A simple method for the selective quantification of polyethylene, polypropylene, and polystyrene plastic debris in soil by pyrolysis-gas chromatography/mass spectrometry

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ABSTRACT

The lack of adequate analytical methods for the quantification of plastic debris in soil challenges a better understanding of their occurrence and fate in the terrestrial environment. With this proof-of-principle study, we developed a simple and fast method for the selective quantification of the three most environmentally relevant polymers polyethylene (PE), polypropylene (PP), and polystyrene (PS) in soil using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In order to facilitate the preparation of calibration series and to better account for the heterogeneity of soil matrix, polymers were dissolved in 1,2,4-trichlorobenzene (TCB) at 120 °C. Thereby, liquid sample aliquots from up to 4 g of solid sample became amenable to pyrolysis without further preparation. To evaluate the performance of this approach, three reference soils with 1.73–5.16 % organic carbon (C_{org}) were spiked at 50 and 250 µg g^{-1} of each polymer and extracted with TCB. A prior cleanup step with methanol, flocculation with $KAl(SO_4)_2$, and Fenton digestion were tested for their suitability to reduce potentially interfering C_{org}. Calibration curves responded linearly (adj. $R^2 > 0.996$) with instrumental detection limits of 1–86 ng corresponding to method detection limits of 1–86 µg g^{-1}. The measurement repeatability was 3.2–7.2 % relative standard deviation. Recoveries of 70–128 % were achieved for plastic contents of 250 µg g^{-1} extracted with TCB without prior cleanup from soils with less than 2.5 % C_{org}. A higher C_{org} particularly interfered with the quantification of PE. The addition of non-target polymers (polyethylene terephthalate, polyvinyl chloride, poly(methyl methacrylate), and tire wear particles) did not interfere with the quantification of the analytes highlighting the selectivity of the method. Further research is needed to determine low plastic contents in soils exceeding 2.5 % C_{org}. With 1–3 h processing time per sample, our method has the potential for routine analyses and screening studies of agricultural systems to be complemented with microspectroscopic techniques for additional information on particle shapes and sizes.

1 INTRODUCTION

The majority of plastic is produced, used, and disposed of on land, where it probably disintegrates into smaller debris such as microplastics (1–1000 µm) or even nanoplastics (<1 µm; Hartmann et al., 2019; Hurley and Nizzetto, 2018; Wagner and Reemtsma, 2019). Whereas previous research has mainly focused on studying plastic debris in the aquatic environment, it remains unknown how and in which quantities such particles may distribute in terrestrial systems and particularly in soil. Currently, atmospheric

deposition, littering, sewage sludge or biosolid applications, and use of agricultural plastic films are being discussed as potential sources of terrestrial plastic pollution, with polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) as the most relevant polymers of interest (Hurley and Nizzetto, 2018; Wang et al., 2019; Steinmetz et al., 2016).

Developing a better understanding of the occurrence and fate of plastic debris in the terrestrial environment requires reliable, quantitative analytical methods for complex environmental matrices (Bläsing and Amelung, 2018; He et al., 2018; da Costa et al., 2018). So far, most studies have relied on optical detection by Fourier transformed infrared spectroscopy (FTIR) with attenuated total reflection or Raman microspectroscopy (Renner et al., 2018). Both techniques require extensive sample pretreatment to separate the plastic particles from sample matrix without losing the polymer analyte (Hurley et al., 2018). When analyzing more complex matrices such as soil or organic wastes, sample preparation may easily take days or weeks (Löder et al., 2017). In addition, particle identification becomes prone to false positive detections, for example, by mistaking natural fibers or sand grains for plastic debris (Bläsing and Amelung, 2018). While this complicates a reliable quantification, optical techniques provide valuable information about particle shapes and sizes. Scheurer and Bigalke (2018) were the first who successfully developed and applied a method for the quantification of plastic debris in soil using a combination of density separation and oxidative matrix digestion followed by FTIR. With their procedure, the authors obtained recoveries of 93–98 % and found a plastic content averaging 5 mg kg^{-1} in Swiss floodplain soil. However, plastic concentrations were estimated from particle sizes and densities without stating limits of detection (LODs) or limits of quantification (LOQs). Similarly, Piehl et al. (2018) screened agricultural soil for plastic debris and found 0.3 ± 0.4 particles ha^{-1}, but neglected all particles smaller than 1 mm due to the challenging sample pretreatment.

In such cases, thermoanalytical techniques such as thermogravimetry/mass spectrometry (David et al., 2018, 2019), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS; Fischer and Scholz-Böttcher, 2017, 2019), or combinations of TGA with GC/MS namely thermal desorption-gas chromatography/mass spectrometry (TED-GC/MS; Dümichen et al., 2015; Duemichen et al., 2019) may demonstrate their inherent benefits. All these methods are based on thermal decomposition of polymer mixtures at temperatures >500 °C and their quantification via indicator pyrolysates. Currently, instrumental detection limits range from 3 to 200 ng for PS (Fischer and Scholz-Böttcher, 2019; Duemichen et al., 2019) and up to 0.5–50 µg for PE, PP, and PET (Duemichen et al., 2019; David et al., 2018). In contrast to optical methods, thermoanalytical techniques are assumed to be more robust against impurities from sample matrix. Yet, interferences may occur when pyrolysis products in plastic and matrix are identical. In addition, thermoanalytical measurements are typically restricted to sample amounts <100 mg, which puts high, hardly attainable requirements on sample homogeneity.

