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Quantification of polyethylene terephthalate microplastics and nanoplastics in sands, indoor dust and sludge using a simplified in-matrix depolymerization method

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ABSTRACT

An effective 3-step method for the quantification of mass of polyethylene terephthalate microplastics and nanoplastics (PET MNPs) in complex environmental matrices was developed based on a simplified in-matrix depolymerization. Liquid chromatography (LC) coupled with ultraviolet (UV) detection was used for detection and quantification. Recoveries for PET-spiked sand samples were $99 \pm 2\%$ (1 mg/L) and $93 \pm 7\%$ (30 mg/L). The limit of quantification (LOQ) for PET was 0.4 $\mu\text{g/g}$ for sand, 1 mg/g for indoor dust and 0.2 $\mu\text{g/g}$ for wet sludge. This method was applied to seven beach sand samples, 20 indoor dust samples and one sewage sludge sample. PET MNPs levels in sand samples were all below the limit of detection (LOD) of LC-UV (0.1 $\mu\text{g/g}$). The concentrations of PET MNPs in indoor dust samples ranged from 1.2 to 305 mg/g and the PET MNPs in liquid sludge was 1.5 mg/L.

1. Introduction

Microplastics are recognized as emerging contaminants of public concern, giving rise to the need for analytical capacity and methods to measure and monitor microplastics in a variety of matrices. Microplastics are defined as plastic particles smaller than 1 mm (International Organization for Standardization), though other definitions have also been convention within the environmental microplastic community, e.g. <5 mm (GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection), 2016). Here we use the abbreviation “MNPs” to represent all small plastic particles with a diameter smaller than 5 mm, including both microplastics and nanoplastics (particle dimensions in nanometer scale).

As most high production volume plastics are not biodegradable, MNPs can accumulate in different environmental compartments like sludge and sediments, terrestrial soils and indoor dust (Liu et al., 2019). Furthermore, MNPs have been detected in human feces (Zhang et al., 2021), lungs (Pauly et al., 1998) and even in human placenta (Ragusa et al., 2021).

1.1. PET as environmental pollutant

In 2020, the world production capacity of polyethylene terephthalate (PET) fiber reached 53 million tons (EMR (Expert Market Research), 2021). The largest application of PET is the production of synthetic fibers (up to 60%) and the remaining is mostly for the production of bottles (30%) and packaging (10%) (Plastics Insight, 2016). Textile microfibers, often consist of PET (Napper and Thompson, 2016; Cai et al., 2021). These microfibers have dimensions ranging from 12 to 18 μm in thickness and their fragments in environmental samples are typically shorter than 1 mm. Research has shown that PET textile garments lose thousands of microfibers (up to 1–2 g for fleece) upon each washing cycle (Browne et al., 2011; Hartline et al., 2016; Napper and Thompson, 2016; Barrows et al., 2018). These microfibers are not degraded in wastewater treatment plants and end up partly in sewage sludge (often turned into biosolids for soil fertilizers) and partly in the treated wastewater effluents that are emitted to surface water (Napper and Thompson, 2016). Besides, PET microfibers released from textile during abrasion and wear pollute both outdoor and indoor

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environments with inhalable sized fibrils (Cai et al., 2021). Another source of secondary PET MNPs is PET packaging and other products that escape waste collection and become litter (Geyer et al., 2017). PET MNPs from fibers in wastewater and from degradation of macroscopic PET items are thus introduced into river systems, oceans, sediments and biota (Browne et al., 2011; Jambeck et al., 2015), as well as air (Liu et al., 2019) and potentially human bodies (Cai et al., 2021; Zhang et al., 2021).

1.2. Analytical approaches

Due to the variety of MNPs regarding shape, size and type, and the complexity of environmental sample matrices, the analysis of MNPs is challenging. Sample pretreatment steps are of critical importance for the performance of the method overall. Qualitative analysis of MNPs, describing their colors, sizes, shapes and identities, is generally conducted using microscopy (e.g. optical, electron, scanning microscopes and etc.) followed by infrared (IR) or Raman spectroscopy (Barbosa et al., 2020). Quantitative analysis of microplastics can be done by identifying and counting plastic particles, preceded by adequate sample pretreatment to remove matrix based on sieving, filtration, destruction of biological samples, or density separation extraction, field flow fractionation etc. (Barbosa et al., 2020; Rocha-Santos and Duarte, 2015). Several other quantitative approaches, based on thermal decomposition followed by mass spectrometry (MS) detection, have been developed (Dümichen et al., 2015; Rocha-Santos and Duarte, 2015; Silva et al., 2018; David et al., 2018). For example, pyrolysis gas chromatography-MS (Py-GC-MS) analysis is used to quantify the chemical composition of the particles and the mass in the sample (Rocha-Santos and Duarte, 2015). Thermal decomposition methods need to balance small sample intake and the challenge of achieving representative samples in which the analyte will be distributed in particle form, which results in a patchy distribution of mass. Some extraction methods (Zhou et al., 2018; Li et al., 2021) have been reported for the preconcentration of nanoplastics prior to the Py-GC-MS analysis to meet the requirement of detection, but the extraction requires multi-step sample pretreatment and also may not be suitable for environmental samples with large volume (e.g. soil). A method that can handle in principle larger sample volumes reduces the chances of non-detects and increases the representativeness of samples

(Besley et al., 2017).

