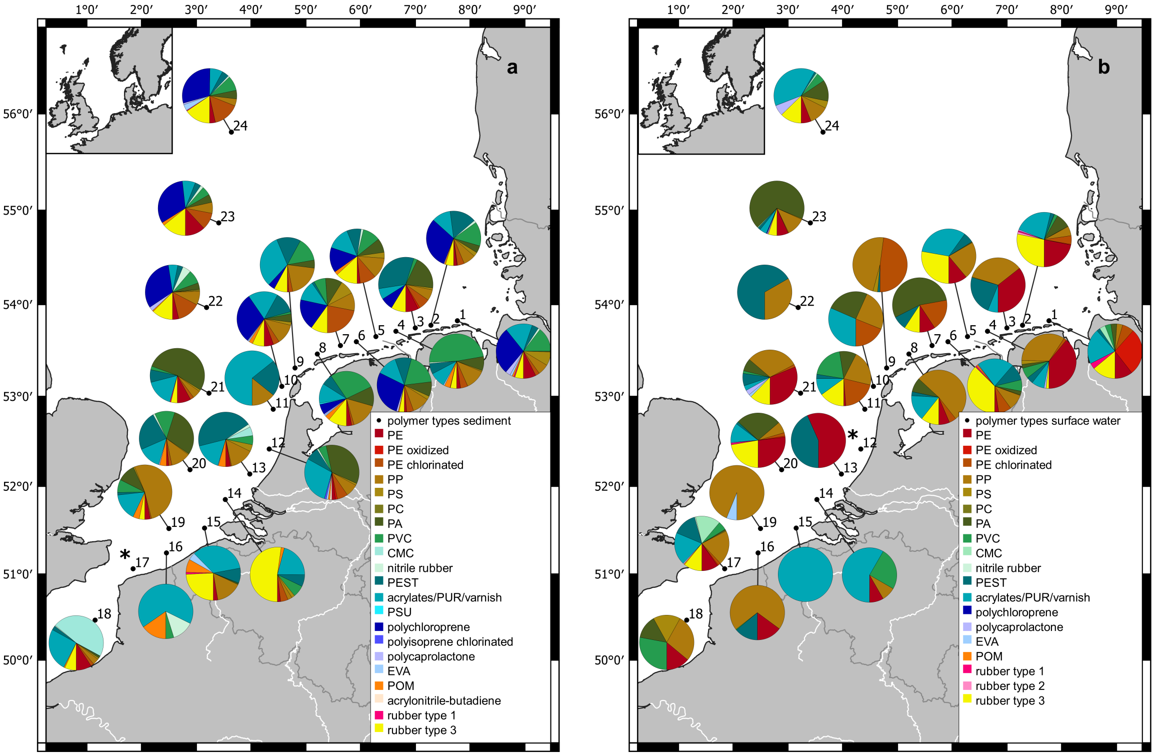
Figure 3 Mean percentage of each polymer type for sediment (red triangle) and surface water samples (blue square). PE: polyethylene, PP: polypropylene, PS: polystyrene, PC: polycarbonate, PA: polyamide, PVC: polyvinyl chloride, CMC: chemically modified cellulose, PEST: polyester/polyethylene terephthalate, PUR: polyurethane, PSU: polysulfone, EVA: ethylene vinyl acetate, POM: polyoxymethylene. Whiskers show the 95% confidence interval.

