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A monitoring and data analysis method for microplastics in marine sediments

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ABSTRACT

In Europe, policy frameworks demand the monitoring of microplastics in marine sediments. Here we provide a monitoring and data analysis method for microplastic particles designed to be used in the context of Marine Strategy Framework Directive (MSFD) and OSPAR policy frameworks. Microplastics were analysed in marine sediments at four different locations in Dutch coastal and transitional waters using replicate sampling to investigate micro-spatial variation. Particle size distribution followed a power law with slope 3.76. Thirteen polymers were identified, with their composition varying between sediments near densely populated West coast areas versus the more rural Wadden Sea area. We quantify differences in the micro-spatial variation of microplastic concentrations between locations using the relative standard error of the mean (RSEM). This metric provides an opportunity to optimize the sensitivity of trend detection in microplastic monitoring networks by selecting locations with relatively low micro-spatial variation. We provide a method to optimize the number of replicate samples for a given location using its relationship with the RSEM. Two replicate samples appear to be cost-effective for relatively homogenous locations, whereas more heterogenous locations require four replicates.

1. Introduction

Due to its ubiquity and persistence (Law and Thompson 2014), plastic litter polluting the marine environment has been embedded in the European Marine Strategy Framework Directive (MSFD) 2008/56/EC (Union 2008). This strategy aims to apply an ecosystem-based approach to the regulation and management of the marine environment, marine natural resources and marine ecological services (Long 2011). Microplastic risks for the marine environment are expected in the near future (Everaert et al., 2020), but as there is uncertainty about microplastic concentrations in the marine environment, there is a clear need for MSFD (Cadiou et al., 2020) and OSPAR (Oslo Paris convention) monitoring and data analysis methods to assess microplastics in marine sediments. The European Commission, who issued the MSFD legislation sets the following demands for microplastic monitoring: "*Micro-litter (particles* $<$ 5 mm*), classified in the categories 'artificial polymer materials' and 'other'. Descriptor 10 (marine litter), Criterion 2 (D10C2, microlitter) — Primary criterion: The composition, amount and spatial distribution of micro-litter on the coastline, in the surface layer of the water column, and in seabed sediment, are at levels that do not cause harm to the coastal and marine environment. Additional specifications for monitoring and assessment: micro-litter shall be monitored in the surface layer of the water column and in the seabed sediment and may additionally be monitored on the coastline. Micro-litter shall be monitored in a manner that can be related to point-sources for inputs (such as harbours, marinas, waste-water treatment plants, storm-water effluents), where feasible. The measurement units are: (a) amount of micro-litter* per *category in number of items and weight in grams (g): (b)* per *kilogram (dry weight) (kg) of sediment for the coastline and for seabed.*"

The OSPAR international environmental cooperation in the North East Atlantic region is not legislative but is an international agreement that The Netherlands has to comply with. These two European demands are leading for the development of the Dutch monitoring method for microplastics. In OSPAR regional cooperation, it has been decided that OSPAR countries will first focus on the monitoring of microplastics (MP) in marine and coastal sediments, because this compartment acts as a sink

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for microplastics and is known to have more stable microplastic concentrations compared to floating microplastics (Lorenz et al., 2019). In addition, it was decided within OSPAR to first focus on microplastics ≥100 μm, because this size range can also be detected by microscopy and is therefore relatively easy to monitor. The methods presented in this paper may also be applicable in the other European marine sea regions, i.e. the Baltic Sea, the Mediterranean Sea and the Black Sea.

Many different methods are used for monitoring of microplastics in marine sediment and consequently results are often incomparable (Möller et al., 2020). This is a general problem in microplastics research (Koelmans et al., 2020). Consequently, reliable knowledge of the presence, distribution and ecotoxicological effects of MP in the (marine) environment is still limited. In order to improve this situation, harmonization efforts for microplastic monitoring and reporting are currently made in the European and OSPAR microplastic expert groups. The agreed method harmonization aspects are currently updated in the EU monitoring guidelines for marine litter (Hanke et al., 2013) and in the OSPAR CEMP microplastic monitoring guidelines which will be finalized in 2023. Among others the length classes 20–49, 50–99, 100–299, 300–999 and 1000–5000 μm are harmonized. These length classes (i.e., 100–299 and 300–999 μm) are used in this study for both MP numbers and total mass (EU, 2017).