1.3. MNPs quantification based on depolymerization

An alternative method for quantification of PET MNPs is based on the analysis of decomposition products of polymeric chains (Wang et al., 2017). This process involves a depolymerization reaction, followed by the analysis of monomers or monomer derivatives, using GC-MS or LC coupled with a MS or UV detector. The advantage of this method is that it allows depolymerization of PET microfibers and fragments without prior isolation or multi-step sample pretreatment. Furthermore, the quantification is reported on a mass basis, a sum of the mass of all PET fragments and fibers in a sample, which is useful for monitoring spatial and temporal trends and for risk assessment. This method also targets a wide range of particle sizes from mm to ultrafine particles in the nanometer range and complements particle-counting based methods.

Wang et al. (2017) reported a quantification method based on alkali-assisted thermal hydrolysis of PET, followed by a water extraction, centrifugation, a cleanup procedure and an LC-MS/MS analysis. This method was successfully applied to quantify polycarbonate (PC) and PET MNPs in several environmental samples, including sludge, marine sediments, indoor dust, mussel and clam extracts, and sea and rock salt. Similar studies have been reported recently in literature and they are presented in Table 1 (Liu et al., 2019; Wang et al., 2017; Zhang et al., 2019a; Zhang et al., 2019b; Zhang et al., 2020; Castelvetro et al., 2020; Müller et al., 2020).

It can be seen from Table 1 that the reviewed studies required extraction steps, oxidation steps, adsorption and desorption (with methanol) and additional cleanup procedures before the instrumental analysis, which is time consuming and increases possible losses, particularly due to the extremely low solubility of terephthalic acid in water (15 mg/L at pH 7.0 and 25 °C) and even lower solubility in methanol. It is recognized that for complicated environmental matrices, the extraction and cleanup steps can optimize the performance of the method (Wang et al., 2017; Castelvetro et al., 2020), but these steps are not always essential for PET MNPs quantification. Besides, more steps of the experimental procedure may induce the loss of analyte and/or increase of the interferences. A high-end instrument like LC-MS/MS is expensive and requires a high level of user knowledge, which is not

Table 1
Examples of PET quantification using thermal hydrolysis followed by LC analysis from literature.

Studies	Sample treatment ^a	Instrument and LOQ for PET (µg/g) ^a	PET Recovery	Samples	PET concentration (µg/g)
Wang et al., 2017	-Water extraction	LC-MS/MS	>98%	Landfill sludge (n = 1)	12
	-SPE cleanup	LOQ = 0.053		Marine sediment (n = 1)	3–10
				Indoor dust (n = 1)	430
				Digestive residue mollusks (n = 2)	6–127
				Sea salt (n = 1)	0.1
Liu et al., 2019	-Water extraction	LC-MS/MS	105% ± 32%	Rock salt (n = 1)	0.002
	-SPE cleanup	LOQ = 0.18		Dust indoor (n = 29)	1550–120,000
Zhang et al., 2019a	-Water extraction	LC-MS/MS	89% ± 6%	Dust outdoor (n = 28)	212–9020
	-SPE cleanup	LOQ = 1.5–2.3		Cat food (n = 35)	<1.5–12
				Dog food (n = 23)	<1.5–46
				Cat feces (n = 41)	<2.3–340
Zhang et al., 2019b	-Water extraction	LC-MS/MS	75% ± 11%	Dog feces (n = 37)	7.7–190
	-SPE cleanup	LOQ = 3.6		Sewage sludge (n = 65)	28–12,000
Zhang et al., 2020	-Water extraction	LC-MS/MS	64–92%	Dust indoor (n = 286)	38–120,000
	-SPE cleanup	LOQ = 5.3			
Castelvetro et al., 2020	-H ₂ O ₂ oxidation	LC-UV-vis	98%	Marine sandy sediment	0.4–0.5
	-SPE cleanup	LOQ = 0.057			
Müller et al., 2020	-Water extraction	LC-UV	94–107%	Beach sediment (n = 2)	<LOD (1.6)
	-SPE cleanup	LOQ = 6.1 ^b		Agriculture soil (n = 2)	<LOD (1.6)
				Compost (n = 3)	<6.1–102
				Fermentation residue bio-plant (n = 3)	210–777
				Sewage sludge (n = 2)	99–142
			Dust (n = 2)	12,500–43,600	

^a SPE = solid phase extraction. LOQ = limit of quantification.

