A new approach in separating microplastics from environmental samples based on their electrostatic behavior☆

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ABSTRACT

Numerous studies on microplastics (MPs; Ø < 5 mm) in the aquatic environment have been published, but knowledge about the occurrence and ecological risks of MPs is limited. This is in part because current data on the distribution of MPs are comparable only to a limited extent, due to the many different methods of investigation. In addition, sample preparation is often difficult such that standard procedures are lacking. The aim of this work was to simplify the preparation of different kinds of MP samples. Our method makes use of the electrostatic behavior of plastic particles to facilitate their separation from sample matter, with up to 99% of the original sample mass removed without any loss of MPs. To determine the efficacy of this approach, four different materials (quartz sand, freshwater suspended particulate matter, freshwater sediment, and beach sand) were spiked with MPs (size: 0.063–5 mm from the seven most common types of plastics, one bioplastic type, polyethylene fibers, and tire wear. A modified electrostatic metal/plastic separator was used to reduce the sample mass and concentrate the plastics based on their physical separation. The recovery achieved with this method was as high as nearly 100% for each type of material. The method was then tested on plastic particles of different shapes and types isolated from the Rhine River. These were successfully electroseparated from the four materials, which demonstrated the utility of this method. Its advantages include the simplified handling and preparation of different field samples as well as a much shorter processing time, because after the last separation step there is hardly any biological material remaining in the sample fraction.

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1. Introduction

The worldwide production of plastics has increased from 1.5 Mt in 1950 to 322 Mt in 2015. Of these, 58 Mt are produced in the European Union, Norway, and Switzerland (PlasticsEurope, 2016), with 18.5 Mt produced in Germany alone (CHEManager, 2016). After their intended use, plastic products often enter the environment by various pathways as plastic litter (Crawford and Quinn, 2017; Dris et al., 2015; Gasperi et al., 2015; Vince and Hardesty, 2017) and, via rivers, finally reach the oceans (BKV, 2017; Koelmans et al., 2014). There, UV radiation, mechanical abrasion, biological degradation, and disintegration act on the plastic litter

(Barnes et al., 2009; Browne et al., 2011; Cole et al., 2011; Song et al., 2017; Pathak and Navneet, 2017) to yield tiny plastic fragments, including those with a size < 5 mm (GESAMP, 2015), referred to as microplastics (MPs). Between 70 and 95% of marine MPs originate from land-based sources (Andrady, 2011; Duis and Coors, 2016; Mehlhart and Blepp, 2012). Moreover, MP contamination has been reported around the world in open water, sediment, and in organisms (Ivar do Sul and Costa, 2014). However, for target-oriented management options of MPs, knowledge about their abundance, distribution, and risk is far from sufficient and further investigations are required (Peng et al., 2017; Wang et al., 2017). Despite the similarity of the various sampling methods used in freshwater and marine environments, the amounts of organic and inorganic compounds in the samples are very different. For example, sediments consist almost exclusively of biomass components (Underwood et al., 2017; Wagner et al., 2014) such that chemical digestion, density separation, and other investigative processes are both difficult and costly (Hanvey et al., 2017).

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Currently, the separation of plastic particles mostly relies on chemical procedures, using solutions that differ in their densities (Hidalgo-Ruz et al., 2012; Imhof et al., 2012). However, this method may not be applicable to MPs with densities higher than those of commonly used solutions, as is the case for alkyd, polyester, and polytetrafluoroethylene. Furthermore, chemical treatment may lead to a partial or complete degradation of the MPs, preventing their further analysis (Rocha-Santos and Duarte, 2015; Nuelle et al., 2014). A key consideration in efforts to simplify MP separation is that the sample mass should be reduced and the biological materials removed without altering the properties of the particles. A reduction in the sample mass would significantly decrease the amounts of chemicals required for further processing. Secondly, less harmful and less costly solvents are needed. A promising physical solution was found for mass reduction in the recycling sector (Dötterl et al., 2000). The Korona-Walzen-Scheider (KWS) provides an electrostatic method that is not limited by particles densities. Devices that make use of the electrostatic properties in different recycling or separating processes (Köhnlechner and Sander, 2009) are manufactured by hamos GmbH (Penzberg, Germany). For this study the procedure was modified for one of them, using the surface charge of synthetic materials (Köhnlechner, 2000) to separate field samples with a previously determined grain size distribution and total organic carbon (TOC) content (Schäfer et al., 2015) into two fractions: one containing most of the natural matter, without any plastics (rest fraction), and another consisting of all MP particles and just a small amount of other substances (sample fraction). It was also examined whether the shape (Rodríguez-Seijo and Pereira, 2017), fouling, or type of the MP influenced the separation process.