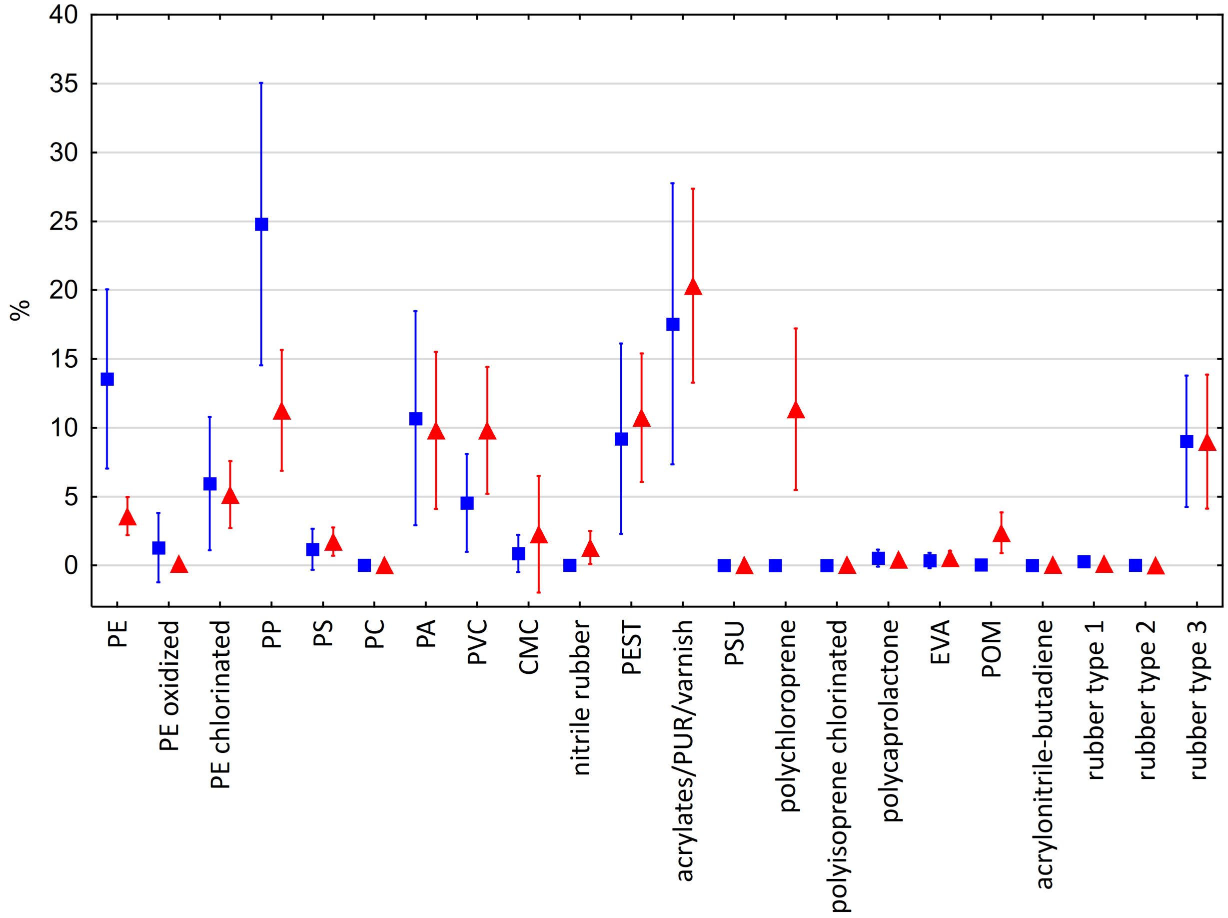
Figure 4 Mean percentage of each size class in µm for sediment (red triangle) and surface water samples (blue square). Whiskers show the 95% confidence interval.