^b In the study of Müller et al., the LOQs were calculated using a calibration based on the initially spiked PET in a reference soil matrix.

always easy to access in a routine laboratory. Thus, a simple and effective method for PET MNPs quantification is proposed here.

1.4. Development of a 3-step method for PET MNPs quantification

Glycolytic depolymerization of PET using an excess of ethylene glycol has been reported in literature for PET recycling (Carta et al., 2003; Dutt and Soni, 2013), in which PET is depolymerized to bis(2-hydroxyethyl) terephthalate (BHET). This method has not yet been applied for the quantification of PET MNPs. The aim of the present study was to develop a robust yet simple method for PET MNPs quantification in complex environmental matrices like beach sand, sewage sludge and dust, using ethylene glycol depolymerization followed by liquid chromatography coupled with UV detection (LC-UV) analysis.

2. Materials and methods

2.1. Reagents and standard preparation

LC-grade water and solvents (acetonitrile and methanol) were purchased from Biosolve (Valkenswaard, the Netherlands). Zinc acetate (purity $\geq 99\%$) and PET fiber (purity $\geq 99\%$, diameter 0.1 mm) were purchased from Fisher Scientific (Landsmeer, the Netherlands). BHET (purity $\geq 99\%$), terephthalic acid (TPA, purity $\geq 99\%$), dimethyl terephthalate (DMT, purity $\geq 99\%$) and ethylene glycol (purity $\geq 99.8\%$) were purchased from Sigma-Aldrich (Zwijndrecht, the Netherlands). Stock solutions of BHET, TPA and DMT were prepared in ethylene glycol (500 mg/L) right before the experiment and stored at 4 °C.

2.2. Quality control

To avoid background contamination during the experiment, several measures were taken. Firstly, PET plastic tools and containers were excluded in the whole experimental procedure, including sampling. Cotton (100%) lab coats and nitrile lab gloves were used. Stainless steel tools, glass jars for sampling and laboratory glassware were cleaned and rinsed with acetone, and baked at 420 °C for 4 h before use. The depolymerization reactions were performed in a fume hood which was vacuum cleaned before each reaction. Reagents and materials were used exclusively for the depolymerization experiments in this study.

As TPA can react with ethylene glycol to yield BHET, to control the contamination before and during the reaction, solvent blanks and procedural blanks were carried out for each environmental sample. Solvent blanks and procedure blanks were analyzed in duplicate with each sample batch to monitor and (if necessary) correct for background contamination. An internal standard (DMT) was used for quantification and monitoring retention time (RT) shifts and signal drift.

2.3. Samples

2.3.1. Environmental sample collection

Environmental samples were collected in the Netherlands between June 2020 and January 2021. Sand samples were collected from the strand line of seven different marine beach locations. In brief, about 1 kg of sand was collected (top 1–5 cm) from the beach using stainless steel spatulas and transported to the laboratory in baked glass jars. Sand samples were air-dried in a fume hood and stored in previously baked glass jars. A piece of aluminum foil was applied on the jar before capping with polypropylene caps. Then all the sand samples were sieved in the fume hood using a stainless steel sieve (5 mm) to eliminate the pebbles and/or shells. No preproduction pellets were found among the sieved pebbles or shells (by naked-eye). Domestic indoor dust samples were sampled in 20 different households and stored in baked glass jars in the same way as the sand samples (each dust donor received a baked glass jar and a pair of nitrile gloves before the collection of dust using a vacuum cleaner). One sludge sample with a solid content of 0.5% was

received from the Waternet water treatment plant in Horstermeer (the Netherlands). The sludge was kept covered for 24 h in a fume hood for sedimentation of solids. Subsequently the water was evaporated from the sludge in a drying oven at 40 °C (named as pre-dried sludge in the text below, and the pre-dried sludge has a moisture content of 70%) before the depolymerization reaction. The organic content of sand, dust and sludge samples was determined by thermogravimetric analysis (TGA) between 25 °C and 600 °C using a Mettler Toledo TGA/DSC 3+ system (Columbus, OH, USA). The details of the samples are given in Table S1.

2.3.2. Burnt sand preparation

500 g of sand from one of the locations was baked at 600 °C for 12 h to eliminate any organic matter including PET. The burnt sand was used as clean matrix in the depolymerization efficiency (recovery) test.

2.4. Depolymerization reaction

2.4.1. Depolymerization of PET with ethylene glycol

In order to quantify PET MNPs chromatographically, it was depolymerized using an excess of ethylene glycol. A reaction temperature of 190 °C was applied, since several studies reported good reaction yields ($>87\%$) at this temperature (Syarifuddeen et al., 2012; Ptiček Siročić et al., 2013). Metal based catalysts are commonly used in PET depolymerization, and zinc acetate is reported to be effective, cheap and relatively non-toxic (Bartolome et al., 2012; Syarifuddeen et al., 2012). In literature, reaction times vary from 30 min to 8 h depending on the reaction conditions (Shukla and Kulkarni, 2002; Syarifuddeen et al., 2012; Ptiček Siročić et al., 2013). However, excessively prolonging the heating time may result in BHET dimerization (Bartolome et al., 2012). In the present study, 6 h was selected and, based on validation experiments, proved to be enough for the reaction and yielded BHET only (see Fig. S1 in Supplementary Materials).

