A new analytical approach for monitoring microplastics in marine sediments

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ABSTRACT

A two-step method was developed to extract microplastics from sediments. First, 1 kg sediments was pre-extracted using the air-induced overflow (AIO) method, based on fluidisation in a sodium chloride (NaCl) solution. The original sediment mass was reduced by up to 80%. As a consequence, it was possible to reduce the volume of sodium iodide (NaI) solution used for the subsequent flotation step. Recoveries of the whole procedure for polyethylene, polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene and polyurethane with sizes of approximately 1 mm were between 91 and 99%. After being stored for one week in a 35% H_2O_2 solution, 92% of selected biogenic material had dissolved completely or had lost its colour, whereas the tested polymers were resistant. Microplastics were extracted from three sediment samples collected from the North Sea island Norderney. Using pyrolysis gas chromatography/mass spectrometry, these microplastics were identified as PP, PVC and PET.

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1. Introduction

Following the invention of the first modern plastic "Bakelit" in 1907, inexpensive high-volume manufacturing techniques were developed. These resulted in the rapidly growing mass production of plastics, which for the most common polymer types commenced in the 1930s and 1940s (Cole et al., 2011). Today, we cannot imagine life without plastics, which are used in a vast array of fields for use in packaging, construction, medicine, electronics, automotive and aeroplane components (Goodship, 2007). In 2009, 230 million tons of plastics were produced globally per year. Europe is the second major region of plastic production (Plastics Europe, 2010). Germany is the third major plastic producer after China and the USA (Abts, 2010). According to sea-based sources such as shipping, fishing and transport activities (Horsman, 1982; Pruter, 1987; Derraik, 2002) and land-based sources such as tourism, adjacent industries or river inputs (e.g. Reddy et al., 2006; Browne et al., 2010), plastics are entering our seas and oceans, "posing a complex and multi-dimensional challenge with significant implications for the marine and coastal environment and human activities all over the world" (UNEP, 2009). For example, in the German Bight (North Sea) anthropogenic debris was one of the three major flotsam categories (32.4 items/km^2); more than 70% of floating debris was made up of plastic items (Thiel et al., 2011). It is assumed that microplastics that are no longer visible to the naked eye represent a major element of the global problem (Cole et al., 2011; Andrady, 2011).

As an amendment to the Marine Strategy Framework Directive (European Parliament and the Council, 2008) the "composition of micro-particles (in particular microplastics) has to be characterised in marine litter in the marine and coastal environment" (European Parliament and the Council, 2010). However, there is still little monitoring data on the occurrence of microplastics in sediments, since analytical methods have yet to be developed. Several attempts have been made to monitor microplastics in sediments based on density separation in solutions of sodium chloride (NaCl) (Thompson et al., 2004; Reddy et al., 2006; Browne et al., 2010; Claessens et al., 2011). Higher density salts such as zinc chloride (Imhof et al., 2012; Liebezeit and Dubaish, 2012) and polytungstate (Corcoran et al., 2009) were used to enable to higher density polymers to be extracted. One important issue in the extraction of microplastics from sediments is the sediment sample mass applied for extraction. When NaCl was used for density separation, 1 kg sediments was usually extracted (Thompson et al., 2004; Reddy et al., 2006; Claessens et al., 2011), with the exception of Browne et al. (2010), who used a sediment volume of only 50 mL. When

expensive higher density salts were used, the sample volume was as low as 500 mL (Liebezeit and Dubaish, 2012) and 68 mL (Imhof et al., 2012). Corcoran et al. (2009) used a sample mass between 150 and 190 g. The reason for using such low sample volumes could be to cut analytical costs by decreasing the amount of high-density salts, which are expensive. However, since the distribution of microplastics in sediments could be very low or heterogeneous in some areas, it is advantageous to have a large sample quantity. Increasing the sample volume increases the prospects of detecting microplastics, and also guarantees that random samples are representative of the study areas.

Another challenge involved in analysing microplastics in sediments is the presence of biogenic organic matter. It often has a low density, meaning that it floats on the surface of the salt solution and adheres to the filter. Shaw and Day (1994) reported difficulties in optically distinguishing plastics from other organic matter when analysing microplastics. For this reason, Liebezeit and Dubaish (2012) suggested pretreating sediments using a solution of 30% H_2O_2 to remove natural organic debris.

The aim of the present study was to develop an extraction technique for separating microplastics from sediments. The technique consists of the following two steps: (i) fluidisation of sediments in a saturated NaCl solution and (ii) a subsequent flotation of microplastics in a high-density salt solution. Since we wish to work with environmentally friendly chemicals and to ensure maximum cost-effectiveness, sodium iodide (NaI) was selected for the second step. The distribution of microplastics in sediments is often heterogeneous, making it necessary to analyse an appropriate amount of sediments. This usually requires a large amount of salt for density separation. In the course of developing the method, emphasis was therefore placed on decreasing the sediment sample mass in the first step to enable the economic use of NaI in the second step. In addition, different solvents for dissolving biogenic matter were tested. The two-step extraction method was applied to sediment samples from the island of Norderney, located off the German North Sea coast. Extracted particles were analysed using pyrolysis gas chromatography/mass spectrometry (Pyr-GC/MS) to identify the types of polymer found.

2. Materials and methods

2.1. Chemicals and materials

In order to prepare a saturated NaCl solution, common food-grade table salt (Suedsalz GmbH, Heilbronn, Germany) containing small amounts of sodium ferrocyanide as an anticaking agent was diluted in distilled water. NaI (grade ≥99.5%) and a 30% stabilised hydrogen peroxide (H_2O_2) solution were purchased from Sigma Aldrich (Steinheim, Germany). Solutions of 35% stabilised H_2O_2 and of 37% hydrochloric acid (HCl) (technical grade) were purchased from AppliChem (Darmstadt, Germany). The latter was diluted to a concentration of 20% by adding distilled water. Solutions of sodium hydroxide (NaOH) with concentrations of 20, 30, 40 and 50% were prepared by dissolving NaOH pellets (AppliChem, Darmstadt, Germany) in distilled water.

In order to perform recovery experiments, plastic particles of approximately 1 mm in size were produced by cutting plastic products made of polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), expanded PS (EPS) and polyurethane (PUR) (see Fig. 1). The types of polymer from all of the products were specified by referring to the respective recycling code. The particles and their origin are described in Table 1.

Plastic pellets and raw plastic materials were used (Table 2) to test 12 different polymer types such as PVC, PET, polyacrylate, acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), PUR, PE, PP, low-density PE (LDPE), linear LDPE (LLDPE), high-density PE (HPDE) and expanded PS (EPS) for resistance against H_2O_2, NaOH and HCl.

2.2. Tests for eliminating biogenic organic matter

Different solvents (H_2O_2, NaOH, HCl) were tested to dissolve biogenic matter of animal and plant origin. Simultaneous experiments were performed to test the resistance of common polymers. In the first test, 4 ml of a 30% H_2O_2 solution was
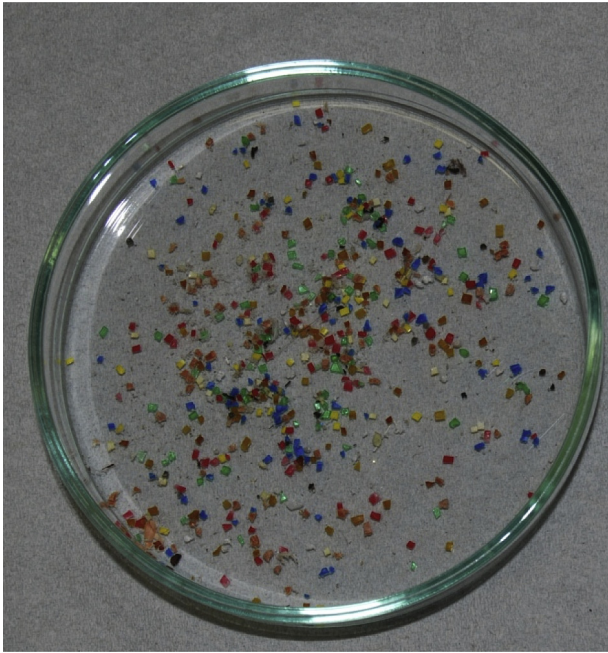

Fig. 1. Plastic particles used for recovery experiments.

added to 10 mL vials containing PVC, PET, PA 6, ABS, PC, PUR, PP, LDPE, LLDPE and HPDE (10 particles between 0.5 and 1 mm and 10 particles between 2 and 3 mm) and different biogenic organic matter of either animal or plant tissue commonly found in beach sand samples, e.g. pieces of bone, chitin carapaces, feathers and pieces of different plant tissues such as seed capsules, fruits, leafs and stems (16 particles between 0.5 and 1 mm and 10 particles between 2 and 3 mm). The vials were then closed. The particles were exposed to a 30% solution of H_2O_2 for seven days. Optical changes were noted for each particle immediately after adding the solvent, and thereafter every 24 h. Optical changes were observed using a stereomicroscope (Wild M3Z Leica Microsystems, Wetzlar, Germany). The intention was to test how long it would take for all biogenic particles in the respective size class to disappear and to determine whether plastic particles would demonstrate resistance.

In the second series of tests, 4 ml NaOH and HCl, respectively, were added to different particles of biogenic organic matter such as parts of leafs and chitin carapaces (four particles between 0.5 and 1 mm and 10 particles between 2 and 3 mm) stored in 10 ml vials. These experiments were performed on a small scale compared to those involving H_2O_2 described above, because it sufficed for an approximate comparison to be made of the three reagents. HCl was only used in a concentration of 20% because it has been reported that many polymers are not resistant to it in a higher concentration (Bürkle, 2010; Amsler and Frey, 2012). The experimental test conditions for HCl and NaOH were identical to those for H_2O_2 described above.

A third experiment was performed using 4 mL of a 35% H_2O_2 solution in reaction with various biogenic organic matter (13 particles between 0.5 and 1 mm and 10 particles between 2 and 3 mm). Likewise, 12 plastic particles in two size classes (<1 mm and between 1 and 5 mm) of the most common polymer materials (PVC, PP,

Table 1
Polymer types, colours, products and sources of plastic particles used for recovery experiments (PE: polyethylene, PP: polypropylene, PVC: polyvinyl chloride, PET: polyethylene terephthalate, PS: polystyrene, EPS: expanded PS, PUR polyurethane).

Polymer type	Colour	Original product	Source
PE	Red	Plastic laboratory bottle	Lab inventory
PP	Blue	GC vial cap	Lab inventory
PVC	Orange–brown	Pipe	Local hardware store
PET	Green	Water bottle	Local discounter
PS	Yellow/white	Yoghurt cup	Local discounter
EPS	White	Styrofoam® packaging	Lab inventory
PUR	Yellow	Raw material	KTK Kunststofftechnik Germering (Germany)

Table 2
Polymer names and types and supplier of plastic particles used for resistance experiments (PE: polyethylene, LDPE: low-density polyethylene, HDPE: high-density polyethylene, LLDPE: linear LDPE, PVC: polyvinyl chloride, PC: polycarbonate nature, PA: polyamide, ABS: acrylnitrile-butadiene-styrene, PET: polyethylene terephthalate, PP: polypropylene, PS: polystyrene).

Polymer name/ product	Polymer type	Supplier
PE laboratory bottle	PE	Lab inventory
LDPE 1840D	LDPE (pellet)	LyondellBasell Industries AF S.C.A., Rotterdam, the Netherlands
HDPE ACP 9255plus	HDPE (pellet)	LyondellBasell Industries AF S.C.A. Rotterdam, the Netherlands
LLDPE 2049E	LLDPE (pellet)	Dow Plastics, Midland, USA
Raw material	PVC	KTK Kunststofftechnik GmbH, Germering, Germany
Raw material	PC	KTK Kunststofftechnik GmbH, Germering, Germany
Raw material	PUR	KTK Kunststofftechnik GmbH, Germering, Germany
Raw material	PA	KTK Kunststofftechnik GmbH, Germering, Germany
Raw material	ABS	KTK Kunststofftechnik GmbH, Germering, Germany
Raw material	PET	KTK Kunststofftechnik GmbH, Germering, Germany
PPHC 904 CF	PP (pellets)	Borealis AG, Vienna, Austria
PS 143E	PS (pellets)	BASF SE, Ludwigshafen, Germany

LDPE, PE, HDPE, PET, PUR, PS, PC, PA, ABS and EPS) were prepared as described above. All particles were photographed using a digital camera coupled to the stereomicroscope in a specified position. The surface area of each particle was determined using "Image J", an image-processing program. After seven days, particles that had not dissolved fully were extracted from the solutions using tweezers and photographed again using the digital camera coupled to the stereomicroscope (Wild M3Z Leica Microsystems, Wetzlar, Germany) in the same position. The surface area of each particle was determined again and compared to the previous surface area.

2.3. Sediment sampling and sample preparation

On 2 November 2011, three sediment samples were taken from a beach on the northern side of the island Norderney, which is about 14 km long and 2.5 km wide. Norderney is one of the eastern Frisian Islands, located on the German coast of the North Sea. Norderney is heavily influenced by tidal streams and periodic storm surges in spring and autumn, producing a high degree of sediment mobilisation. The northern side of the island, which is part of Lower Saxony's Wadden Sea National Park, is characterised by beaches with a width of more than 250 m, far away from the urban area, which is concentrated in the western part of the island. The randomly chosen sampling sites were located in the 'recreation zone' (Zone III), containing the main tourist beach areas. The maximum distance between sampling sites was approximately 80 m. The coordinates were 53.722067°/7.243967° for sample 1.6u, 53.722383°/7.247033° for sample 2.6u and 53.722383°/7.247025° for sample 2.6 l. Approximately 3 kg sediments were taken randomly from a depth of about 3 cm and placed in precleaned brown glass bottles using a stainless steel spoon. The spoon was cleaned using sea water and lint-free paper between each sample. The bottles were sealed and stored at room temperature in the laboratory until analysis. Next, 2 kg wet sediments from each bulk sample was transferred to ceramic bowls, which were subsequently covered with aluminium foil. The bowls were placed in a drying oven at 60 °C until the sediments had dried out. A total of 1 kg dry sediments (approximately 600 ml) was weighed out and sieved through a 1 mm mesh. The <1 mm fraction was further analysed for the presence of microplastics using the procedure described in Sections 2.4 and 2.5, with the exception that the sediment samples from Norderney did not undergo treatment with H_2O_2 because they contained only small quantities of biogenic material.

Ten samples of 1 kg aquarium sand (grain size 0.1–0.9 mm, Rosnerski Baustoffe, Koenigslutter, Germany) were spiked with seven types of plastic particles (PE, PP, PVC, PET, PS, EPS and PUR, see Fig. 1 and Table 1) in order to determine the recoveries of different types of plastic particles for the total extraction procedure. Recoveries were determined for the two-step extraction procedure without ($n = 6$) and including a step to remove organic matter ("oxidation" step) by using a solution of 35% H_2O_2 ($n = 4$) (see Section 2.2). Recoveries were obtained by calculating the plastic particles remaining on the filter. The independent two-sample t-test was used to test for any significant difference between these two series of tests.

Two samples of 1 kg aquarium sand (grain size 0.1–0.9 mm, Rosnerski Baustoffe, Koenigslutter, Germany) were used in order to determine the procedural blank of

the total extraction procedure. Two procedural blank samples were extracted as described in Sections 2.4 and 2.5, one (blank 1) using a four times reused NaCl solution for pre-extraction (see Section 2.4) and the other (blank 2) using a newly prepared NaCl solution to test for a higher background contamination risk from reusing the NaCl solution.

2.4. Fluidisation (first extraction step)

Seeking to avoid background contamination, the following preventive measures were taken during the extraction procedure: all materials and vessels used for the first time for one sample were cleaned in the dish washer if possible, or otherwise thoroughly by hand, and covered with aluminium foil immediately after washing them. Lab coats were worn at all times during analysis; all materials and vessels were covered with aluminium foil after each individual step; and the workplace for stereomicroscopic analysis was cleaned before opening and analysing the petri dishes in which microplastics were stored.

Microplastics were extracted from sediment samples by applying a two-step extraction procedure. The basic idea was to use a combination of fluidisation of sediments in a lower density salt followed by flotation of microplastics in a higher density salt. First, the air-induced overflow (AIO) method was developed to pre-extract sediments by fluidisation using a saturated NaCl solution. The aim of this first step was to decrease the sediment sample mass for the second density separation step by flotation. The principle of the AIO method is shown in Fig. 2. In order to prepare a saturated NaCl solution (26% weight/weight) with a density of 1.2 g/cm^3 (Schäfer and Synowietz, 1984), NaCl (food-grade table salt) was dissolved in distilled water. A 2 L glass beaker was placed inside a glass vessel (25 × 30 cm). Approximately 1.5 L from the 6.5 L of saturated NaCl solution was pumped from a glass storage tank into the 2 L glass beaker using an indoor fountain pump (Gardena, Ulm, Germany). The pump was then stopped, and moderate bubbling was generated by a constant air flow (air flow rate of approximately 0.1 L/s) introduced into the NaCl solution. The sediment sample (1 kg) was added quickly to the NaCl solution. The air-generated turbulent gas bubbles induced a stochastic process that forced specific lighter particles to move more frequently and quickly to the top layer of the solution than specifically heavier ones. The remaining NaCl solution was pumped into the beaker with a constant flow rate of about 2.4 L/min, inducing an overflow of the top layer into the outer glass vessel. Once 4 L of the NaCl solution had been transferred, the air flow rate was increased to approximately 0.2 L/s. The overflowing mixture of NaCl solution and floating particles was collected in the outer glass vessel (see Fig. 2). After the separation process, a series of thorough rinsing steps was performed to rinse the beaker with the saturated NaCl solution, which was then collected in the outer vessel. The aim of applying numerous rinsing steps was to ensure the efficient transfer of plastic particles from the beaker to the outer vessel. The beaker was rinsed in several steps using a saturated NaCl solution filled in a wash bottle: first of all, the outer upper edge of the beaker was rinsed to remove any potential microplastics that had adhered to the outer wall. The beaker was then lifted by holding it by the previously cleaned upper edge of the vessel; the NaCl supernatant was decanted into the outer vessel. The bottom of the beaker was subsequently rinsed from the outside while still being held by the upper edge. The beaker was then put on a glass plate that was placed across the outer vessel (sustained by two parallel metal rods and the edges of the outer vessel) and rinsed inside and outside. In this way, any adherent particles were washed into the collecting vessel below. Finally, the glass plate was rinsed over the collecting vessel. The original sediments that remained in the beaker were then discarded. Since it was too time consuming to directly transfer the total supernatant through a filter paper, the supernatant in the outer vessel was then transferred stepwise into a 25 μm stainless-steel sieve installed on a collecting pan with outlet using a stainless steel ladle (both Retsch, Haan, Germany). The 'sieved' NaCl solution was stored for reuse for a maximum of six subsequent runs. The residue in the sieve containing sediments and microplastics was rinsed again with 250 ml distilled water into the outer glass vessel. The residue was then decanted from the outer glass vessel by thoroughly rinsing with about 800 ml NaCl solution onto a folded filter paper placed in a glass funnel. The filter cake was additionally rinsed with 700 ml distilled water to clean sodium chloride from the sample material.

The filter was dried in an oven at 60 °C for 12 h, after which the filter residue was carefully added to a glass beaker (500 mL) using a stainless steel laboratory spoon (residues were thoroughly removed from the folded filter using the spoon).