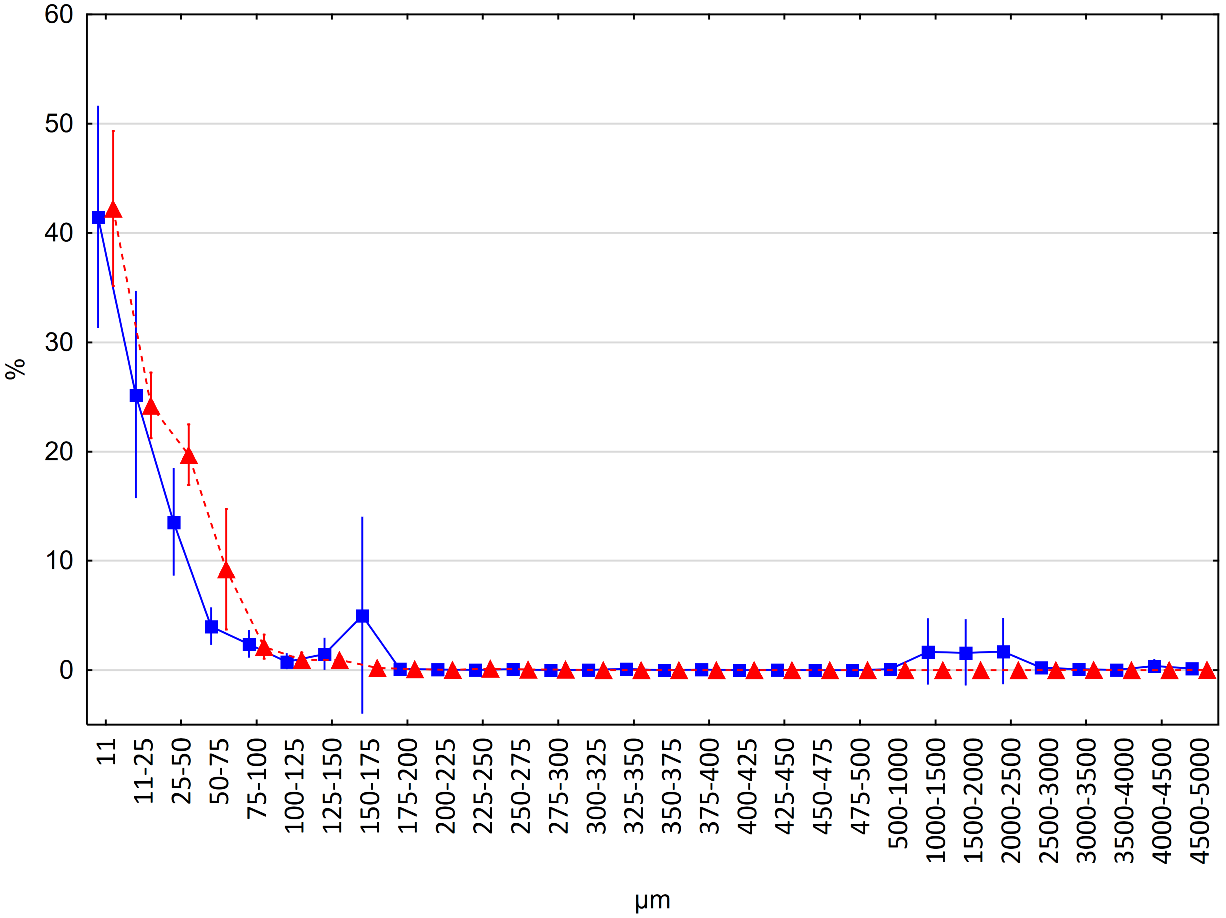
Figure 5 Map of the southern North Sea with the 24 stations of sediment (a) and surface water sampling (b) and their assigned groups (different colors) respectively based on kR-clustering. Stations where no sample was analyzed are marked with *.