In the present study, the reaction condition for PET depolymerization is shown in Fig. 1. In brief, each sample was added to 100 mL ethylene glycol containing 10 mg zinc acetate in a round-bottom flask. A magnetic stirrer was placed inside the round-bottom flask and the sample was stirred at 300 rpm during the reaction. The flask was heated at 190 °C for 6 h in an oil bath. The condensers were cooled at 20 °C with a cooling fluid. After reaction, the mixture was cooled down to room temperature and spiked with DMT (internal standard) to yield a DMT concentration of 1 mg/L. Subsequently, the mixture was filtered through a 0.2 μm polytetrafluoroethylene (PTFE) filter (Fisher Scientific, the Netherlands) directly into 2 mL LC glass vials and stored in the fridge at 4 °C until LC analysis.

To validate the depolymerization reaction conditions, 50 mg analytical grade PET (purity $\geq 99\%$) was treated under the reaction condition mentioned above. After reaction, the final product mixture was analyzed using proton nuclear magnetic resonance (^1H NMR) spectrometry (Bruker AV400, Billerica, MA, USA). The NMR analysis indicated that BHET is formed during the depolymerization reaction; no other unknown peak was detected in the NMR spectra (see Fig. S1 in Supplementary Materials).

2.4.2. Recovery test

The burnt sand was used as clean matrix to test the PET recovery (calculated on the basis of BHET yield). About 50 g (± 0.5 g) of burnt sand was weighed into three round-bottom flasks, each containing 100 mL ethylene glycol and 10 mg zinc acetate. Then, to one flask, 0.1 mg (low-level spike) and to another flask, 3 mg (high-level spike) analytical grade PET was added. A third flask without PET was used as procedural blank. All three mixtures were treated under the same conditions as mentioned in Section 2.4.1. The recovery test was performed in triplicate. The recovery reported in Section 3.1 is the mean of the three replications.

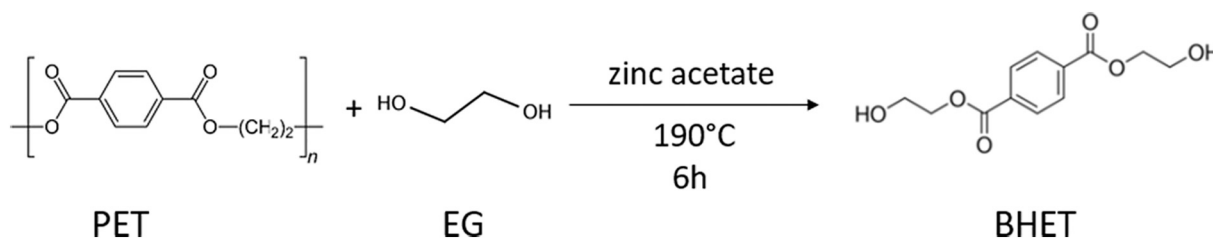


Fig. 1. Depolymerization of PET with excess ethylene glycol and zinc acetate (EG = ethylene glycol).

2.4.3. Application in real environmental samples

To investigate the level of PET MNPs in sand, indoor dust and sludge, these environmental samples were depolymerized following the same procedure as described in Section 2.4.1. The weights of the environmental samples, analyzed with the developed method, were selected based on the expected PET content reported in literature (Müller et al., 2020; Zhang et al., 2020). In brief, 50 g of sand, 20 mg of indoor dust and 500 mg of pre-dried solid sludge were weighed for reaction, respectively. The full procedure was conducted in duplicate for each sample.

2.5. Instrumental analysis

2.5.1. LC-UV

Reaction mixtures were analyzed using an Agilent 1260 Infinity II LC system (Agilent Technologies, Santa Clara, USA) coupled with a diode array detector (DAD) (G1315A) (Agilent Technologies, Santa Clara, USA). LC separation was conducted on a Poroshell 120 Phenyl Hexyl column (Agilent Technologies; 2.7 $\mu\text{m} \times 3.0 \text{ mm} \times 100 \text{ mm}$) fitted with a Poroshell 120 Phenyl Hexyl guard column (Agilent Technologies; 2.7 $\mu\text{m} \times 3.0 \text{ mm} \times 10 \text{ mm}$). The mobile phase (flow rate: 0.5 mL/min) consisted of a mixture (gradient mode) of water (solvent A) and methanol (solvent B). The percentage of organic mobile phase B increased linearly and the gradients were as follows: 10% at 0 min, then increased to 90% at 15 min, 100% at 18 min, and maintained at 100% during 18–19 min; at 22 min, the eluent was restored to the initial conditions

$$\text{PET mass in reaction mixture} = \text{BHET mass in reaction mixture} / \text{Molecular weight of BHET} \times \text{Molecular weight of PET monomer} \quad (1)$$

for 1 min to re-equilibrate the column for the next injection. The injection volume was set at 5 μL and the column temperature was maintained at 40 $^\circ\text{C}$. The UV spectrum was recorded at 245 nm ($\lambda_{\text{max}} = 245 \text{ nm}$, determined by DAD full scan mode). Agilent OpenLAB software (Agilent Technologies, Santa Clara, USA) was used for data acquisition, processing and peak integration.

2.5.2. LC-ESI-MS

To test whether the LC-UV analytical results were comparable to those generated with a different instrument, the reaction mixtures of environmental samples (all sand samples, one dust sample, one sludge sample and their procedure blanks) were next analyzed by LC-electrospray (ESI)-MS (Thermo Finnigan LTQ system) (Thermo Fisher, Waltham, MA, USA). The LC separation was conducted using the same method as LC-UV analysis. Samples were analyzed under ESI positive mode (ESI+) with a source voltage of 3.2 kV and a capillary temperature at 275 $^\circ\text{C}$. Nitrogen was used as the drying gas and the gas flow was 5 L/min. MS data were acquired in the m/z 50–1000 range. The targeted m/z is 255 $[\text{M} + \text{H}]^+$ for BHET and 195 $[\text{M} + \text{H}]^+$ for DMT.

2.6. Method validation

To validate the instrument performance, a set of matrix-matched

calibration standards (50 $\mu\text{g/L}$ to 150 mg/L of BHET, 1 mg/L for DMT) were assessed for LC-UV. Another set of matrix-matched calibration standards (10 $\mu\text{g/L}$ to 5 mg/L of BHET, 1 mg/L for DMT) were assessed for LC-ESI-MS. The linearity of the instrument response was assessed using the response of the calibration standards prepared in ethylene glycol with burnt sand matrix. The limit of detection (LOD) was calculated as three times the standard deviation of procedural blanks. If the analyte was absent in all procedural blanks, the LOD was determined as the concentration of the target analyte in matrix that yielded a peak signal-to-noise ratio of 3 (Bayen et al., 2013). The LOQ was determined as the concentration of the target analyte in matrix that yielded a peak signal-to-noise of 10. The relative standard deviation (RSD) for the inter-day precision was calculated based on the analysis of three replicates of standard sample on different days. An inter-day precision (RSD) lower than 15% was deemed acceptable.

2.7. Calculations

It is assumed that all quantified BHET resulted from the depolymerization of PET in the reaction mixture (see 3.2 for explanation). The PET amount in environmental samples was calculated through the analytical quantification of BHET according to Eq. (1), where the molecular weight of PET monomer is 192.04.

The recovery was calculated using Eq. (2).

$$\text{PET recovery (\%)} = \text{PET mass in reaction mixture} / \text{PET mass spiked} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Method validation

The LC-UV calibration curves for BHET were linear with the coefficient of determination (r^2) higher than 0.99. The LOD and LOQ for BHET were 82 $\mu\text{g/L}$ and 259 $\mu\text{g/L}$, respectively, which is equal to 62 $\mu\text{g/L}$ and 197 $\mu\text{g/L}$ for PET in the reaction mixture. The LODs for PET was 0.1 $\mu\text{g/g}$ for sand, 0.3 mg/g for dust and 0.1 $\mu\text{g/g}$ for wet sludge using LC-UV analysis. The LOQ for PET in the three environmental sample matrices was 0.4 $\mu\text{g/g}$ for sand, 1 mg/g for indoor dust and 0.2 $\mu\text{g/g}$ for wet sludge using LC-UV analysis. The LOQ for PET in sand using LC-UV analysis in the present study is lower than those reported by Müller et al. (2020) (see Table 1).

The LC-ESI-MS response for BHET calibration standards was also linear ($r^2 > 0.99$), and the LOD and LOQ for BHET were 15 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, respectively. The equivalent LOD and LOQ for PET in the reaction mixture were 11 $\mu\text{g/L}$ and 38 $\mu\text{g/L}$, respectively. The LODs for PET

measured using LC-MS was 0.02 µg/g for sand, 0.06 mg/g for dust and 0.01 µg/g for wet sludge.

The mean recoveries for PET depolymerization in sand measured by LC-UV were 99 ± 2% (low-level spike) and 93 ± 7% (high-level spike), which indicates the robustness of depolymerization with ethylene glycol. The recovery for PET depolymerization in dust and sludge matrices was not evaluated due to the absence of a reference sample (certified dust or sludge with no PET), but the quantification results of dust and sludge samples suggested the validity and applicability of the current method (see Section 3.2). The inter-day precision (RSD) for LC-UV and LC-MS analysis was below 1.5%. No BHET and TPA were detected in solvent blanks and procedural blanks, which indicates that the environmental samples were the exclusive sources of BHET in the reaction mixtures. BHET has not been reported that naturally present in the environment; although TPA could theoretically be present in environmental samples and introduced into the depolymerization reaction, the concentration of TPA is expected to be at trace level and multiple orders of magnitude lower than PET (Wang et al., 2009). Therefore the interferences of TPA and BHET in the environment are negligible in the present study. Thus, it can be assumed that PET is the exclusive source of BHET quantified in the environmental samples (Section 3.2).

Table 2
PET content in environmental samples.

Environmental samples	Replicate	LC-UV	LC-ESI-MS
		PET content (mg/g)	PET content (mg/g)
Sand 1–7	2 per sample	<1 × 10 ⁻⁴	< 2 × 10 ⁻⁵
Dust 1	1	78	NA
	2	83	NA
Dust 2	1	35	NA
	2	26	NA
Dust 3	1	47	NA
	2	42	NA
Dust 4	1	17	NA
	2	31	NA
Dust 5	1	134	NA
	2	14	NA
Dust 6	1	7.1	NA
	2	18	NA
Dust 7	1	17	NA
	2	16	NA
Dust 8	1	7.4	NA
	2	8.2	NA
Dust 9	1	3.8	NA
	2	5.5	NA
Dust 10	1	29	NA
	2	21	NA
Dust 11	1	28	NA
	2	26	NA
Dust 12	1	30	NA
	2	36	NA
Dust 13	1	49	NA
	2	305	NA
Dust 14	1	20	NA
	2	27	NA
Dust 15	1	16	NA
	2	28	NA
Dust 16	1	13	NA
	2	15	NA
Dust 17	1	101	NA
	2	213	NA
Dust 18	1	35	NA
	2	58	NA
Dust 19	1	121	NA
	2	137	NA
Dust 20	1	<0.31	0.39
	2	1.2	1.3
Sludge (pre-dried)	1	0.30	0.31
	2	0.32	0.32

Note: NA = not analyzed.

3.2. Analysis of environmental samples

The results of the quantification of PET in environmental samples are given in Table 2. PET was present (>LOQ) in all the dust samples, with concentrations ranging from 1.2 to 305 mg/g measured by LC-UV (Table 2). The depolymerization was conducted in duplicate for each sample, however, the reproducibility has not been evaluated for the environmental samples due to their heterogeneity (Fig. S2). Thus, the PET content is reported for individual samples rather than a mean value. The median value of PET content in indoor dust samples in the present study (28 mg/g) is higher than the values reported in the literature for Greece (9.7 mg/g), Romania (9.1 mg/g), United States (8.9 mg/g), and China (3.7 mg/g) (Zhang et al., 2020). The concentration range of PET in dust reported here is in the same order of magnitude as the ranges reported by Liu et al. (2019) and Zhang et al. (2020).

BHET was detected in the sludge reaction mixture, which proves the presence of PET in the sludge sample. The PET concentration was approximately 300 µg/g in pre-dried solid sludge (which is 1.5 mg/L in raw liquid sludge). Müller et al. (2020) reported PET concentrations of 99 µg/g and 142 µg/g in two sludge samples (air-dried) using LC-UV. However, the sludge samples they analyzed were air-dried (water content was not reported) and therefore cannot be directly compared with those in the present study.

Using LC-UV detection, the levels of BHET in reaction mixture of sand samples were all below the LOD (82 µg/L, which is equal to 0.1 µg/g for PET in sand).

The results of LC-ESI-MS analysis are also shown in Table 2. No BHET was detected in sand samples with this method either, (all values were below the LC-ESI-MS method LOD of 0.02 µg/g). Several previous studies have reported the presence of MNPs in beach sand from different countries worldwide, but the number of particles varies a lot between sampling locations (Besley et al., 2017). In the case study from the Netherlands presented by Besley et al. (2017), the microplastics were absent in beach sand samples from certain sampling locations. The inherent patchy distribution of plastic particles in sample matrices and the typically relatively small sample intake mass for MNPs analyses contribute to the challenges of representative sampling.

In addition to the LC-UV, the reaction mixture of Dust 20 (two replicates) was analyzed by LC-ESI-MS (Table 2). The concentration of PET in Dust 20 was relatively low in comparison to the concentrations determined in other dust samples in this study. One of the reasons for the low PET level in Dust 20 may be the sample's structure, as it was sandy, inhomogeneous and had low organic content (see Table S1). All indoor dust samples were donated by different individuals and their living environments may differ from each other (e.g. the degree to which there are carpets, curtains, furniture and clothing made of synthetic PET fibers in use in the home), however such metadata collection was outside the study's scope. In the present study, only about 20 mg of dust sample was weighed for the quantification reaction. For future analysis, it is possible to increase the sample weight in order to help overcome the problem of sample inhomogeneity. The results of sand, dust and sludge from the LC-ESI-MS analysis indicate that peaks at RT 7.8 min (Fig. 2) are only BHET (m/z is 255 [M + H]⁺), and these results showed good agreement with the LC-UV measurements (Table 2).

LC-UV has been reported for PET MNPs using quantification via depolymerization only recently (Castelvetto et al., 2020; Müller et al., 2020), and the present study proved the practicability of LC-UV in MNPs quantification using depolymerization, and aimed to increase awareness in the analytical community of this as yet rather uncommon approach to MNP analysis.

3.3. Validity of the developed method in current study and future perspectives

3.3.1. Validity of the developed method in current study

The present study aimed to develop a simplified method for PET

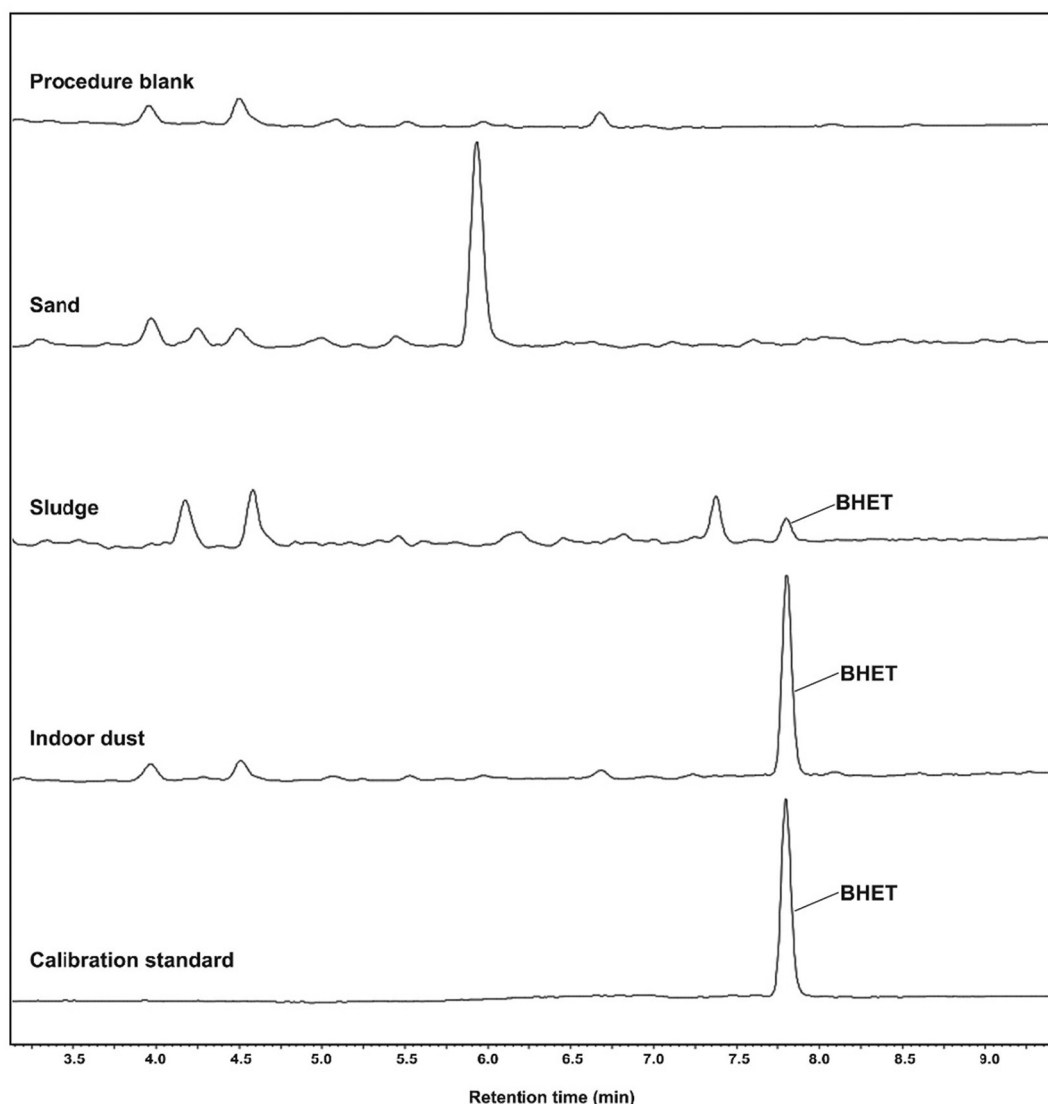


Fig. 2. Examples of LC-UV chromatograms of BHET in the reaction mixtures of depolymerized PET for procedure blank, environmental samples and calibration standard (BHET calibration standard: 20 mg/L).

MNPs quantification in environmental samples, and the results have demonstrated the performance of the developed method, which will be explained below in terms of sensitivity, accuracy, and versatility towards different matrices.

When comparing the LOQs of the current study (Section 3.1) with those of the literature for PET MNP quantification (Table 1), the LOQs (based on LC-UV analysis) in the present study for dust and sludge are lower than the values reported by Zhang et al. (2019b) (LC-MS/MS), Zhang et al. (2020) (LC-MS/MS) and Müller et al. (2020) (LC-UV). The LOQ (LC-UV) for sand in the current study is higher than the one reported by Castelvetro et al. (2020) for marine sandy sediment (LC-UV), but much lower than the one reported by Müller et al. (2020) (LC-UV). The PET MNPs concentrations measured in dust and sludge are in similar ranges as we have seen reported in the literature (Table 1). The method developed in the present study is sensitive enough for PET MNPs quantification, and the LC-MS results (Section 3.2) have demonstrated the accuracy of the LC-UV measurement in current study. Although, the developed method has been applied here in only three different environmental matrices (sand, dust and sludge), it has been designed with the intention of applicability of trace analysis of PET in other matrices, after validation.

3.3.2. Advantages and future perspectives

The method developed in this study is one of the simplest methods for PET MNP quantification to date, as it requires almost no sample pretreatment, which limits background contamination, requires no extraction and centrifugation step nor solvent change, no oxidation step nor SPE clean-up step using and adjustment of the pH of the reaction solution is not required. Furthermore, the developed method can be performed under ambient pressure (allowing the use of simple laboratory glassware) and makes use of four main chemicals, ethylene glycol and a catalytic amount of zinc acetate, an internal standard (DMT) and a calibration standard (BHET). It is well recognized that LC-MS has many advantages (e.g. low LOQ, high sensitivity and high selectivity) in chemical analysis. However, the LC-UV may more accessible in routine laboratories than other instruments, like LC-MS or GC-MS, because it is relatively inexpensive and operation and data interpretation are less complicated, and as such can be considered as a complementary method and part of the current suite of options available to the analytical community. The developed 3-step method (depolymerization of PET to BHET) offers an alternative way for PET MNPs quantification with an acceptable data quality, and of course, its sensitivity could be further optimized when LC-MS is accessible and very low PET concentrations or very tiny sample volumes need to be analyzed. The ability of the

developed 3-step method to capture submicron particles, which are considered more bioavailable than large-size microplastics, makes it potentially of interest to studies of PET residues in biota and food as well as other environmental and consumer product matrices where PET nanoparticles might be expected.

Given the high volume of PET waste, the wide application of PET in food contact materials, and the PET MNP pollution already signaled in the outdoor and indoor environments (Napper and Thompson, 2016; Rocha-Santos and Duarte, 2015; Huang et al., 2020), a simple yet robust and sensitive quantification method can contribute to our understanding of the dynamics of this particular type of MNP pollution. Awareness of PET MNP pollution can be strengthened by quantitative mass analysis, and support decision making and assessment of effectiveness of pollution abatement measures taken. Combining the qualitative analysis (e.g. microscopy coupled with IR or Raman spectroscopy) with the developed quantification method can offer a better knowledge for the risk assessment of human exposure to PET MNP.

It must be noted that this type of solvent depolymerization is limited to condensation polymers. It is certain that it works for polyesters like PET, but it could, with some adaptations to the method, potentially also be applied to polycarbonates or polyamides, most importantly nylon, which is another high production volume polymer applied in textiles. Work towards developing and improving quantification methods for MNPs of all types, (especially polyolefins that are used in bulk such as polyethylene, polypropylene, polyvinylchloride and polystyrene), is ongoing in the scientific community. These efforts are important in answering the need for exposure and risk assessment of MNPs, which relies on robust exposure data for both ecosystems and humans.

4. Conclusion

A quantification method specifically targeting PET MNPs based on in-matrix depolymerization using ethylene glycol and LC analysis was developed and applied. In the present study, no PET MNP was detected in beach sand samples. The amount of PET MNPs in a liquid sewage sludge sample was 1.5 mg/L. PET MNPs were detected in indoor dust samples at levels up to about 30% of total dust mass, adding further evidence for indoor dust as a potential source of human exposure to PET MNPs in the living environment. These results demonstrated the practicability of the developed 3-step method, which can be validated in future studies for other environmental matrices, including diverse biological tissues, effluents, sediment, etc.

CRedit authorship contribution statement

Lei Tian and Ewa Skoczynska are both first authors as they have equal contributions to this study including conceptualization, sampling, formal analysis, investigation, data curation, writing - original draft, and writing - review & editing. Deepti Siddhanti did the pre-experiment test. Prof. dr. Gert-Jan Gruter and Dr. Robert-Jan van Putten are responsible for conceptualization and manuscript review and editing. Dr. Heather A. Leslie is responsible for co-writing the grant proposal, co-supervising the pilot phase analytical development, and had a major role in manuscript editing.

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2022.113403>.

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