The aims of this study therefore are (a) to develop and test a monitoring method of microplastics in marine sediments to contribute to monitoring within MSFD and OSPAR policy frameworks, and (b) to develop and test data analysis methods such as sample number optimization and modelling of particle size-number relations for microplastic monitoring data. These aims are pursued using replicate sediment samples taken from four national chemical monitoring locations along the Dutch coast. We investigate replicate sampling to provide insight in the micro-spatial variation at the location level which is relevant to select monitoring locations and to recommend a cost-effective number of replicate samples. Based on the results of this study recommendations for an OSPAR and MSFD microplastic monitoring and data analysis method for marine sediments are made. Since the EC specifications request information on the relationship between monitoring locations and point-sources, the present study was designed to address coastal site monitoring first. **Offshore locations** will be included in future Dutch monitoring. Furthermore, the following specifications have been added to the desired protocol. The method should be selective for plastic and rubber microparticles, be relatively simple and practical to perform, have acceptable reference material recoveries, and should result in both total number and total mass data. Furthermore, the analytical method should comply with common QA/QC criteria (Koelmans et al., 2019; Redondo-Hasselerharm et al., 2022).

Previously, microplastics have been measured in North Sea sediments, including Dutch coastal and offshore locations, using density extraction, clean-up and visual microscopic methods (Leslie et al., 2017; Maes et al., 2017). However, recent insights regarding data quality indicate that polymer identification with e.g. FTIR spectroscopy is an essential part of microplastic analysis to avoid false positive results (Hermsen et al., 2018). Furthermore, polymer information can be helpful in relating polymer types found in samples to possible riverine and estuarine sources. When data on particle numbers, size and polymer identity are required for microplastics, μFTIR has become the standard method for analysis (Primpke et al., 2017). Consequently, we used FTIR-microscopy combined with automated image analysis using the SiMPle and MPAPP software (Primpke et al., 2019) in combination with the reference database provided by (Primpke et al., 2018). Data analysis included an approach to optimize required sample replication based on the measured relationship between the standard error of the mean (SEM) of the microplastic number concentration and the number of replicate samples per location. Furthermore, data analysis included a probability density function for particle length, which can be used to rescale concentration data to a default microplastic size range of 1–5000 μm, or to probabilistically assess exposure and risks.

2. Methods

2.1. Sampling and sample conservation

Sediment samples were taken at four Dutch coastal locations (Table S1). Vlissingen (VLIS, estuarine location) and Noordwijk2 (NW2, coastal location) are situated near the densely populated South-West of the Netherlands, close to or on the route to important international ports (Rotterdam and Antwerp). The locations Bocht van Wattum (BVW) and Kornwerderzand (KWZ) are both situated on the Dutch north coast, in the Ems-Dollard estuary and Wadden Sea, respectively. At all these locations three separate samples were taken. Subtidal samples were taken using a Rheineck boxcorer; only at Kornwerderzand intertidal samples were taken using a metal shovel (Table S1). These replicate samples were taken within 10 m horizontal distance. In both cases, the top 5 cm were scraped off, transferred into stainless steel jars and stored at 4 °C. In the laboratory these top layer samples of each individual box core or shovel sample (approximately 3 L) were homogenized carefully using a metal spoon. Subsequently, for the samples from BVW and KWZ one subsample (150 g wet weight) of each individual sample was taken and transferred into glass jars, sealed with aluminium foil, and stored again at 4 °C until extraction. For the samples from VLIS and NW2, three subsamples were taken from each boxcore sample for a more detailed analytical and statistical analysis of the micro-spatial variation.

2.2. Chemicals and materials

Perdrogen™ 30% hydrogen peroxide (H_2O_2) and technical grade (>98%) zinc chloride ($ZnCl_2$) were purchased from Boom (The Netherlands). Potassium hydroxide (KOH) was purchased from Merck (Germany). MilliQ water with a resistivity >18 MΩ was used for all rinsing steps and to make a $ZnCl_2$ solution with a density of 1.6 g/cm^3 as well as a 12.5% KOH solution. All chemical solutions were filtered over a 20 μm metal mesh filter prior to usage. Anodisc filters 25 mm with a pore size of 200 nm were purchased from Whatman®. Fluorescent green polyethylene microspheres (90–106 μm) were purchased from Cospheric (USA) and used to determine the recovery rate of the applied extraction process.