2. Material and methods

2.1. Electrostatic separator

The hamos separators are used in sorting plastics and other materials as well as in metal detection, including metal deposition. In this study a hamos electrostatic metals/plastic separator, referred to as the KWS, was used. It divides non-conductive material, such as common plastics, from metal particles <8 mm in diameter using a dry separation process (Köhnlechner and Sander, 2009). Due to the conductive properties of sediments and other particulate matter, these can be separated from non-conductive MPs. An absolutely prerequisite is the use of carefully dried and unconsolidated samples; otherwise, the separator cannot completely divide the materials (hamos, 2016). The mixture to be separated is introduced via a vibrating conveyor into a rotating grounded metal drum and transported to the area of a corona electrode, where it is electrostatically charged with up to 35 kV (Fig. 1). The standard KWS has throughputs of several tons per hour, but for our purpose a trade fair demonstration device with dimensions of 60 cm × 60 cm × 60 cm and a weight of 57 kg was used. The filling funnel is 20 cm × 15 cm × 20 cm, allowing samples up to this volume to be separated directly. However, as the collecting trays can be emptied continuously, unlimited quantities can be separated. The KWS is operated via a touch panel from sigmatek (Landau, Germany) that enables all settings (voltage, rotation speed, vibration) to be saved and exported (hamos, 2016).

2.2. Grain size distribution

Natural materials must be used to show that their composition has no effect on the separating process used for natural samples. Grain size fractions were quantified by sieving four natural materials, quartz sand, freshwater suspended particulate matter (SPM),

freshwater sediment, and beach sand (Fig. 2, A-D), through a series of sieves with different mesh sizes (20, 63, 200, 630, and 2000 μm). A mixture of 20 g of freeze-dried material, 100 mL of bidistilled water, and agate balls was added into the 2000 μm sieve, sieved in a sonication bath for 1 min, and sieved again by hand. The sieved fraction was collected and sieved in the same way in sieves with mesh sizes of 630, 200, 63, and 20 μm. The procedure was repeated ten times with each sieve. The material fractions remaining in the sieves were centrifuged at 2000–3000 × g, dried at 105 °C, and weighed. Dry residues of the material were gravimetrically determined by drying 1 g of wet sediment at 105 °C on an aluminum plate in a moisture analyzer (MA 35, Sartorius AG, Göttingen, Germany). Dry residue measurements were repeated twice and the mean values (%) of the dry residues were calculated as described by Schäfer et al. (2015).

2.3. Total organic carbon (TOC) determination

The TOC content of the four different sample materials was analyzed by first acidifying 100–700 mg of freeze-dried sample material with 1 mL of hydrochloric acid (1 M) for 3–4 h. TOC measurement was conducted in a Eltra Helios Carbon/Sulfur analyzer CS-580A (Eltra GmbH, Haan, Germany) (Schäfer et al., 2015).

2.4. MP production

Products made up of the seven most frequently produced plastic varieties were used to produce MP standards to determine recovery: high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), (non-foamed) polystyrene (PS), polyvinyl chloride (PVC), and polymethyl methacrylate (PMMA) (PlasticsEurope, 2015). Standards were also prepared from three other plastics types: polylactic acid (PLA), polyethylene fibers, and self-made tire wear. The densities of the ten plastics types covered a range from 0.85 g/cm³ to 1.58 g/cm³ (Andrady, 2011). All plastics were characterized by pyrolysis-gas chromatography-mass spectrometry (PyGCMS), as specified by the manufacturer (Fries et al., 2013). MPs, including the tire wear, were produced by freeze-milling with liquid nitrogen using the freezer/mill 6800 (SPEX SamplePrep, Metuchen, NJ, USA). Each material was sieved into three size fractions (63–200 μm, 200–630 μm, 630–2000 μm), except the fibers, available only with a size in the range of 630 μm to 5 mm. Five-mm particles were punched from the materials (Fig. 2E). All particles were counted before and after the three separations in the four different sediments. The procedure was repeated using triplicate samples. The particles had a characteristic color, size, and shape, which prevented their confusion with naturally occurring MPs.

2.5. Recovery

To verify the validity and reliability of the KWS, recoveries were carried out using four different purified sample materials: quartz sand, freshwater suspended particulate matter, freshwater sediment, and beach sand (Fig. 2A–D). For each sample material, 150 g was spiked with ten particles of each plastic type (see "MP production") and size fraction (63–200 μm, 200–630 μm, 630–2000 μm, and 5000 μm). The lower limit of the particle diameter was 63 μm since smaller particles cannot be counted individually. The largest particles had a diameter of 5000 μm and were defined as such by the National Oceanic and Atmospheric Administration (NOAA) (Arthur et al., 2009). The spiked MPs were separated from the different sample materials using the KWS (Fig. 1) to sort the materials according to their conductivities