Water Research 85 (2015) 451–457

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method

Erik Dümichen [a], Anne-Kathrin Barthel [a], Ulrike Braun [a, *], Claus G. Bannick [b], Kathrin Brand [b, c], Martin Jekel [c], Rainer Senz [d]

[a] BAM Federal Institute for Material Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
[b] UBA Umweltbundesamt, Wörlitzer Platz 1, 06844 Dessau-Roßlau, German
[c] Technical University of Berlin, Water Urban Area, Strasse des 17 Juni, 10623 Berlin, Germany
[d] Beuth University of Applied Sciences, Luxemburger Straße 10, 13353 Berlin, Germany

ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
28 August 2015
Accepted 3 September 2015
Available online 7 September 2015

Keywords:
Microplastic
Identification and quantification of polymers
Thermogravimetric analysis
Evolved gas analysis
Gas chromatography mass spectroscopy

ABSTRACT

Small polymer particles with a diameter of less than 5 mm called microplastics find their way into the environment from polymer debris and industrial production. Therefore a method is needed to identify and quantify microplastics in various environmental samples to generate reliable concentration values. Such concentration values, i.e. quantitative results, are necessary for an assessment of microplastic in environmental media. This was achieved by thermal extraction in thermogravimetric analysis (TGA), connected to a solid-phase adsorber. These adsorbers were subsequently analysed by thermal desorption gas chromatography mass spectrometry (TDS-GC-MS). In comparison to other chromatographic methods, like pyrolyse gas chromatography mass spectrometry (Py-GC-MS), the relatively high sample masses in TGA (about 200 times higher than used in Py-GC-MS) analysed here enable the measurement of complex matrices that are not homogenous on a small scale. Through the characteristic decomposition products known for every kind of polymer it is possible to identify and even to quantify polymer particles in various matrices. Polyethylene (PE), one of the most important representatives for microplastics, was chosen as an example for identification and quantification.

1. Introduction

Synthetic polymers are important materials, especially for packaging and construction, due to the broad range of their application and material characteristics, their low production and processing costs, and their flexible forming. Used for many decades, their amounts are increasing year by year. In 2013 the consumption of synthetic polymers in Germany was about 17 million tons, and about 280 million tons worldwide (PlasticsEurope, 2013).

Due to the high consumption of plastic worldwide, it was only a question of time before plastic debris or particles entered the environment, especially the aquatic environment (Cole et al., 2011; Ivar do Sul and Costa, 2014; Moore, 2008; Thompson et al., 2004). Since the 1970s plastics particles have been detected in marine ecosystems (Carpenter and Smith, 1972). The size and shape of observed plastic particles varies significantly as does their chemical composition. Plastic debris and plastic particles can be detected on the sea surface, in the water column and sediment. The problem of contamination by plastic debris is not restricted to oceans; the presence of plastics is also documented in urban rivers (Mc Cormick et al., 2014), lakes (Free et al., 2014; Imhof et al., 2013) and wastewater treatment plants (Magnusson and Norén, 2014). It is described in the literature that biota ingest plastic particles (Murray and Cowie, 2011; Ugolini et al., 2013) and that plastic particles adsorb and concentrate toxic chemicals (Hirai et al., 2011; Teuten et al., 2009) Cauwenberghe et al. showed the uptake of microplastic by mussels (Van Cauwenberghe et al., 2015). Through this pathway, microplastic thus also may be accumulating in the human food chain. Therefore, the problem of plastic contamination is not merely an aesthetic one.

For monitoring and assessment, the European Working Group on Marine Litter has proposed a classification system for the size of synthetic polymers in the marine environment, which is to be applied uniformly in Europe. They defined polymer particles larger 25 mm as macroplastic and between 5 and 25 mm as mesoplastic.

* Corresponding author.
E-mail address: ulrike.braun@bam.de (U. Braun).

http://dx.doi.org/10.1016/j.watres.2015.09.002
0043-1354/

Polymer particles between 1 and 5 mm are called large microplastic and smaller 1 mm they are called small microplastic. In the present work, we focus in particles smaller 1 mm.

A distinction is made between primary and secondary microplastic. Primary microplastics are tailored specifically for use, for example, as industrial abrasives, but also in cosmetic products like peelings and shower gels, which predominantly contain PE (Fendall and Sewell, 2009). Secondary microplastics are formed from macroscopic debris due to the influence of mechanical forces or to oxidation and photochemical processes that are triggered by sunlight.

In the literature, the monitoring, sorting and analysis of plastic particles in the environment is still an area of controversial methods and discussion (Claessens et al., 2013; Hidalgo-Ruz et al., 2012; Imhof et al., 2012; Nuelle et al., 2014). The various environmental matrices (e.g. water, suspended solids, biota or soil and sediment) require different sampling methods. To sample water different methods are used, here the dimension of the filter, net or the sieve and the amount of water filtered determining what particles are detected. Often the received filtrates require further concentration (visual identification or chemical/biological treatment). For sediment sampling visual (microscopic) or flotation methods are often applied. In these methods the particles' shape (or colour) and the different densities of various polymers preclude any comprehensive selection of plastic particles. For a biological assessment, the classification of particle size and numbers in various matrices may be sufficient. However, for a detailed understanding of the origin and the assessment of the pathways of these particles, identification and quantification are necessary.

Today microplastics are identified by Fourier transformed infrared (FTIR) (Claessens et al., 2011; Frias et al., 2010; Thompson et al., 2004) or Raman spectroscopy (Imhof et al., 2012). In both methods the polymers are determined on the basis of the energy absorption of characteristic functional groups. These methods work well with high certainty and have the advantage of being nondestructive. In addition, because these methods produce visual images, the dimension of the particles can be determined. In principle, “quasi-quantification” by known polymer density and shape is possible but not practical: the data evaluation of the imaging techniques is very time-consuming, requires skilled personnel and is difficult to automate, and not all particles can be detected (size limitation of the methods). Therefore, a pre-selection of samples (e.g. by microscope, filtering or flotation) is done before the measurements. However, this selection limits the species that can be detected using the given selection method. Further approaches (Fabbri, 2001; Fries et al., 2013) use Py-GC-MS. In this method, isolated plastic particles can be identified with high certainty by their characteristic decomposition products.

For the quantification of different microplastic particles in the environment, no comprehensive metrological test methods are available yet. In much of the currently published data, values are limited to numbers of particles per mass or volume of environmental samples (Claessens et al., 2013; Cole et al., 2011; Hidalgo-Ruz et al., 2012; Imhof et al., 2012; Ivar do Sul and Costa, 2014; Moore, 2008; Nuelle et al., 2014; Thompson et al., 2004). No polymer-specific, comprehensive value exists. However, SI-based values of microplastic concentration in environmental samples are needed for monitoring and to set regulatory limits.

This article will present a new method (Duemichen et al., 2014) that allows the identification and even the quantification of polymers in different, solid environmental samples. In the method used, thermoextraction and desorption coupled with gas chromatography-mass spectroscopy (TED-GC-MS), environmental samples are pyrolysed and the decomposition gases are analysed. Identification and quantification of characteristic decomposition products of each polymer allows the determination of microplastics in various environmental samples. In contrast to the use of Py-GC-MS (Fries et al., 2013), we are able to analyse the polymer particles in environmental samples without any pre-selection.

We will show in this work that is possible to identify PE microplastics with certainty in environmental samples using TED-GC-MS by examining the characteristic decomposition products that differ from the complex decomposition products of the matrices. This is carried out by measuring PE-spiked environmental matrices that were taken from natural sources (PE-free). Besides polypropylene (PP), and polystyrene (PS), PE is the most frequently identified micro particle in the environment (Claessens et al., 2011; Frias et al., 2010; Ivar do Sul and Costa, 2014; Thompson et al., 2004). This is caused by the fact that PE (low and high density) as well as PP are produced in great quantities (PlasticsEurope, 2013) and used for many consumables and packing products. Especially low-density PE (LDPE) is used for packing materials and is a high potential precursor for microplastics. Therefore for this work LDPE was chosen as an example polymer for the experiments. As environmental matrices, soil, suspended solids and mussels were used. In addition we will show that TED-GC-MS is also suited to quantify PE in environmental samples. Therefore this method enables the determination of SI-based concentration values in the percent of PE per gram weight of the environmental sample. This will be the first step to implement a method for routine analytics to determine concentration values of the specific polymers in complex environmental samples to monitor and limit values.

2. Material and methods

2.1. Samples

The mussel sample and the sample of suspended solids are from the Environmental Specimen Bank (ESB) UBA, Germany. The mussels were taken from the Elbe River and processed in accordance with the relevant standard operating procedures (SOP). The suspended solids were taken from the Spree River in Berlin, also according to the SOP of ESB. The soil sample was taken at a site in Berlin. It was from the surface layer of soil on a sandy substrate under oak trees. This layer is dominated by the presence of a large amount of organic matter. All matrices were homogenized by cryomilling. The LDPE of common plastic bag was used for identification as well as for quantification. It was cut into small pieces (about 1 mm). In preceding tests we were able to verify that for the measurements the PE content is independent of particle size. This is because most common thermoplastics melt before they decompose independent of their particle size, morphology and structure.

For the external matrix calibration, standards of 1.64 wt%, 3.10 wt%, 4.94 wt%, 9.58 wt% and 15.21 wt% of LDPE in soil material were prepared by adding soil material to LDPE particles in a crucible until a total weight of (4 ± 0.04) mg was reached.

2.2. TED-GC-MS (TGA-SPE/TDS-GC-MS)

Samples of 4.00 ± 0.04 mg were placed in 150 μL aluminum oxide crucibles for thermogravimetic analysis (TGA). All measurements were carried out with a single-arm horizontal thermobalance TGA/SDTA 851 (Mettler/Toledo, Gießen, Germany) equipped with an auto sampler. All samples were measured under nitrogen from 25 to 600 °C at a heating rate of 10 °C min^{-1}. A gas flow of 90 ml min^{-1} was set.

For thermal extraction twisters (polydimethylsiloxane, 10 mm x 0.5 and 1.0 mm, Gerstel, Mülheim a/d Ruhr, Germany) were used. These adsorber specimens were fixed in a desorption tube (OD 6.0 mm) with two stainless sieves and coupled directly to the TGA