2.3. Sample preparation

The sample preparation was based on previously reported methods (Fig. S1) (Mintenig et al. 2018, 2020). Each subsample (150 g) was suspended in MilliQ water. The suspension was then sieved through a 500 and a 60 μm metal mesh cascade. The particles retained by the 500 μm sieves were re-suspended in Milli-Q water and analysed visually under a stereomicroscope (see "microscopic analysis" section). The particles retained by the 60 μm filter were transferred into a glass beaker and 600 mL of pre-filtered $ZnCl_2$ solution (density 1.6 g/cm^3) were added. The beakers were placed on a stirring plate and stirred for 15 min using a magnetic stirrer with a glass surface (60 × 8 mm, 120 rpm). After another 15 min settling time the supernatant was filtered over a 20 μm stainless steel filter using a vacuum pump and a filtration setup with a Teflon tube. This procedure was repeated with another 600 mL of $ZnCl_2$ solution. The filter with the supernatant material was transferred into a beaker with 75 mL KOH (12.5%), covered with aluminium foil and left standing for 5 days at 35 °C. Subsequently, this suspension was filtered again through the same 20 μm metal filter. In the next step the remaining particles were transferred into a beaker with 50 mL H_2O_2 (30%) and left standing for 1 day at 35 °C. The sample was filtered again through the same metal filter, and the remaining particles were transferred into a separation funnel using 100 mL $ZnCl_2$ solution. The funnels were shaken and left overnight to enable settling of denser materials. The settled material was discarded by continuously turning the valve of the funnel to prevent clogging, re-suspension and loss of plastics. About 10 mL of the liquid remained in the funnel and was filtered over the 20 µm metal filter. From there, the residues were transferred onto anodisc filters using Milli-Q water.

2.4. Instrumental analysis

2.4.1. Microscopic analysis

The solids from the 500 µm filter were re-suspended in Milli-Q water, placed in a Bogorov chamber (PMMA, 70 mL, HydroBios, Germany) and examined under a stereomicroscope (Nikon Stereo SMZ2T).

2.4.2. Analysis of particles >500 µm

All particles larger than 500 µm, and potentially made from plastic were sorted manually. Individual particle characterisation was achieved for all sorted particles using attenuated total reflectance (ATR)-FTIR (Varian 1000 FT-IR, Agilent USA). The polymer types were identified based on the recorded spectra (600–4000 cm^{-1}) and under consultation of the Hummel Polymer and FTIR Spectral Library' (ThermoFisher Scientific, USA).

2.4.3. Analysis of particles <500 µm

All particles smaller than 500 µm were filtered on anodisc filter which were analysed using µFTIR mapping in the laboratories of Wageningen University and Research (Nicolet iN10, ThermoFisher). Of each filter an area of approximately 6 × 15 mm was mapped, representing 45% of the total filter area. For this, anodisc filters were placed on a calciumfluoride (CaF$_2$) crystal (EdmundOptics, Germany) to avoid filter bending. IR spectra were recorded with a spatial pixel resolution of 30 µm and in a wavenumber range of 1250–3200 cm^{-1}. The spectral resolution was set as 16 cm^{-1}, and 1 scan per pixel was conducted. Generated FTIR data were analysed using automated image analysis with the software SiMPle and MPAPP (Primpke et al., 2019) in combination with the reference database presented by (Primpke et al., 2018), which provides information on the particle polymer type, size measurements and mass estimates. Based on criteria by Primpke et al. polymer specific thresholds were determined by evaluating the IR spectra of four samples manually (Table S5). The particles counted on the 45% of the filter area of each sample and negative control can be found in the SI (Table S6). Data were extrapolated to the whole filter area and corrected for polymer specific blank contamination and extraction recovery (see section Quality assurance and control).

2.4.4. Data reporting

For each microplastic particle (plastic and rubber) the length, width, polymer type and estimated mass is determined based on the method by Simon et al., (2018). The total number of particles ≥100 µm per kg dry weight, as well as the size fractions 100–300 µm and 300–1000 µm are reported using particle length data. The total estimated mass of polymer particles per sample per kg dry weight, for the size fractions 100–300 µm and 300–1000 µm, are also reported. The mean and median total number of particles and total mass per kg dry sediment are provided per location and date (Table 1).

The polymer composition of the samples was calculated for the individual locations and for all locations combined. All polymers with a relative abundance (based on particle number) of more than 5% in at least one location were reported. The resulting set of polymers is: polyethylene (PE), chlorinated polyethylene (Cl-PE), polypropylene (PP), polystyrene (PS), polyamide (PA), ethylene propylene diene monomer rubber (EPDM) and acrylates-polyurethanes-varnish (APV). The remaining polymers are grouped into 'Other polymers' (O) as their relative abundance (particle number) was <5% in all samples.

2.5. Quality assurance and control

Quality assurance and control (QA/QC) complied to the most recent criteria for the determination of microplastic in sediment (Redondo-Hasselerharm et al., 2022), with a total accumulated score (TAS-score) of 15 out of 20 points and no zero scores (Table S7). Four points were deducted because not enough sample material was used, the positive controls were run with only one type of polymer, a laminar flow cabinet could not be used always and 45% of the anodisc filter was mapped during analysis. To mitigate contamination, all laboratory surfaces were cleaned with ethanol, equipment was rinsed with ethanol and covered immediately with aluminium foil, and a cotton lab coat was worn at all times. Solutions of chemicals were filtered prior to use. The materials used avoid the use of plastic as much as possible (e.g., a metal filter setup with a Teflon tube, the separation funnels made of glass). Note that possible Teflon contamination (density 2.2 g/mL) is not recovered with density extraction (1.6 g/mL). Further, a negative control was treated in parallel to each batch of actual samples to determine the degree of background contamination resulting in a total of six negative controls. Concentration data of the samples were corrected for the polymer-specific mean values of these negative controls. For the positive controls a known number of plastic particles (green fluorescent PE, average diameter 90–1 06 µm, Cospheric, USA) were added to a sample (six samples in total) and treated the same way as the actual samples. The recovery was determined after visually counting these PE spheres under a microscope. The mean recovery of six recovery tests was 73 ± 16% which was used to correct the results. This recovery represents a good recovery for marine sediments. For example, In a comparative study the majority of the reported recoveries for microplastic reference materials from marine sediments was below 70% (Cashman et al., 2020). During µFTIR analysis, 42% of the each Anodisc filter area was scanned and mapped.

2.6. Statistical analysis

Outlier analysis of the microplastic total number data within triplicate measurement results was performed using the Dixon's Q test (Rorabacher, 1991).

The total microplastic number concentrations determined in the replicate samples of the four locations were tested for significant differences of the location mean values using a *t*-test in the Excel Data

Table 1

Mean and median number and mass concentrations for marine sediments in Dutch coastal regions. The column Mean count 100–5000 µm is the sum of the colums Mean count 100–300 µm and Mean count 300–1000 µm. The column Mean est. mass is the sum of the columns Mean est. mass 100–300 µm and Mean est. mass 300–1000 µm.

Location code	N samples	Mean count 100-1000 µm [/kg dw]	RSEM Mean count [%]	Mean count 100–300 µm [/kg dw]	Mean count 300–1000 µm [/kg dw]	Median count [/kg dw]	Mean est. mass 100–1000 µm [mg/kg dw]	RSEM Mean est. mass [%]	Mean est. mass 100–300 µm [mg/kg dw]	Mean est. mass 300–1000 µm [mg/kg dw]	Median est. mass 100–1000 µm [mg/kg dw]
VLIS	9	313	26	287	26	318	6.95	83	0.44	6.51	0.77
NW2	9	493	9.5	423	70	471	16.43	86	1.04	15.39	0.69
KWZ	3	829	8.3	785	44	797	0.03	100	0.00	0.03	0.00
BVW	2	311	1.1	267	44	312	7.52	57	0.47	7.04	7.51

Analysis Toolpack, assuming unequal variances per location and using the two-sided p-value.

The Relative Standard Error of the Mean (RSEM), defined as SEM/mean (Miller and Miller, 1993) of total microplastic numbers was calculated at the location level using the SEM-tool (provided as Supplementary Data). The relative error (RSEM) is used as a statistical metric for the location micro-spatial variation instead of the absolute standard error of the mean (SEM) because the variation of environmental data is usually proportional to the measured values (Manchuk et al., 2009). For the locations with 9 replicates (NW2 and VLIS) the relation between the number of replicates and the RSEM was calculated using a bootstrapping method. Bootstrapping included 100,000 draws of sample microplastic concentrations from the set of 9 replicates samples per location with replacement. Accuracy of the results was quantified down to 1000 draws, below which the accuracy was considered insufficient.

We propose the following criterion to optimize the number of replicate samples for a specific location. For each additional replicate, the improvement of the RSEM is evaluated. When the reduction of the RSEM with the increase of one replicate becomes <0.05 (Table S4) it is concluded that this additional replicate is not cost-effective and therefore not needed. Note that this decrease of the RSEM <0.05 is equivalent to the reduction of the SEM with <5% compared to the mean value.

Following (Kooi et al., 2021) the distribution for particle length (x) was analysed by pooling all available sample data and fitting a power law distribution $y = bx^{-\alpha}$. The power law exponent α was estimated as $\widehat{\alpha} = 1 + n\left[\ln\sum_i \frac{x_i}{\widehat{x}_{min}}\right]^{-1}$, using a maximum likelihood estimation (MLE) method (Clauset et al., 2009; Newman 2005). Each fit was bootstrapped, to obtain means ($\widehat{x}_{min}$ and $\widehat{\alpha}$) and standard deviations for the mean for both $\widehat{x}_{min}$ and $\widehat{\alpha} < ! - -Q4:$ **Fig. 1** was not cited in the text. Please check that the citation(s) suggested are in the appropriate place, and correct if necessary. $- - >$ (see Fig. 1).

3. Results and discussion

3.1. Number and mass based microplastic concentrations

Microplastic number concentrations (MNC) show that the concentrations at NW2 and VLIS are not significantly different ($p = 0.08$), that BVW has significantly lower concentrations than NW2 ($p = 0.005$) and that KWZ has significantly higher concentrations than the other locations ($0.001 < p < 0.017$) (Table 1). The relatively high MNC for KWZ can be explained by its location at the outlet sluice of lake IJsselmeer into the Wadden Sea, where microplastics from inland rivers and other discharges may accumulate. For all locations, mean and median MNC are comparable (Table 1), which suggests that the MNCs are distributed

Fig. 1. Coastal and estuarine sampling locations used in this study. The location codes (names) are: VLIS (Vlissingen), NW2 (Noordwijk2), KWZ (Kornwerderzand), BVW (Bocht van Watum).

normally. The average mean MNC varies from 287 to 785 kg^{-1} dw among locations (Fig. 2). The highest MNC was found in an individual sample from KWZ (962 kg^{-1} dw; Table S2), whereas the lowest MNC was found in a sample from VLIS (27 kg^{-1} dw; Table S2).

Table 1, Fig. S2 and Fig. S3 show the MNC and the microplastic mass concentration (MMC) for the size classes 100–5000 μm (i.e. the targeted microplastic range), 100–300 μm and 300–1000 μm, respectively. At each location about 90% (282–785 particles/kg dw) of all particles fall within the 100–300 μm size range, while 10% (26–70 particles/kg dw) are in the 300–1000 μm size range. Particles larger than 1000 μm were not detected. This does not mean that larger particles are not present in the sediments that we investigated. Most likely our sample size was too small, causing the detection limit for these less abundant large particles to be too high. It is common that larger microplastics are found less frequently (Bäuerlein et al., 2022; Mintenig et al., 2020). For mass-based concentration data the opposite is observed, with the highest MMC mostly found in the larger (300–1000 μm) size fraction (Table 1). This result is expected, since large particles are relatively heavy and thus have a relatively high contribution to the mean mass concentration (Kooi et al., 2021). The RSEM values show substantially lower values for mean total numbers compared to the mean total masses. This is caused by the fact that the few large microplastic particles (≥300 μm), which are more sampled by chance, have a relatively large contribution to the total mass, resulting in a larger mass variation. This result shows that mean total number is a more precise indicator to analyse and report than the mean total mass.

3.2. Assessment of micro-spatial variation

We assessed the relation between the number of replicate samples per location, the mean and the relative standard error of the mean (RSEM, Fig. 3, Fig. S4). Note that this variation is the combination of micro-spatial variation at one site and the analytical variation related to extraction, cleanup and instrumental analysis. Additional experiments would be necessary to determine the micro-spatial variation and the analytical variation separately.

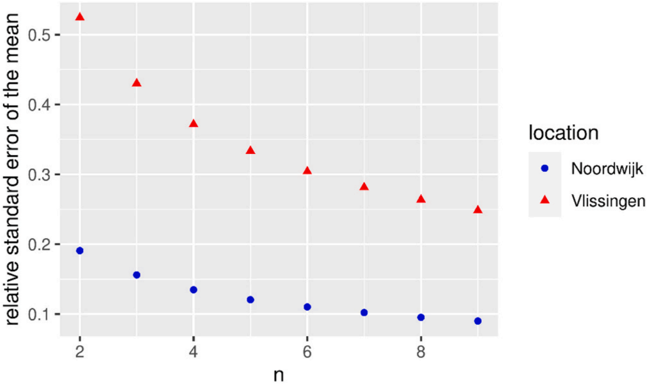

Fig. 3. Relation between the number of replicate samples and the relative standard error of the mean (RSEM) for the locations Noordwijk (NW2) and Vlissingen (VLIS), respectively.

The RSEM for location VLIS is approximately 2.7 times higher than the RSEM for location NW2 (Fig. 3). This is not unexpected as the highly dynamic conditions at the estuarine site VLIS, and the resulting micro-habitats, apparently result in a higher variation of microplastic concentrations compared to the more homogenous NW2 coastal conditions. This shows that the location VLIS is less suitable for trend detection in the context of microplastic monitoring because of its larger micro-spatial variation. An alternative location nearby with less variation can thus be more suitable for monitoring purposes. For the locations BVW and KWZ

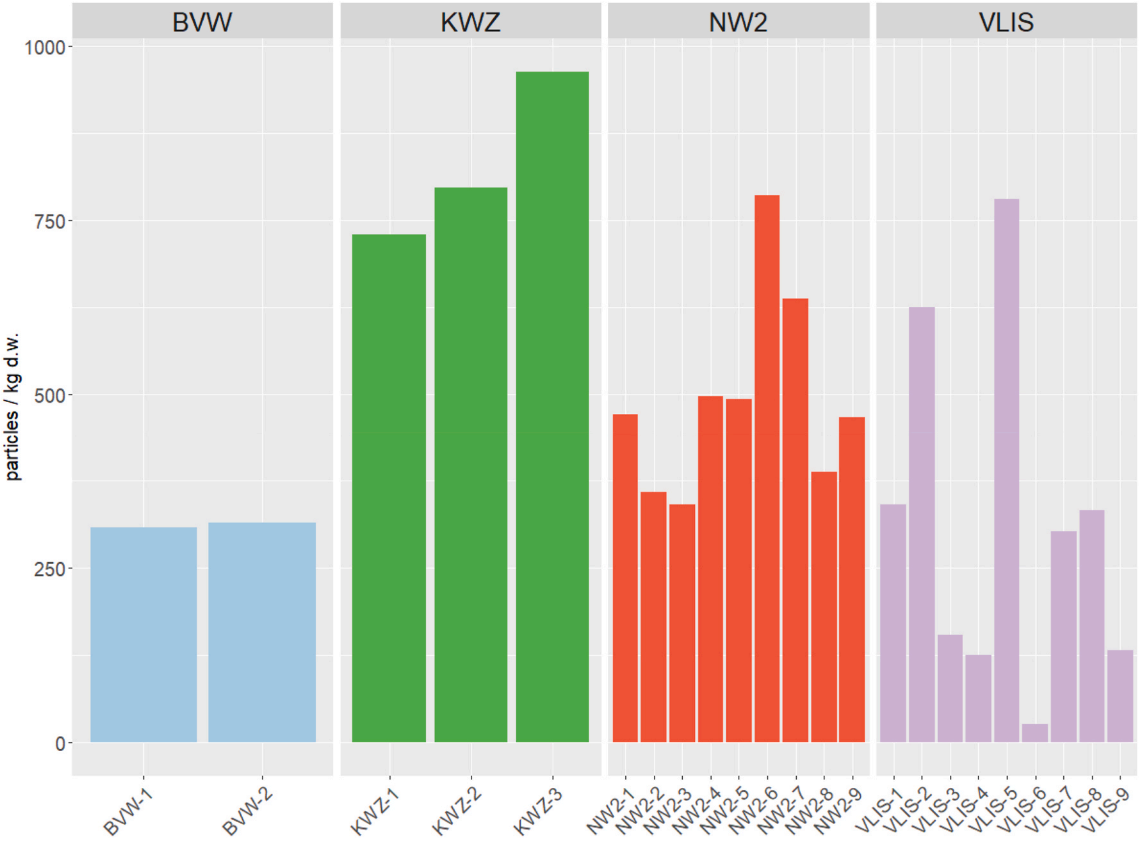

Fig. 2. Variation of total microplastic concentrations per location and sample. Boxplots of these data are shown in Fig. S3. One outlying low sample result for BVW was omitted based on it's Dixon's Q value (0.977).

the number of data points is too low (i.e. 2,3) to assess the micro-spatial variation.

It appears from these bootstrapping results that the mean value is independent of n (Fig. S4). The RSEM clearly decreases with increasing numbers of subsamples (Fig. 3). Using the proposed optimization criterion, that is to only increase n if the reduction of the RSEM is > 0.05, it appears that for location NW2 two replicate samples are already sufficient; and that for VLIS four replicates are necessary, respectively (Table S4). This information is relevant for the optimization of the number of samples per location with regard to monitoring costs. Microplastic sampling and analyses in general have relatively high costs, and the number of microplastic analyses is therefore often constrained by the monitoring budget. The proposed values for the number of replicates per location (Noorwijk2, 2; Vlissingen, 4) are in line with commonly used number of replicate analyses per location (see e.g. Bronzo et al., 2021).

The SEM tool and sample optimization criterion can also be applied to optimize the number of subsamples to be taken for a single (composite) boxcore, grab or shovel sample (Pan et al., 2021). If e.g. 10 subsamples are taken from a single sample, analysed and the data are analysed using the SEM tool, the homogeneity of the sample can be presented and a cost-effective number of subsamples can be derived using the presented optimization criterion.

