



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% H₂O₂ 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/km²); 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

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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% H₂O₂ 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 (H₂O₂) solution were purchased from Sigma Aldrich (Steinheim, Germany). Solutions of 35% stabilised H₂O₂ 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, acrylnitrile-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 H₂O₂, NaOH and HCl.

2.2. Tests for eliminating biogenic organic matter

Different solvents (H₂O₂, 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% H₂O₂ solution was

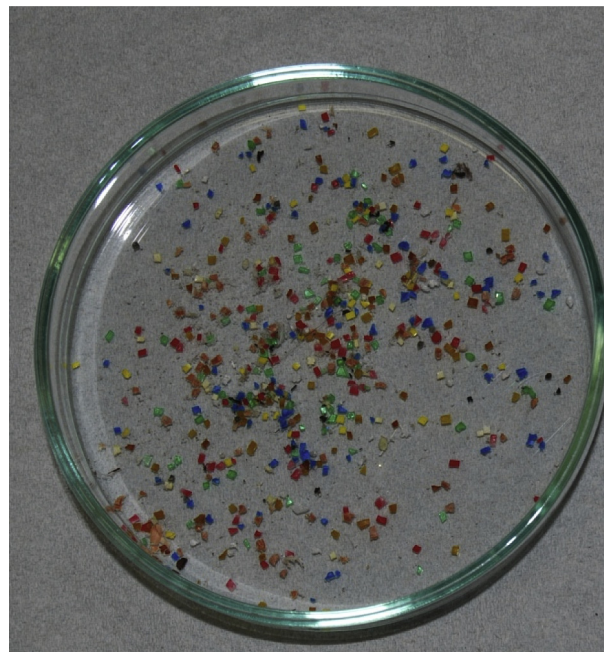


Fig. 1. Plastic particles used for recovery experiments.

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, leaves 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 H₂O₂ 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 stereo-microscope (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 leaves 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 H₂O₂ 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 H₂O₂ described above.

A third experiment was performed using 4 mL of a 35% H₂O₂ 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)

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