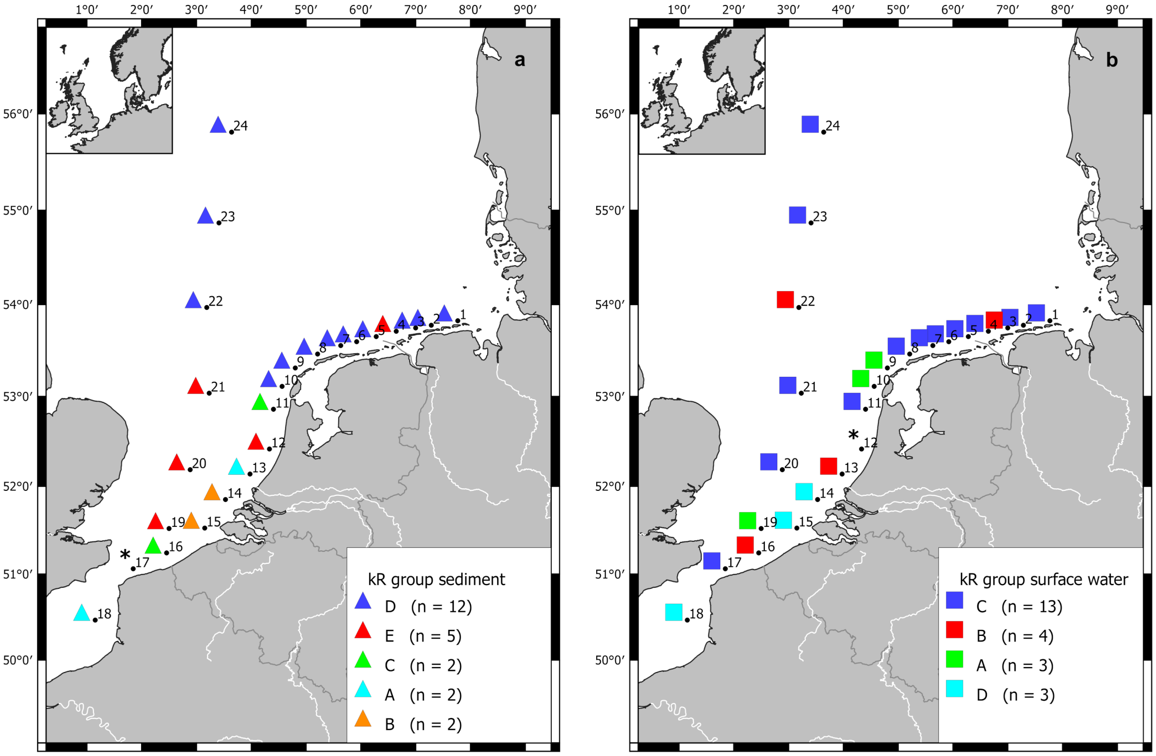


a
b
MP concentration
0 - 50
50 - 100
100 - 150
150 - 200
200 - 250
250 - 300
300 - 350
350 - 400
400 - 450
450 - 500
500 - 550
550 - 600
600 - 650
650 - 700
700 - 750
750 - 800
800 - 850
850 - 900
900 - 950
950 - 1000
1000 - 1050
1050 - 1100
1100 - 1150
1150 - 1200
1°0′
2°0′
3°0′
4°0′
5°0′
6°0′
7°0′
8°0′
9°0′
56°0′
55°0′
54°0′
53°0′
52°0′
51°0′
50°0′
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
*


1°0′
2°0′
3°0′
4°0′
5°0′
6°0′
7°0′
8°0′
9°0′
56°0′
55°0′
54°0′
53°0′
52°0′
51°0′
50°0′
a
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
*
polymer types sediment
PE
PE oxidized
PE chlorinated
PP
PS
PC
PA
PVC
CMC
nitrile rubber
PEST
acrylates/PUR/varnish
PSU
polychloroprene
polyisoprene chlorinated
polycaprolactone
EVA
POM
acrylonitrile-butadiene
rubber type 1
rubber type 3
b
polymer types surface water
PE
PE oxidized
PE chlorinated
PP
PS
PC
PA
PVC
CMC
nitrile rubber
PEST
acrylates/PUR/varnish
polychloroprene
polycaprolactone
EVA
POM
rubber type 1
rubber type 2
rubber type 3


40
35
30
25
20
15
10
5
0
%
PE
PE oxidized
PE chlorinated
PP
PS
PC
PA
PVC
CMC
nitrile rubber
PEST
acrylates/PUR/varnish
PSU
polychloroprene
polyisoprene chlorinated
polycaprolactone
EVA
POM
acrylonitrile-butadiene
rubber type 1
rubber type 2
rubber type 3


60
50
40
30
20
10
0
%
11
11-25
25-50
50-75
75-100
100-125
125-150
150-175
175-200
200-225
225-250
250-275
275-300
300-325
325-350
350-375
375-400
400-425
425-450
450-475
475-500
500-1000
1000-1500
1500-2000
2000-2500
2500-3000
3000-3500
3500-4000
4000-4500
4500-5000
µm


a
b
1°0′
2°0′
3°0′
4°0′
5°0′
6°0′
7°0′
8°0′
9°0′
56°0′
55°0′
54°0′
53°0′
52°0′
51°0′
50°0′
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
*
kR group sediment
▲ D (n = 12)
▲ E (n = 5)
▲ C (n = 2)
▲ A (n = 2)
▲ B (n = 2)
kR group surface water
■ C (n = 13)
■ B (n = 4)
■ A (n = 3)
■ D (n = 3)

Highlights

- All 46 analyzed sediment and surface water samples contained microplastics
- Microplastic concentrations were higher in sediment than surface water samples
- Polymer composition differed significantly between surface waters and sediments
- Microplastics <500 µm were more abundant and divers in polymer type than large ones
- Particles smaller 100 µm dominated clearly in both environmental compartments

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: