

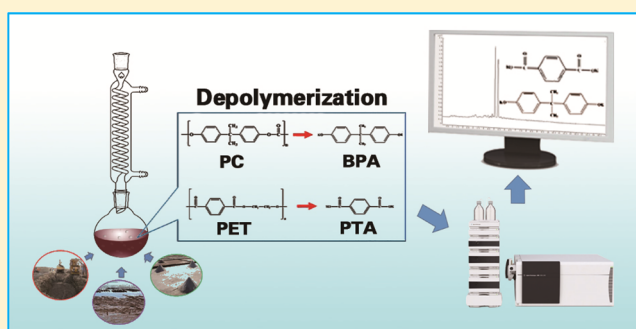
A Simple Method for Quantifying Polycarbonate and Polyethylene Terephthalate Microplastics in Environmental Samples by Liquid Chromatography–Tandem Mass Spectrometry

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S Supporting Information

ABSTRACT: Microplastics (MPs) have frequently been found in the environment. However, studies of the quantification methods for MPs are still needed. Plastics are polymers with different degrees of polymerization. In this study, alkali-assisted thermal hydrolysis was applied to depolymerize two plastics containing ester groups, polycarbonate (PC) and polyethylene terephthalate (PET), in a pentanol or butanol system. By determining the concentrations of the depolymerized building block compounds, i.e., bisphenol A and *p*-phthalic acid, we quantified the amounts of PC and PET MPs in environmental samples. Recoveries of 87.2–97.1% were obtained for the PC and PET plastic particles spiked in the landfill sludge. The method was successfully applied to determine the occurrence of PC and PET MPs in samples of sludge, marine sediments, indoor dust, digestive residues in mussel and clam, and sea salt and rock salt. High concentrations of 246 and 430 mg/kg were determined for PC and PET type MPs, respectively, in an indoor dust. In addition, concentrations of 63.7 mg/kg for PC and 127 mg/kg for PET were detected in the digestive residues of a clam.



INTRODUCTION

Microplastics (MPs) are members of the newest emerging group of contaminants in the environment.¹ Global plastics production was estimated to be ~300 million metric tons,² while around 10% of the produced plastics eventually will enter the environment and fragment into MPs.³ Considering the low degradability of most plastics, high levels of MPs might accumulate in the natural environment.⁴

Methods of analysis for MPs mainly focus on their morphological and physical characterization using different microscopy and spectroscopy instruments,⁵ while MPs were chemically characterized by infrared and Raman spectroscopy.^{5,6} However, MPs are quantified mainly by counting, which requires that MPs be pre-separated from the samples, and might lead to large systematic errors.⁵ Chemical identification of MPs is seldom performed with mass spectrometry. For example, a pyrolysis–gas chromatography–mass spectrometry (Py–GCMS) method was used to identify the separated MPs from marine sediments.⁷ Very recently, Py–GCMS was applied to directly analyze spiked MPs in fish.⁸ However, it failed to quantify MPs in the original fish samples, because of the weak indicator signals for quantification.⁸

Polycarbonate (PC) and polyethylene terephthalate (PET) are important plastics with estimated global annual production of 4.4 and 53.3 million tons, respectively.^{9,10} Although PC and PET MPs have been reported in the environment,^{11–17} the detailed concentrations of these MPs in the environmental

samples are still unknown. To quantify PC and PET MPs in the environment, we developed a direct quantification method by depolymerizing these plastics and determining the emerging building block compounds.

MATERIALS AND METHODS

Chemicals and Environmental Samples. Standards bisphenol A (BPA, ≥99%), *p*-phthalic acid (PTA, 99%), and bisphenol A diglycidyl ether (BADGE, ≥95%) as well as 1-pentanol (>99%) and 1-butanol (99%) solvents were used. The PC and PET particles (0.075–0.15 mm) were provided by Yineng Plastic Co. (Dongguan, China).