2.5. Flotation (second extraction step)

The second extraction step was performed using the principle of the flotation of lower density microplastics in a saturated NaI solution with a density of 1.8 g/cm^3 (Schäfer and Synowietz, 1984). Different volumetric flasks (volumes 50–200 mL) were used for this purpose. The volume of the volumetric flask was chosen according to the sediment mass resulting from the first extraction step. The sediment sample was added to the volumetric flask, and a 60% (weight/weight) NaI solution was added to roughly three-quarters of the flasks. It turned out that it was important to ensure the NaI volume remained below the angle of the belly of the volumetric flask to make sure that the content of the flask could be
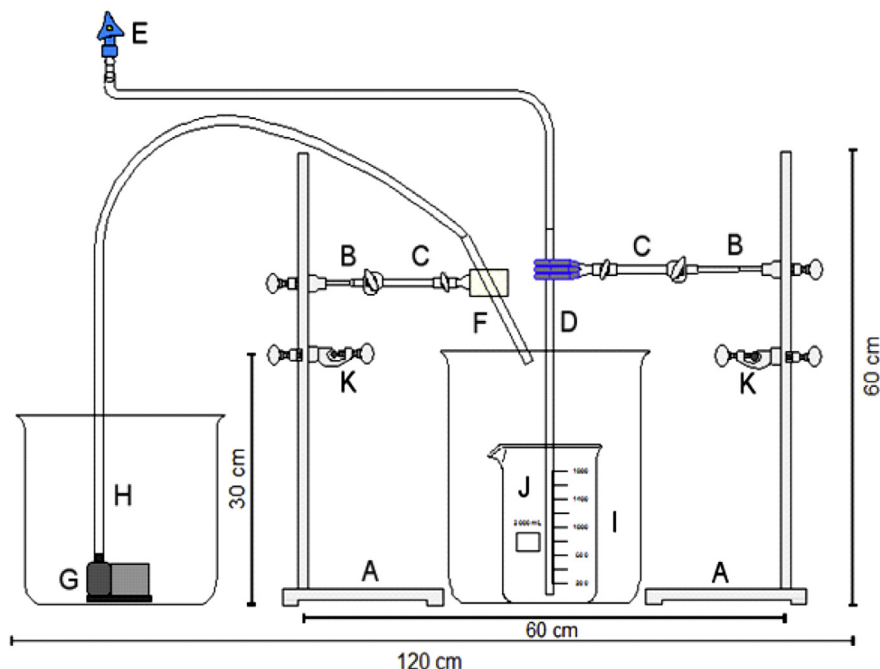
1mm

Fig. 2. Experimental setup for the AIO method (first extraction step). A: laboratory stands, B, C: clamps, D: glass tube, E: laboratory fume, F: glass tube, G: indoor fountain pump, H: storage tank for NaCl (25 × 25 cm), I: outer glass vessel (25 × 30 cm), J: inner glass beaker (2 L), K: double sockets with parallel metal rods.

mixed completely by shaking. The flask was shaken by hand for about 20 s and then filled with NaI solution to the highest calibration mark. The flask was then shaken again for approximately 10 s to limit the amount of minerals on the solution surface due to adhesion and surface tension. The flask was then filled with NaI solution to 1 cm below the rim. After a settling time of 10 min, the supernatant was decanted into a 200 mL glass beaker up to about 1 cm below the angle of the belly, enabling the suspension to be shaken again for 10 s. The procedure of shaking, refilling, shaking, refilling, sedimentation and decantation was replicated five times. The supernatant in the 200 mL glass beaker was subsequently poured into a vacuum filtration unit using a nitrocellulose filter (0.45 μm pore width, Mili, China). The glass beaker was rinsed thoroughly with about 250 ml distilled water into the vacuum filtration unit. The filtered NaI solution was collected for reuse and the filter was air-dried for further analysis. The filter in the vacuum filtration unit was then washed with 750 ml more distilled water to remove any salt residues from the filter.

If H_2O_2 was applied to eliminate biogenic organic particles from the filter cake, a further filtration step involving passing the supernatant through a new filter was tested to remove NaI from the filter. To this end, the filter cake was rinsed thoroughly with about 75 ml distilled water into the 200 ml glass beaker. The content of the glass beaker was filtered again by vacuum filtration through a new filter, and washed with approximately 500 ml distilled water to remove any residues of NaI. The filter was subsequently rinsed with about 20 ml of a 35% H_2O_2 solution into a glass beaker and stored in the solution at room temperature for seven days.

Since some of the particles on the filter had stuck to the protruding upper edge of the top glass funnel of the vacuum filtration unit, these adhered particles were rinsed carefully with a small amount of distilled water into a glass petri dish. Finally, the filter was transferred to the second glass petri dish. The filtered NaI solution was collected for reuse, and the content of both petri dishes was air-dried for further analysis and covered with aluminium foil.

In addition, an investigation was carried out to ascertain whether a separatory funnel (with volumes of 0.25, 1 and 2 L) is applicable as a suitable alternative to volumetric flasks. Sediments were taken from the 500 mL glass beaker and placed in the separatory funnel, and the NaI solution was added to roughly three-quarters of the funnels. After shaking for approximately 10 s and following a settling time of 10 min, the deposited sediments were drained off the funnel by opening the stopcock. Shortly before the sinking surface layer and the floating microplastics reached the zone above the stopcock, the stopcock was instantaneously closed. As a consequence, only the surface layer of the solution with the floating plastics remained in the funnel. The content of the funnel was then filtered as described above.

An optical analysis of the filters was performed using a stereomicroscope (Wild M3Z, Leica Microsystems, Wetzlar, Germany) providing 6.5-fold up to 40-fold magnifications. Optical images of particles were taken using a digital camera, which was connected to the microscope via a phototube. Particles that were optically identified as potential plastics were separated using tweezers.

2.6. Pyr-GC/MS analysis

Extracted particles were analysed using Pyr-GC/MS by applying a Multipurpose Sampler 2XL equipped with the thermal desorption system (TDS 3) (Gerstel, Muelheim, Germany). Pyrolysis GC is used to obtain structural information about macromolecules by carrying out a GC/MS analysis of their thermal degradation products. Ten polymer types of the most common standard polymers (PVC, PC, PUR, PA, ABS, PET, LDPE/EVA, PP, PS and EVA, see Table 2) were also analysed using Pyr-GC/MS to obtain a pyrogram database. Details on the polymers, experimental conditions and resulting pyrograms are provided by Fries et al. (2013). Briefly, the particle was pyrolysed at 700 °C for 60 s. The temperature of the transfer line was 350 °C. In order to separate and detect pyrolysis products, the TDS was interfaced to a gas chromatograph (GC) 7890A coupled to a mass selective detector (MS) 5975C (both Agilent Technologies, Santa Clara, USA). A 30 m HP-5MS capillary column (Agilent Technologies, Santa Clara, USA) with an inner diameter of 250 μm and a film thickness of 0.25 μm was used to achieve chromatographic separation. The GC oven was programmed from 40 to 180 °C at 15 °C/min and then to 300 °C at 5 °C/min, held for 12 min. The carrier gas was helium (purity 5.0) with a vent flow of 60 mL/min. Mass spectra of organic plastic additives (OPAs) and pyrolysis products were obtained by running the MS in full scan mode with a mass range between 10 and 600 amu. Pyrolysis products were identified by consulting the NIST05 mass spectra library.

3. Results

3.1. Removal of biogenic organic matter

First, the results for the 30% H_2O_2 solution are presented. Concerning biogenic organic particles >1 mm, 50% (most of which was of animal origin) had completely dissolved after seven days. The other 50% also demonstrated obvious reactions, i.e. they became discoloured or transparent, or had partly dissolved. Results for biogenic particles <1 mm were similar (56% had dissolved completely while the other particles were either discoloured and/or had partly dissolved). For all polymer types from both size classes, a reaction was observed in that gas development occurred to different extents. The experiment with polymer particles >1 mm in size also showed visible changes for PA, PC and PP, which were more transparent, smaller and/or thinner after exposure. Definite optical changes were also determined for PET (brownish colour) and LLDPE (fragmented). For particles <1 mm, one range of

polymers was slightly more transparent, thinner or smaller (PVC, PET, PA, PUR, PP, LDPE, LLDPE). It was observed that PC was definitely thinner than before.

Results of the experiments involving NaOH and HCl revealed that overall optical changes to biogenic organic particles were weaker than the reaction using 30% H_2O_2. None of the biogenic organic particles had dissolved completely or become fully transparent. A strong reaction was only observed with 30% NaOH and 20% HCl, respectively, with a beetle carapace.

The experiments involving the 35% H_2O_2 solution revealed that each biogenic organic particle showed a visible, measurable reaction, as with the particles exposed to the 30% H_2O_2 solution. The outcome regarding biogenic organic particles >1 mm was that four particles had dissolved completely, eight were transparent and one was inconsistent. About 92% of particles had dissolved completely or were becoming discoloured. Regarding micro-particles (<1 mm), 25% had dissolved completely. Six particles were discoloured or had become transparent, three had dissolved, two showed a considerable reduction in size and two were inconsistent. None of the plastic particles showed a significant change in size, except for PP and PE particles in the <1 mm size category, which showed a reduction in size of 17.2% and 15.9%, respectively. To test the applicability of a treatment involving a 35% H_2O_2 solution using the AIO/flotation method developed here, a beach sand sample collected from the island of Fehmarn located in the Baltic Sea was used since they contained large quantities of biological organic material. Fig. 3 shows what the filter looked like after the two extraction steps had been taken before (Fig. 3a) and after (Fig. 3b) having been treated with 35% H_2O_2. Treatment of the finally extracted fraction on the filter with 35% H_2O_2 showed a visible effect compared to the non-treated one to the extent that the treated filter contained visibly fewer biological organic particles that were completely bleached.

3.2. Separating microplastics from sediments

During the first extraction step, the original sample mass of 1 kg was reduced to values between 43.9 and 122.7 g by fluidisation of the sediments in a NaCl solution (see Table 4). Volumetric flask sizes (ml) and volumes of NaI solution recommended for different sediment sampling masses are shown in Table 3. For sediment sample masses between < 50 and 200 g, volumes of NaI solution between <90 and 255 mL turned out to be sufficient. The NaI volume and the volume of the volumetric flask had to be increased in line with the sediment mass.

Recovery rates calculated for the total extraction procedure with and without the oxidation step using H_2O_2 are shown in Table 4. No significant differences were observed concerning recovery rates for any tested polymer types between the two series of tests ($p > 0.05$,

Fig. 3. Biogenic matter on the filter of a beach sand sample from Fehmarn a) before and b) after treatment with H_2O_2.

Table 3
Volumetric flask size and volume of NaI solution used for different sediment sampling masses resulting from the first extraction step.

Volumetric flask size (ml)	Sample mass (g)	NaI consumption (ml)
50	<50	≤90
100	50	170
100	75	125
100	85	110–115
200	100	255
200	125	215
200	150	200
200	175	190
200	200	195–200

unpaired student's *t*-test). The results demonstrated that additional filtration and rinsing during the application of the oxidation step had no effect on extraction efficiencies. Thus mean recoveries were determined for all 10 runs. Mean recovery rates for PE, PP, PVC, PET, PS, EPS and PUR ranged between 91% (relative standard deviation, RSD: 0.4%) for PET and 99% (RSD: 3.0%) for PE. Only the extremely low dense EPS exhibited a lower recovery rate of 68% (RSD: 0.4%) (Table 4).

3.3. Background contamination

The results of the optical analysis of procedural blanks 1 and 2 are shown in Fig. 4a–d. Blank 1 contained 39 coloured fibres, mainly blue and light blue, and red and black. A total of 33 coloured fibres, mainly blue, light blue and red, were extracted from blank 2. The processing and storing of aquarium sand could not completely be ruled out as a source of these fibres. In addition, between three and five fibres were found in each petri dish exposed to laboratory air for five days with an optical appearance resembling that found in the procedural blank samples.

3.4. Occurrence of microplastics in sediments from Norderney

Optical images of five particles, which could potentially be microplastics, are shown in Fig. 5. Two particles were found in sample 1.6u (# 1, #2), one in sample 2.6u (#3) and two in sample 2.6 l (#4, #5). The following pyrolysis products were identified in the pyrograms obtained by the Pyr-GC/MS analyses of particles #2 and #5 and of a PET standard (the retention times, RT, for individual compounds are given in brackets): 1,2-propanedione-1-phenyl (RT: 6.675 min), benzenecarboxylic acid (RT: 7.370 min), divinyl terephthalate (RT: 10.622 min), terephthalatic acid (RT: 11.064 min), 2-(benzyloxy)ethyl vinyl terephthalate (RT: 25.145 min) and ethan-1,2-diyl divinyl diterephthalate (RT: 31.252 min). Several terephthalate-based compounds are also described as pyrolysis products for PET in Tsuge et al. (2011). A comparison of the pyrogram of particle #3 with that obtained from the Pyr-GC/MS analysis of PVC revealed a match of 13 major peaks, albeit with different relative peak intensities. The following characteristic peaks were identified (RT are given in brackets): o-xylene (RT: 3.989 min), p-xylene (RT: 4.223 min), napthalene (RT: 7.213 min), 1-methylnapthalene (RT: 8.312 min), 2-methylnapthalene (RT: 8.419 min), acenaphthene (RT: 9.976 min), fluorene (RT: 10.925 min) and anthracene (RT: 13.171 min). Hence, an original PVC-based polymer is likely. A comparison of the pyrogram obtained from the pyrolysis of PP and the transparent white particle #4 revealed that this particle was PP. Important evidence for the presence of PP was the first peak, which was identified as 2,4 dimethyl-1-heptene − a typical pyrolysis product of PP (Tsuge et al., 2011). It was not possible to identify particle #1 because there was no comparable type of pyrogram in the database of analysed polymer types.
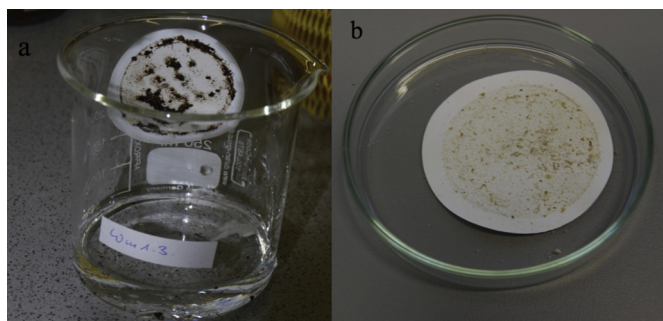
Table 4
Recoveries for seven different polymer types from sediment samples ($n = 6$ for two step-extraction, $n = 4$ for two step-extraction including H_2O_2 oxidation of the material on the filter) including mean recoveries (PE: polyethylene, PP: polypropylene, PVC: polyvinyl chloride, PET: polyethylene terephthalate, PS: polystyrene, EPS: expanded PS, PUR: polyurethane, RSD: relative standard deviation). The given sample mass is the mass of sediments resulting from the first extraction step.

Run	Reduced sample mass (g)	Polymer type						
		PE	PP	PVC	PET	PS	EPS	PUR
		Particles counted on the filter						
1	74.1	10	8	10	10	9	9	10
2	78.1	10	10	10	10	10	3	10
3	87	10	10	10	9	10	8	10
4	43.9	10	9	10	8	10	5	10
5	74.9	10	10	10	10	8	10	10
6	122.7	10	10	10	9	7	7	10
Mean recovery rate without "oxidation step" $n = 6$ (%)		100	95	100	93.3	90	70	100
7	69.3	10	9	9	8	10	2	7
8	74	10	10	10	7	10	8	10
9	45.5	10	10	10	10	9	8	10
10	56.7	9	10	8	10	9	8	9
Mean recovery rate with "oxidation step" $n = 4$ (%)		97.5	97.5	92.5	87.5	95	65	90
Mean recovery rate $n = 10$ (%) (SD)		99 (3.0)	96 (6.6)	97 (6.4)	91 (10.4)	92 (9.8)	68 (24.8)	96 (9.2)

All sediment samples collected from Norderney contained fibres with a length from about 0.5 mm to a few centimetres, with a diameter of less than 100 μm. These samples were divided into coloured and uncoloured groups. The latter also contained black, brown and beige fibres in addition to mainly translucent fibres to distinguish fibres of a probable natural origin from obviously coloured fibres — mainly blue, red and green — where an artificial origin was more likely. The numbers of uncoloured and coloured fibres were 213 and 21 in sample 1.6u, 55 and 14 in sample 2.6u, and 194 and 10 in sample 2.6.l.

4. Discussion

4.1. Removing biogenic organic matter

The task was to define an appropriate reagent and reaction conditions that cause the effective deletion of biogenic organic substances whilst ensuring that plastics remain resistant to it. The first step taken before testing a reagent was to verify and compare chemical resistance tables issued by plastics manufacturers. Some polymers such as PET, PUR, PA and PC are reported to be non-inert or only constrictively inert to H_2O_2, NaOH and HCl (Bürkle GmbH, 2010; Polydraack GmbH, 2006). However, tests under respective test conditions are recommended. Generally, concentrated acids and alkalis are known to destroy biological tissue by essentially cleaving proteins, carbohydrates and fats. However, biogenic organic particles were dissolved to a lower extent following the use of NaOH and HCl than when H_2O_2 was applied. Consequently, H_2O_2 was used for further processing. A 30% H_2O_2 solution was found to be the ideal reagent for deleting about 50% of biogenic organic matter, However, a number of visible changes in some polymers were also observed, including the development of gas bubbles, indicating a chemical reaction between H_2O_2 and the polymers. The optical analysis of polymers before and after exposure to H_2O_2 was

Table 5
Densities of polymer types, and European demand for commonly used polymers, densities of minerals mainly present in sediments, and densities of saturated salt solutions used in this study (w/w: weight/weight).

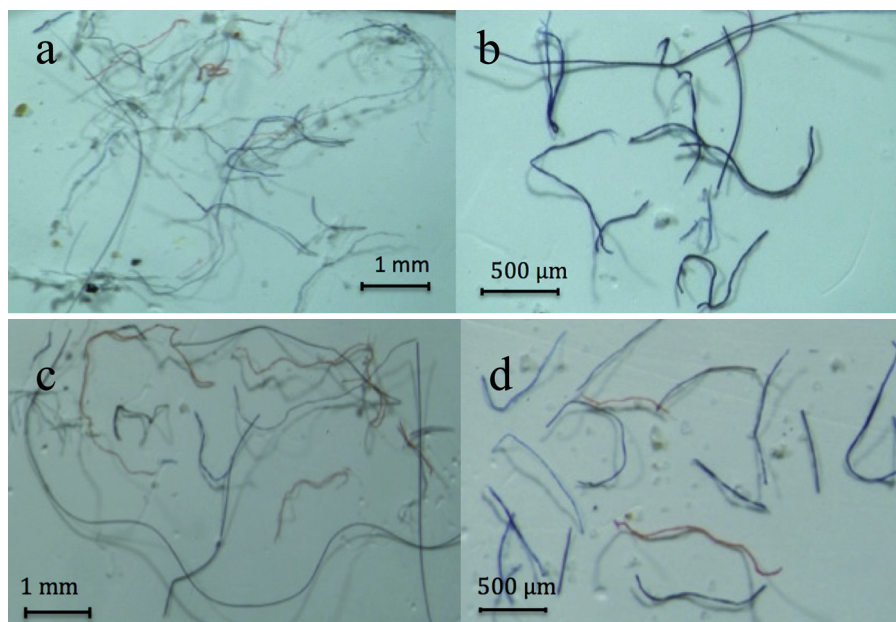| Polymer abbr.	Polymer name	European demand [%] (Plastics Europe, 2010)	Density [g/cm³] (US EPA, 1992)	Density with Additive [g/cm³] (US EPA, 1992)	Mineral	Density [g/cm³] (Matthes, 2001)	Salt solution (saturated)	Density [g/cm³] (Schäfer and Synowietz, 1984)
HDPE	High-density polyethylene	12	0.94–0.97	1.18–1.28 (PE)	Quartz	2.65	NaCl (26% w/w)	1.2
LDPE	Low-density polyethylene,	17	0.89–0.94		Potassium Feldspar	2.56	NaI (60% w/w)	1.8
PP	Polypropylene	19	0.89–0.91	1.04–1.17	Light Mica	2.80		
PVC	Polyvinylchloride	11	1.3–1.58	1.3–1.7	Magnetite	5.2		
PET	Polyethylene terephthalate	8	1.29–1.40		Calcite	2.7		
PS	Polystyrene	8 (incl. PS-E)	1.04–1.08	1.2–1.5				
EPS	Expanded polystyrene		0.015–0.03[a]					
PA	Polyamide	2.3	1.07–1.08	1.13–1.62				
PC	Polycarbonate	1.2	1.20					
PMMA (acrylic)	Polymethyl-methacrylate	0.9	1.17–1.20					
SAN	Styrolacrylnitrile	1.9 (incl. ABS)	1.02–1.08					
ABS	Acrylonitrile/butadiene/styrene		1.01–1.08	1.18–1.61				
PUR	Polyurethane	7	1.17–1.28					

[a] BASF SE (2011).

Fig. 4. Fibres extracted from procedural blank 1 (a, b) and procedural blank 2 (c, d).

found to be insufficient for evaluating the resistance of polymers to H_2O_2. In contrast, it emerged that calculating the reduction in surface areas of polymers before and after exposure was an appropriate tool for determining their resistance to a solution of 35% H_2O_2. However, it must be mentioned that applying the surface area calculations apparently caused significant measurement inaccuracy. This could be seen in the frequent positive values for the change in surface area. Since an increase in particle size due to reaction with H_2O_2 is unlikely, the positive values act as an indicator of the magnitude of measuring error. Thus an absolute
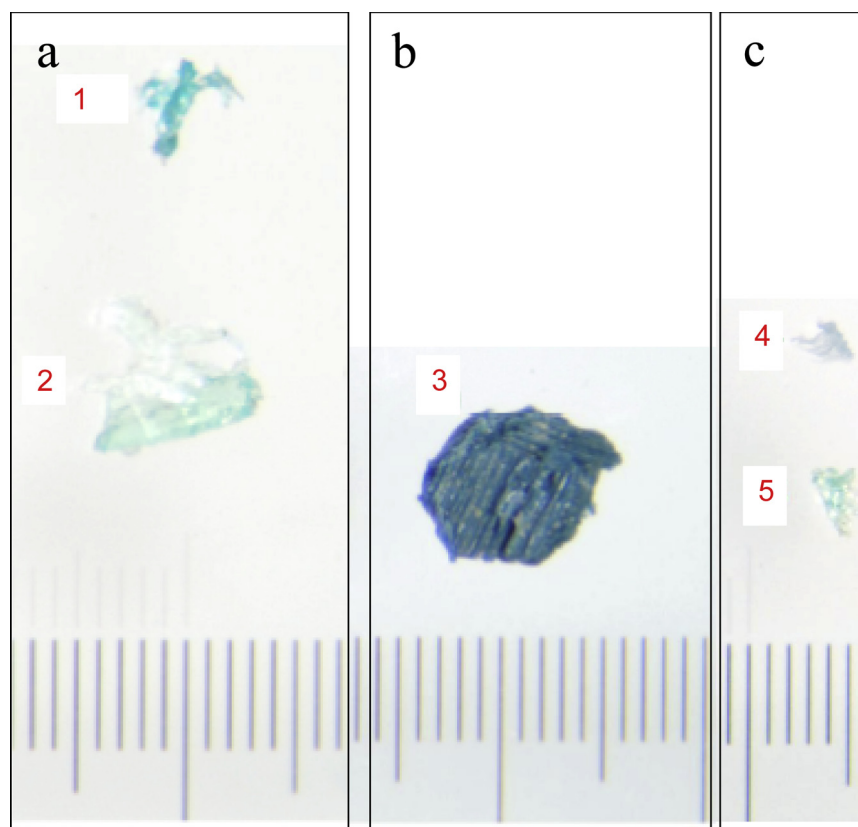

Fig. 5. Microplastics extracted from sediments collected at Norderney (a: sample 1.6u, b: sample 2.6u, c: sample 2.6 l). The scale bar at the bottom is divided into 100 μm markings (the length between elongated markings is 1 mm).

measurement error was estimated from the mean of positive values for surface change, amounting to 6.2% for particles of <1 mm in size and 2.5% for particles of >1 mm in size. When taking this into account, the reduction in size of PP and PE particles <1 mm was approximately 10%. Together with the fact that PP and PE exhibited no considerable change in size in the >1 mm size class, these results could be interpreted as a minimal change in PP and PE in contact with H_2O_2. In summary, a week-long treatment using a 35% H_2O_2 solution is suitable for removing biogenic organic particles whilst ensuring that all tested polymer types are resistant to it. The results of the present study show that the remaining particles became discoloured, i.e. white or transparent, after H_2O_2 treatment. Since other studies report that microplastics found in marine sediments are often naturally coloured white or transparent (reviewed in Hidalgo-Ruz et al., 2012), it must be mentioned that H_2O_2 could also complicate optical analysis rather than facilitate it, since natural particulates can then no longer be distinguished from plastics that are whitish or transparent. To conclude, the oxidation step during analysis is only recommended if there is a large amount of organic matter on the filter comprising almost a layer of particles, making visual selection impossible. It is therefore recommended that this "oxidation step" is not applied routinely in the extraction procedure, but should be determined on a case-by-case basis for each sample, depending on the quantity of biogenic matter obtained in the filter following extraction. In contrast to Liebezeit and Dubaish (2012), it is also recommended to expose filters to H_2O_2 instead of the whole original sediment sample, since it may be difficult to treat 1 kg sediments. Since iodide ions act as catalysts, causing an undesirable decomposition of H_2O_2 into water and oxygen, a reaction of NaI and H_2O_2 must be avoided by all means. The reaction is extremely exothermic, and causes strong gas development. After having conducted a few trials, it became evident that residues of NaI can only be eliminated fully by additional filtration and rinsing through a new filter.

4.2. Separating microplastics from sediments

Our results demonstrate the importance of performing blank samples to obviate overestimations of microplastic pollution of marine sediments when taking microplastic fibres into account. From our experience gained whilst developing the method, we assume that extraction methods for microplastics in general are highly susceptible, particularly to background contamination by fibres from the working environment. Since fibres contained in samples were optically very similar to those found in procedural blanks (Fig. 4), contamination of samples with fibres must be avoided by all means during sampling and analysis. The sources of fibre background contamination were not proven. It was found that recycling the NaCl solution had no significant impact on background contamination. The problem of fibre background contamination has been touched upon in the past (Fries et al., 2013), and a comparison of background contamination levels among laboratories was urgently recommended by Hidalgo-Ruz et al. (2012). However, it is likely to be difficult to find appropriate sediments that are free of fibres for running the procedural blank.

By applying the two-step separation method, it was possible to efficiently extract common polymers of about 1 mm in size from 1 kg sediments. Recovery rates can be fed as correction factors into evaluations of environmental sample analyses, as suggested by Claessens et al. (2011). Since EPS had the lowest density of those polymers tested, its lower recovery rate may be attributed to loss processes other than flotation. A loss of EPS was observed due to its strong adherence behaviour to glass surfaces. Up to now, recovery rates for extracting microplastics from sediments have only rarely been reported. The recovery rates of fibres and granules/spheres

reported in Claessens et al. (2011), using the method of Thompson et al. (2004) with a number of minor modifications, ranged from 68.8% to 97.5% (no information is given on recoveries for particular polymer types). Imhof et al. (2012) achieved a mean recovery rate of 95.5 ± 1.8% for 0.1 g microplastic particles from seven environmentally relevant plastic types (PA, PE, PVC, PC, HDPE, PET, and PP) with a diameter <1 mm in 1 L sediments using a $ZnCl_2$ solution.

A solution of NaCl (Thompson et al., 2004; Browne et al., 2010) or tap water (Zurcher, 2009) was used to separate microplastics from sediments by flotation of lighter particles on the solution surface. The use of NaCl for flotation is also recommended in the tool sheet for analysing microplastics in technical recommendations for implementing MSFD (JRC, 2011). One advantage of NaCl is that it is a relatively inexpensive salt, and also eco-friendly. However, the maximum density achieved using a saturated NaCl solution is only 1.2 g/cm³. Several common polymers such as PET, PVC, and PUR, as well as HDPE, PS, PA and ABS, which contain additives (US EPA, 1992), exceed this density (see Table 5 for an overview of the density ranges of common polymers, common minerals in sediments and saturated solutions of NaCl and NaI). The density of lighter polymers can be enhanced by the presence of additives, fillers or bio fouling processes (US EPA, 1992; Braun, 2003; Thompson et al., 2009; Moret-Ferguson et al., 2010; Hidalgo-Ruz et al., 2012). The use of NaCl or tap water may therefore lead to an underestimation of the microplastic content in sediments because the solution density is too low to enable their flotation. Instead, the density of the saturated NaI solution used in the present study is high enough to separate common polymers (including those containing additives) from higher density minerals (Table 5). However, two-step extraction is more time consuming than flotation using NaCl only. It was previously assumed that only lower density plastic particles with the capability of floating in sea water are present in beach sediments (Zurcher, 2009), which would mean that it would suffice to use only NaCl. However, it must be mentioned that higher density sediments and debris (Liebezeit, 2008; OSPAR, 2009; Browne et al., 2010) are also washed ashore. Consequently it must be assumed that the entire range of polymer types can potentially occur as microplastics in sediments on shorelines (Moret-Ferguson et al., 2010). Since high-density microplastics are present in beach sediments, flotation in a high-density solution is necessary to extract polymers of a broad density range. However, it must be said here that Browne et al. (2010) also extracted PVC from sediments using an NaCl solution for extracting microplastics from sediments.

As with all other higher density salts, NaI is a relatively expensive salt. In contrast to previously described methods involving large volumes of high-density salts (Imhof et al., 2012) or smaller sample masses (Corcoran et al., 2009; Liebezeit and Dubaish, 2012), we managed to reduce the volume of NaI solution by reducing the original sediment mass in the first extraction step. A relatively high sample amount of 1 kg enables a higher statistical relevance to be achieved when extrapolating from random samples to the overall test area. By applying our methodology, the analytical cost of extracting microplastics from sediments is cut remarkably, which is important for a routinely applicable monitoring method for microplastics in sediments. In addition, according to the German Water Hazard Classification (WGK), higher density salts such as $ZnCl_2$ and polytungstate which have been used in the past (Corcoran et al., 2009; Imhof et al., 2012; Liebezeit and Dubaish, 2012) are "severely hazardous to waters" (WGK3) and "hazardous to waters" (WGK2), respectively, whereas NaI poses only a "minor threat to waters" (WGK1) (Sigma Aldrich, product data sheets). An additional benefit of the AIO/flotation method presented here is that all materials used are available in any conventional lab setting and that no extra

apparatus needs to be constructed, which is the case for the apparatus invented by Imhof et al. (2012).

In previous studies, separatory funnels were often used for flotation (e.g. Thompson et al., 2004; Browne et al., 2010). In the present study, the use of separatory funnels with different volumes for flotation was compared to the use of volumetric flasks. Flotation in 1 and 2 L separatory funnels entailed a relatively large amount of minerals in the floating fraction due to the surface tension of the relatively large solutions' surface. In addition, numerous rinsing steps were required due to the large inner surface of the separatory funnels. Decantation of the solution in a volumetric flask turned out to be more effective than draining off from a separatory funnel with high volumes (1 and 2 L) in order to minimise rinsing steps to save NaI. It was impossible to use a smaller separatory funnel (250 mL) because the outlet clocked according to the low bore width (a larger bore width was not commercially available).

The two-step extraction method enabled microplastics to be extracted from environmental samples collected from a National Park of an East Frisian Island (Norderney) in the North Sea. The results of the Pyr-GC/MS analysis revealed the presence of higher density polymers such as PET and PVC, demonstrating the necessity to use higher density salts than NaCl. The occurrence of microplastics in sediments from a National Park indicates that marine plastic debris can potentially result in the contamination of protected areas with sensitive habitats by microplastics, which ought to be of special concern.

5. Conclusions

The AIO/flotation method based on two-step extraction using NaCl for pre-extraction to decrease the original sediment sample mass and NaI for the subsequent flotation of microplastics was found to be efficient for extracting common polymer types, including higher density polymers, from marine sediments. One particular advantage is that a lower solution volume of high-density salt (NaI) was required thanks to the reduction in mass of the sample achieved in the first step. Compared to previous attempts based on flotation in higher density salts, this method is eco-friendly, it incurs low material costs, and the equipment is easily obtainable. The device for applying the AIO/flotation method can easily be established in laboratories to monitor the occurrence of microplastics in sediments, even in countries with only standard laboratory equipment at their disposal. Since marine plastic pollution is a global problem, this would be a great advantage. Due to the high contamination potential for fibres, additional research is required to avoid contamination of samples by fibres from the working environment. Inter-laboratory comparisons and standardised protocols are necessary in the future as a prerequisite to implementing MSFD in Member States. In this way, quantitative data on microplastics will be less speculative, due to possible overestimations or underestimations. The results of applying the new method to environmental sediments indicate the occurrence of microplastics in sediments in Lower Saxony's Wadden Sea National Park, which contains sensitive habitats that deserve particular protection. Further studies are required to quantify and analyse the spatial distribution patterns of contamination by microplastics on Norderney and other islands along the North Sea coast.

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