3.3. Particle size distribution

The particle size distribution (PSD) plotted according to Kooi et al. (2021), shows that the smaller the particles the more abundant they are (Fig. 4, Table S2). The linear relationship (Fig. 4) is often lost at the lowest and highest side of the range due to measurement artefacts. The power law slope α of the PSD based on length is 3.76 (±0.18). This is substantially higher than an earlier reported value for marine sediment of 2.57 ± 0.20 (Kooi et al., 2021). For length, the slope (α) can hypothetically range between 0 and 3 (Kooi and Koelmans 2019). Values around 3 indicate a three-dimensional (3D) fragmentation pattern of the particles with full mass conservation, while lower values imply fragmentation in two dimensions, e.g. erosion of films or sheets. In this case, such an interpretation is surrounded by uncertainty. Indeed, we analysed the distribution for all particles from all sample locations, representing a broad coastal area. Many processes other than fragmentation can take place at such a scale, such as size, shape and density dependent transport, aggregation and sinking. Besides differences due to different instrumentation used, such hydrodynamical processes may explain the difference with the value reported for other marine sediments (Kooi et al., 2021). Nevertheless, the current alpha value would still be the best proxy to use in data alignments for risk assessments for marine benthic communities at the scale of these Dutch coastal waters (Koelmans et al., 2022).

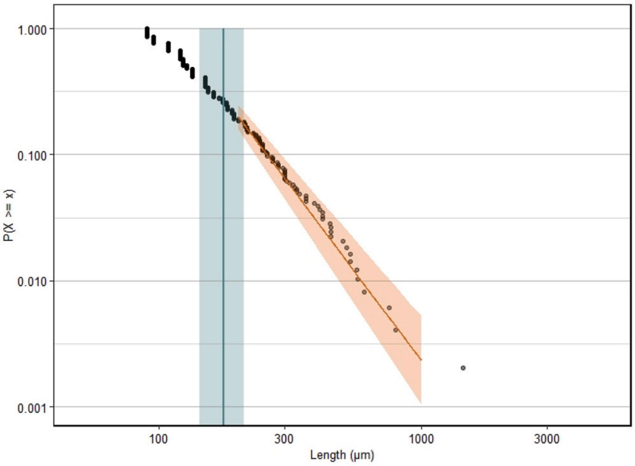

Fig. 4. Particle size distribution for particle length. The brown band shows the SD of the relation. The green vertical line indicates the lower end where the log-transformed relationship stops to be linear, with the green zone indicating the SD.

Particles larger than 1000 µm were not detected in any of the samples. As the overall percentage of larger particles is low, finding such a particle is merely a matter of chance (Kooi and Koelmans 2019). Larger sample amounts are necessary to get an accurate number concentrations for these larger particles. Analysing large amounts of sediment is, however, not feasible in cost-effective monitoring.

3.4. Microplastic characterization and spatial differences

In total 13 different polymers were found. The relative amount differed only slightly between the different size classes. In both size classes, rubber, PS, PP, PE-Cl and PE make up more than 95% of the plastics in terms of number, with PE being the most abundant plastic (±60%) (Fig. S5). Only small amounts of other polymer types (ethylene vinyl acetate, polycarbonate and polyoxymethylene) can be found (±5%). PE and PP having the largest share based on particle numbers is largely in line to earlier findings (Haave et al., 2019; Lorenz et al., 2019; Mintenig et al., 2020). The relative polymer compositions between the fractions 100–300 µm and 300–1000 µm appear to be comparable (data not shown).

Polymer composition appear to be different between the samples from the Wadden sea area (BVW, KWZ) and the West coast (NW2, VLIS). The samples from the Wadden sea area seem to contain relatively more PS and PP, whereas rubber is noticeably absent in these samples (Fig. 5). The differences in rubber concentrations can probably be attributed to differences in anthropogenic pressures. The West coast locations (VLIS, NW2) are located in a densely populated area, with intense car traffic, industry and international harbours (Rotterdam and Antwerpen), whereas the location KWZ lies in the relatively pristine Wadden sea area. The location KWZ situated at the end of the river Ems, which flows through a less densely populated area with some harbours and industry upstream, is the only location where a significant concentration of PA is present. The rubber found on the West coast may, at least in part, originate from the rivers Rhine and Maas. Earlier, it was shown that between 10 and 15% of the polymers in the river Meuse are rubbers (Mintenig et al., 2020; Roscher et al., 2021). Note however that more monitoring data and statistical analysis are planned to obtain reliable assessments of differences in polymer composition between locations in the near future.