Landfill sludge was collected from a municipal sludge landfill in Tianjin, China. Two marine sediments were collected from Bohai Bay, with the information about the sites shown in Figure S1. An indoor dust sample was collected from a student dorm by sweeping of floors. The digestive residues from two mussels and two clams purchased from a local market were also collected for quantification of MPs. Commercial crude sea salt and rock salt were randomly purchased from a supermarket.

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Environmental samples were stored at $-20\text{ }^{\circ}\text{C}$ after lyophilization.

Depolymerization of PC and PET MPs. The alkali-assisted heating depolymerization method has been studied for plastic recycling.¹⁸ In this study, depolymerization of PC and PET was performed according to alkaline hydrolysis reactions (Figure 1a,b). In brief, PET or PC particles together with KOH

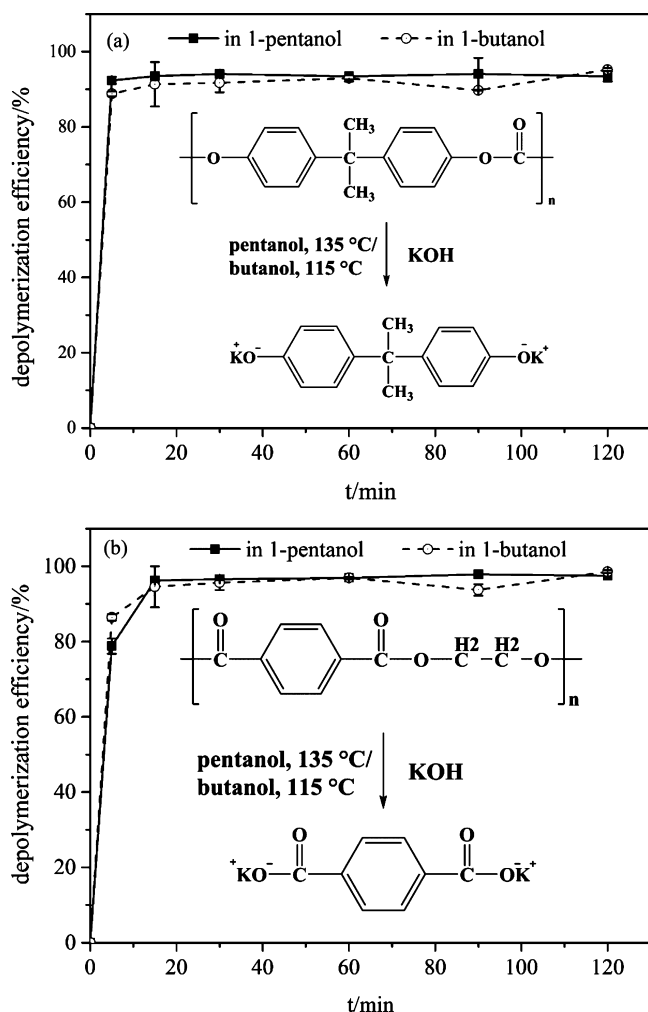


Figure 1. Depolymerization efficiencies of (a) PC and (b) PET plastics at different time in 1-pentanol and 1-butanol. The diagram depicts average values of triplicate measurements, while the error bar represents the standard deviation.

were added to a 1-pentanol solution. The system was heated at $135\text{ }^{\circ}\text{C}$ for different periods of time. Then the depolymerization products in the pentanol solution were extracted with water. The water extracts were diluted 1×10^5 times, and 1.0 mL of the diluted extract was taken out and spiked with [$^{13}\text{C}_{12}$]BPA and [D_4]PTA (10 ng each) before the liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis of the newly formed BPA and PTA. The detailed depolymerization procedure is shown in Table S1. The depolymerization experiments were performed in triplicate. The control experiments indicated BPA and PTA were stable during the depolymerization process, while the procedure blank showed no detectable background of BPA or PTA.

Depolymerization was also performed in the solvent 1-butanol (Figure 1). Then the butanol solvent was removed by

rotary evaporation, and the solutes were redissolved in a 1:1 (v/v) water/acetonitrile solvent for LC–MS/MS analysis.

Spiking and Recovery of PC and PET MPs in Sludge. The recoveries of PC and PET MPs spiked in the landfill sludge were determined at three spiking levels, i.e., 10, 100, and 1000 mg/kg, with the detailed spiking procedure presented in Table S1. After sufficient mixing, 1.0 g of the sludge containing 1000 mg of spiking MPs per kilogram was weighed and transferred to the 1-pentanol depolymerization system as described above. At the optimized reaction time, the free forms of BPA and PTA were extracted twice with 30 mL of water and then 20 mL of water. The water extract was diluted 100 times, and 1.0 mL of the diluted extract spiked with 10 ng of [$^{13}\text{C}_{12}$]BPA and 10 ng of [D_4]PTA was purified by solid phase extraction (SPE) as shown in Table S1, before the LC–MS/MS analysis.

To determine the concentrations of BPA and PTA in the depolymerization systems of samples with spiking MPs of 10 and 100 mg/kg, water extracts were diluted 100 and 10 times, respectively, before the SPE treatment. At each MP spiking level, six parallels of spiked sludge samples were analyzed to identify the error in the determination. Six sludge samples without MPs spiked were analyzed as blank controls. Therefore, the contribution of the spiked MPs to the newly formed BPA and PTA can be calculated. Accordingly, amounts of spiked PC and PET MPs can be calculated, with the equations introduced below.

Application of the Method. To identify PC and PET MPs in the sludge sample, BPA and PTA in the original sludge were first detected in a control experiment. Sludge was treated in a similar manner, only without the heating process. Therefore, the amount of newly formed BPA and PTA from the depolymerization of PC and PET MPs can be calculated by subtracting the amount of BPA and PTA in the original sludge from the total amount of BPA and PTA in the depolymerized systems, and then the corresponding occurrence of PC and PET MPs can be quantified. The assessment of PC and PET MPs in marine sediments, indoor dust, and digestive residues from biological samples was also performed with the same procedure. It should be noted that, although BPA is also commonly used as the monomer of epoxy resin,¹⁹ BADGE, the monomer of epoxy resin, proved to be stable in the depolymerization system, while no emerging BPA was detected. Also, in addition to PET, the newly formed PTA during depolymerization may also come from other terephthalate type plastics, such as polybutylene terephthalate (PBT) and polytrimethylene terephthalate (PTT). However, considering the much lower level of production of PBT and PTT and their similar structure and application with PET plastics,²⁰ PET calculated in this study could represent the occurrence of all three of these plastics.

Two hundred grams of the sea salt or rock salt were weighed and dissolved in hot water. The insoluble matter was filtered with $0.22\text{ }\mu\text{m}$ nylon membrane filters and dried to a constant weight at $48\text{ }^{\circ}\text{C}$ for 24 h. Then the insoluble matter was depolymerized in 1-butanol for 30 min. After the addition of 10 ng of [$^{13}\text{C}_{12}$]BPA and 10 ng of [D_4]PTA, butanol was removed by rotary evaporation, and the target compounds were redissolved in a 1:1 (v/v) water/acetonitrile solvent and filtered with a nylon membrane filter before analysis.

For each sample of sludge, marine sediment, dust, digestive residue, or salt, two parallel samples were analyzed, and the average values were calculated. It should be noted that the newly formed BPA and PTA during the depolymerization were

Table 1. BPA, PTA, and Calculated PC and PET MPs in Environmental Samples (milligrams per kilogram)^a

	BPA _{non-depolym}	BPA _{depolym}	PC MP	PTA _{non-depolym}	PTA _{depolym}	PET MP
sludge	5.03	14.1	10.1	2.41	12.7	12.0
sediment A	0.0214	1.47	1.60	0.482	9.31	10.3
sediment B	0.208	0.898	0.765	0.318	2.84	2.93
indoor dust	0.770	222	246	217	587	430
mussel digestive residue A ^b	1.20	3.30	2.33	4.17	69.0	75.4
mussel digestive residue B ^b	0.234	4.20	4.41	4.31	19.4	17.5
clam digestive residue A ^b	0.740	58.1	63.7	7.04	116	127
clam digestive residue B ^b	0.659	4.91	4.72	14.8	19.8	5.81
SIM ^c in sea salt	<LOQ	24.1	26.7 (87.5 μg/kg) ^d	3.32	30.0	31.1 (102 μg/kg)
SIM ^c in rock salt	2.14	2.37	0.249 (0.122 μg/kg)	3.45	6.69	3.77 (1.85 μg/kg)

^aBPA_{non-depolym} and BPA_{depolym} are BPA concentrations in samples before and after depolymerization, respectively. PTA_{non-depolym} and PTA_{depolym} are PTA concentrations in samples before and after depolymerization, respectively. PC and PET MP concentrations were calculated according to eqs 1 and 2. ^bSamples of the digestive residues were collected from of the digestive tract of two mussels and two clams, which were ~150 mg of dry weight for each from mussels and 60 mg of dry weight for each from clams. ^cSIM represent solid insoluble matter, while SIM was depolymerized in 1-butanol systems and concentrated by rotary evaporation before the LC–MS/MS analysis. ^dThe calculated MP concentrations in salts are given in parentheses.

assumed to be derived entirely from the depolymerization of PC and PET in the samples. This will be further discussed in detail below.

Instrument Analysis. Detailed information about chromatographic separation and the tandem MS system for quantifying BPA and PTA is listed in Tables S2 and S3. The MRM chromatograms of BPA and PTA in the depolymerized sludge are shown in Figure S2, and their concentrations were corrected by the corresponding internal standards, i.e., [¹³C₁₂]BPA and [D₄]PTA, respectively.

RESULTS AND DISCUSSION

Depolymerization of PC and PET MPs in Pentanol and Butanol. Both PC and PET MPs can be readily depolymerized via hydrolysis within 30 min in a 1-pentanol or 1-butanol solution with potassium hydroxide. The visual disappearance of PC and PET particles in the 1-pentanol and 1-butanol solutions can be observed. Accordingly, formation of BPA and PTA can be assessed. For example, at 30 min, 0.42 g of BPA was detected in the 1-pentanol system initially containing 0.5 g of PC MPs (Figure 1a). On the basis of the structural formula of the PC polymer, i.e., [-O-C₆H₄-C(CH₃)₂-C₆H₄-O-C(O)-]_n, the unit of (BPA-2H) accounts for approximately 89.5% [*f*_(BPA-2H) (w/w)] in PC plastic, indicating a theoretical mass of 0.45 g of emerging BPA might form from 0.5 g of depolymerized PC plastic. Therefore, a depolymerization efficiency of >93% for PC plastic within 30 min can be verified.

Similarly, 0.42 g of PTA formed at 30 min in the hydrolysis system containing 1-pentanol and 0.5 g of PET plastic (Figure 1b). According to the PET polymer structural formula, i.e., [-C(O)-C₆H₄-C(O)-O-CH₂-CH₂-]_n, (PTA-H₂O) accounts for approximately 77.4% [*f*_(PTA-H₂O) (w/w)] in PET plastic. Therefore, 0.43 g of emerging PTA might form from 0.5 g of depolymerized PET. This demonstrated that almost all of PTA (98%) depolymerized from PET plastic. Similar depolymerization efficiencies were also obtained in 1-butanol. Therefore, by determining the amount of hydrolysis products, i.e., BPA and PTA, we can quantify PC and PET plastics according to eqs 1 and 2

$$PC_{\text{amount}} = \frac{(BPA_{\text{depolym}} - BPA_{\text{non-depolym}}) \times MW_{(BPA-2H)}/MW_{BPA}}{f_{(BPA-2H)}} \quad (1)$$

$$PET_{\text{amount}} = \frac{(PTA_{\text{depolym}} - PTA_{\text{non-depolym}}) \times MW_{(PTA-H_2O)}/MW_{PTA}}{f_{(PTA-H_2O)}} \quad (2)$$

where *f*_(BPA-2H) and *f*_(PTA-H₂O) are the mass percentages of BPA-2H and PTA-H₂O in PC and PET plastics, respectively, and MW represents the molecular weight.

The unheated control indicates that heating is necessary for depolymerization. At room temperature (25 °C), the plastic particles were insoluble in pentanol and butanol, with mass changes of PC or PET particles of <2%.

Quality Assurance and Quality Control. As mentioned above, a mass ratio of newly formed BPA (ΔBPA = BPA_{depolym} - BPA_{non-depolym}) and the depolymerized PC MPs of 90% can be theoretically assumed, and the method recovery of PC MPs could be calculated as (ΔBPA/90%)/PC_{added} × 100%. Similarly, recovery of PET MPs spiked in sludge samples could be calculated by the amount of newly formed PTA (ΔPTA = PTA_{depolym} - PTA_{non-depolym}) as (ΔPTA/86%)/PC_{added} × 100%. Ideal recoveries of PC and PET MPs spiked in sludge samples can be obtained for MPs at three levels in 1-pentanol. In sludge samples with 1000 mg of PC or PET MPs spiked per kilogram, 843 mg of BPA/kg or 850 mg of PTA/kg can be determined in the depolymerized samples. In comparison, 14.1 mg of BPA/kg or 12.7 mg of PTA/kg was detected in the background samples without spiked MPs. This gives concentrations of newly formed BPA and PTA of 829 and 837 mg/kg, respectively (Figure S3a), accounting for recoveries of 92.0 ± 1.1 and 97.1 ± 2.1% for spiked PC and PET MPs in sludge, respectively (*n* = 6) (Table S4). Using the same method, the amounts of newly formed BPA by depolymerization of the spiked PC MPs at 100 and 10 mg/kg in the sludge were determined to be 72.3 and 8.73 mg/kg, respectively, while the amounts of newly formed PTA were 78.9 and 7.56 mg/kg, respectively (Figure S3a). Therefore, ideal recoveries of 87.2–92.0% (for PC) and 87.9–

97.1% (for PET) can be obtained for the different spiking levels of MPs in sludge (Table S4). Depolymerized BPA and PTA were also detected in the 1-butanol depolymerization systems, but with greater deviation values, especially for the spiked MPs at 100 and 10 mg/kg (Figure S3b). Detection recoveries of PC and PET particles were lower if the 1-butanol depolymerization and rotary evaporation concentration process was applied (Table S4). This was due to the more significant matrix interference effects of this method, because no purification treatment was included in the butanol depolymerization and rotary evaporation process. In comparison, both water extraction and SPE used in the 1-pentanol depolymerization method could purify the samples efficiently.

Instrumental calibration was verified by the injection of a 10-point calibration standard ranging in concentrations from 0.1 to 20 $\mu\text{g/L}$ for BPA and from 0.5 to 200 $\mu\text{g/L}$ for PTA, with the regression coefficients (R) of the calibration curves being ≥ 0.99 . Accordingly, the linear ranges of this method for PC and PET MPs in sludge were 5.56–1110 and 29.1–11600 $\mu\text{g/kg}$, respectively. The limits of quantification for PC and PET MPs were calculated to be 8.32 and 53.0 $\mu\text{g/kg}$, respectively, based on the instrumental limits of quantification (S/N of 10) and the recoveries of BPA and PTA.

Determination of PC and PET MPs in Environmental Samples. To determine PC and PET MPs in the environmental samples, the concentrations of original free form BPA and PTA should be deducted. For the unheated treatment, 5.03 mg of BPA/kg and 2.41 mg of PTA/kg were determined in sludge samples. After these background monomers were deducted, the level of PC MPs in the sludge was calculated to be 10.1 mg/kg, while that of PET was 12.0 mg/kg (Table 1), according to eqs 1 and 2, respectively. Although MPs in the marine sediments and lagoon sediments were quantified by counting,^{12,16,21} no detailed mass concentration of MPs has been reported until now. In this study, in marine sediment A, 1.60 mg of PC MPs/kg and 10.3 mg of PET MPs/kg were detected (Table 1). Very high concentrations of PC (246 mg/kg) and PET (430 mg/kg) MPs were detected in the indoor dust sampled in Tianjin, indicating a high risk of exposure of humans to these MPs through dust.

Bivalves are commonly used as indicators of environmental contaminants.²² PC MPs of 2.33 and 4.41 mg/kg were detected in the digestive residues from mussel samples A and B, respectively, while the concentrations for PET MPs were calculated to be 75.4 and 17.5 mg/kg, respectively (Table 1). In addition, much higher PC and PET MPs were detected in the digestive residues from a clam, with concentrations of 63.7 and 127 mg/kg, respectively.

MPs can be detected in sea salts.¹⁴ In the two commercial salts, i.e., a sea salt and a rock salt, the amounts of solid insoluble matter were determined to be 3280 and 490 mg/kg, respectively. This solid matter was depolymerized in 1-butanol. In the insoluble matter from sea salts, PC and PET MPs were calculated to be 26.6 and 31.0 mg/kg, respectively, in the insoluble matter. Therefore, the concentrations of PC and PET MPs in the sea salts were 0.088 and 0.102 mg/kg, respectively (Table 1). By comparison, much lower concentrations of MPs, 1×10^{-4} mg/kg for PC and 2×10^{-3} mg/kg for PET, were detected in the rock salts.

For the method presented here, separation of MPs from the samples is unnecessary, which increases the analyzing efficiency and prevents the loss of MPs or error picking caused by separation. Attention should also be paid to the specificity of

the building block compound of MPs. For instance, for PC MPs containing other key building block compounds, e.g., bisphenol S (BPS), detection of only BPA will lead to an underestimation. Besides, the BPA and PTA newly formed during the depolymerization process were assumed to be derived entirely from the hydrolysis of PC and PET MPs in the samples, respectively. Although BPA was also added to some plastic materials as an antioxidant, it may affect PC quantification only slightly. First, the contribution of the BPA additive is much smaller than that of the building block BPA in PC. For example, BPA released from a PVC plastic was 6 orders of magnitude lower than that from the depolymerized PC plastic (Table S5). Second, most released BPA from the PVC particles can migrate in the nondepolymerization treatment (Table S5), which can be deducted as “BPA_{non-depolym}” according to eq 1. Similarly, PTA is also added to PVC plastic as a plasticizer in the form of lipids. However, emerging PTA released from PVC plastics during the depolymerization process was 4–5 orders of magnitude lower than that from PET (Table S5), indicating the limited contribution of PVC to detected PTA after the depolymerization process. In addition, it should be noted that the particle size distribution of MPs in the samples cannot be analyzed by this method. In addition, if polymers containing the same building block compound are present and can be depolymerized under the same condition, it will be difficult to distinguish the source of the depolymerization products.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00454.

Detailed procedure for depolymerization, MP spiking, and SPE (Table S1); HPLC gradient elution programs for BPA and PTA (Table S2); MS parameters for the analysis of BPA and PTA (Table S3); recoveries of spiked MPs in sludge samples (Table S4); amounts of BPA and PTA (milligrams) released from 0.5 g of PVC, PC, or PET plastics before and after depolymerization (Table S5); sampling location of marine sediment samples (Figure S1); chromatograms of BPA and PTA from the extracts from depolymerized sludge without or with PET and PC MPs spiked (Figure S2); and detected concentrations of BPA and PTA depolymerized from spiked MPs at different spiking levels in a 1-pentanol or 1-butanol system (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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