The polymer compositions at the four locations seem to be different from the compositions at the locations in an earlier study (Lorenz et al., 2019). These differences can possibly be explained by the fact that the locations studied by Lorenz et al. are on the Wadden Islands side facing the Atlantic Ocean, while BVW and KWZ are close to the mainland. The plastic composition of the latter locations is most likely more influenced by the influx of plastic from fresh inland waters (river Ems and Ijsselmeer, respectively). For these two locations (VLIS and NW2) the close proximity to the Dutch West coast might explain the notable differences in polymer type composition compared to Lorentz et al. (2019). Another reason might be the size range that has been investigated. Lorenz et al. focused on particles larger than 20 µm, whereas in the present study particles larger than 100 µm were analysed. More Dutch monitoring data are needed to enable quantitative statistical comparisons with data for different locations and with data from the literature.

4. Conclusions

We have improved a monitoring and data analysis method with potential relevance for MSFD and OSPAR monitoring of microplastics in marine sediments. Strict QA/QC criteria were followed which resulted in a reliable dataset, which is one of the first for Dutch marine coastal

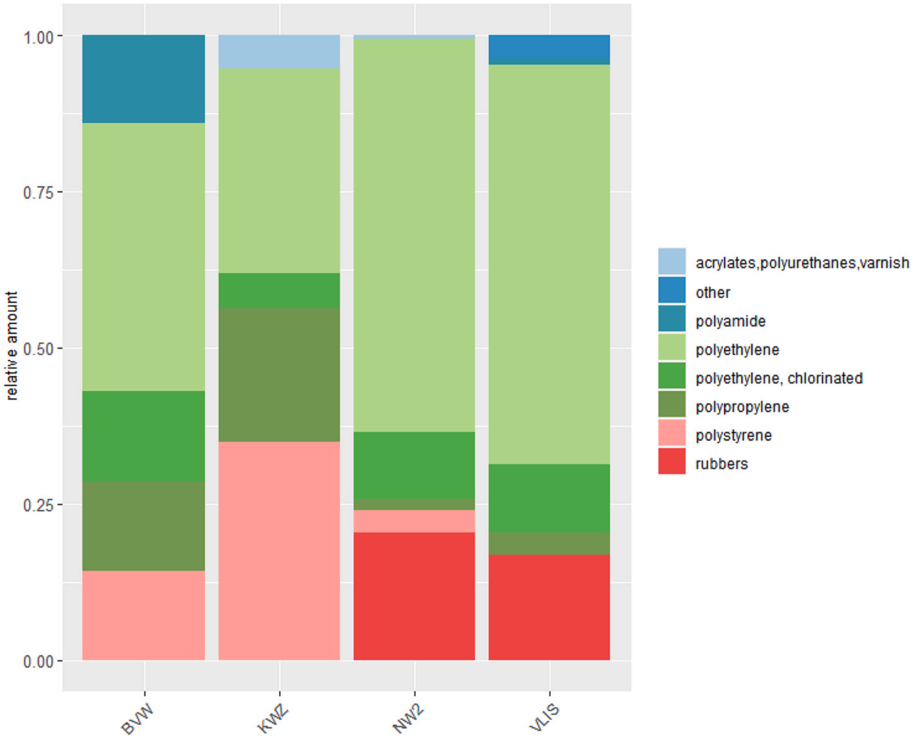

Fig. 5. Relative polymer type amount for the four locations. Rubbers: mostly rubber type 3. Other: ethylene-vinyl-acetate, polyester, polycarbonate and polyoxymethylene.

sediments. State-of-the-art μFTIR and validated data processing software provided accurate information on polymer composition, length, width, volume and estimated mass of the particles, as required by the MSFD. A data analysis method is provided that allows for the optimization of the number of replicates used for a specific location, using the standard error of the mean (RSEM) as the statistical optimization metric. This metric provides a measure of micro-spatial variation of microplastic concentrations at the location level. This is relevant for the selection of monitoring locations with relatively low micro-spatial variation, which are more suitable for the detection of trends. It is shown that for relatively homogenic locations two samples can be cost-effective, while for more heterogenic locations four samples can be necessary. Furthermore, the SEM tool can also be applied to investigate the effect of the number of subsamples from a single (composite) sample on the RSEM, by measurement of e.g. ten subsamples and processing the results. The resulting RSEM model can be used for a cost-effective choice of the number of subsamples to be analysed.

Data available on request.

Author statement

Patrick S. Bäuerlein: Writing - Original Draft, Writing - Review & Editing, Visualization, Conceptualization, Data Curation, Formal analysis, Maarten W. Erich: Investigation, Conceptualization, Willem M.G. M. van Loon: Writing - Original Draft, Writing - Review & Editing, Conceptualization, Methodology, Svenja M. Mintenig: Writing - Original Draft, Investigation, Conceptualization, Albert A. Koelmans: Supervision, Conceptualization, Writing - Original Draft, Writing - Review & Editing, Resources.

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Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marenvres.2022.105804.

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