These challenges may be overcome by combining an adequate sample pretreatment with the selectivity of Py-GC/MS analyses. Therefore, we developed and validated a new Py-GC/MS method for the quantification of PE, PP, and PS by using 1,2,4-trichlorobenzene (TCB) as a solvent both for the preparation of readily measurable polymer standards and for the extraction of plastic debris from different soil types. TCB is a typical eluent for size exclusion chromatography (SEC) of polymers (Bivens, 2016) and has been assessed for quantitative ^{1}H nuclear magnetic resonance relaxometry of polymers (Peez et al., 2019). Very recently, Dierkes et al. (2019) took a comparable approach by extracting PE, PP, and PS with tetrahydrofuran (THF) from various solid matrices using accelerated solvent extraction (ASE). Although the polymers needed to be reprecipitated in silica gel and could not be analyzed directly via Py-GC/MS. Unlike THF, TCB is not classified as teratogenic and has a more than 100-fold lower vapor pressure according to the respective material and safety data sheets. This makes TCB easy to handle in batch extraction set-ups. Moreover, sample pretreatment and extraction can be carried out in a single tube which reduces the contamination potential and facilitates scalability for routine analyses.

2 MATERIAL AND METHODS

2.1 Preparation of polymer standards

The polymers used in this study were PE (CAS 9002-88-4, beads of 500 µm average particle size) purchased from Alfa Aesar, Kandel, Germany, PP (CAS 9003-07-0, isotactic, pellets) from Aldrich Chemistry, Taufkirchen, Germany, and PS (CAS 9003-53-6, 250 µm average particle size) from Goodfellow, Huntingdon, United Kingdom. PP pellets were ground using a commercially available coffee mill with stainless steal lining (Cloer 7580, Arnsberg, Germany) to pass a 1000 µm sieve. All polymer standards

Table 1. Overview of physicochemical soil properties

Soil	Texture	Clay [%]	Silt [%]	Sand [%]	pH	C_{org} [%]
RefeSol 06-A	Silty clay	47.2	41.3	11.5	7.39	2.5
LUFA 2.2	Loamy sand	8.6	15.7	75.7	5.6	1.73
WR	Clayey silt	25.0	70.0	5.0	5.0	5.16

were prepared in TCB (CAS 120-82-1, 99 % purity, Alfa Aesar, Kandel, Germany) containing 0.015 % butylated hydroxytoluene (CAS 128-37-0, ≥99 %, Merck, Darmstadt, Germany) as antioxidant (Bivens, 2016). To this end, 50 mg of PE, PP, and PS were weighed individually and as an equal mixture of all three polymers into glass culture tubes (16 × 100 mm, GL18, VWR, Darmstadt Germany). The tubes were equipped with a polybutylene terephthalate screw cap and a polytetrafluoroethylene (PTFE)-coated sealing (Carl Roth, Karlsruhe, Germany). The plastic particles were mixed with 5 mL of TCB and heated to 120 °C for 30 min to facilitate dissolution. After having cooled down to room temperature, the polymers formed a sol-like phase within the TCB that could easily be dispersed upon manual agitation before diluting the polymer standards. Dilution series of 5, 10, 20, 50, 100, and 150 µg mL^{-1} were prepared using 10–100 µL positive displacement pipettes with glass capillaries (Transferpettor micro, Brand, Wertheim, Germany) and 2–5 mL volumetric glass flasks. Standard solutions were kept in 2 mL ND9 glass vials with PTFE sealed caps.

2.2 Extraction of plastic debris from soil

For the recovery experiment, three soils with different textures and organic carbon (C_{org}) contents were selected (Table 1). RefeSol 06-A (Fraunhofer IME, Schmallenberg, Germany) and LUFA 2.2 (Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Germany) as previously used by David et al. (2018) served as reference soils from organically managed arable areas. In addition, a pristine forest soil was taken from a continuous observation site of the Landesamt für Geologie und Bergbau in Wallmerod (WR), Rhineland-Palatinate, Germany (Meyer et al., 2018).

In order to assess the efficacy of TCB for extracting PE, PP, and PS from different soil types, soil triplicates of 4 g were weighed into glass culture tubes and spiked with 0.2 and 1.0 mg PE, PP, and PS using a microscale (Sartorius SE 02-OCE, Göttingen, Germany). With that, a nominal content of 50 and 250 µg g^{-1} of each polymer was obtained. Soil without any plastic supplement served as control. One batch of LUFA 2.2 soil was further spiked with 0.2 mg of plastics not targeted in our analysis to evaluate whether their pyrolysates interfere with PE, PP, and PS extraction and quantification. This non-target plastic mixture consisted of 19 % PET from recycled bottles (PETKA CZ, Brno, Czech Republic), 11 % poly(methyl methacrylate) (PMMA) ground from a commercial plexiglass (Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany), 41 % polyvinyl chloride (PVC) (Aldrich Chemistry, Taufkirchen, Germany), and 29 % tire wear particles (TWP) from a test rig at Bundesanstalt für Straßenwesen, Bergisch Gladbach, Germany. Content and composition of the non-target polymers were based on findings by Piehl et al. (2018) to reflect realistic conditions in agricultural soil.

Since natural soil polymers may also interfere with plastic quantification, additional sample cleanup procedures were tested for WR soil with a C_{org} of 5.16 %. The selected cleanup procedures were intended to be fast (<2 h processing time for a 12-sample batch), easily scalable and reproducible, robust against external contamination, and compatible with the subsequent dissolution of polymers in TCB. To this end, soil C_{org} was either preextracted with methanol, oxidatively digested using Fenton reagent, or flocculated with $KAl(SO_4)_2$ prior to TCB extraction. The methanol cleanup was simplified from Fuller and Gautam (2016). In brief, spiked soils were topped off with 8 mL methanol (CAS 67-56-1, 99.9 %, Carl Roth, Karlsruhe, Germany) and agitated for 60 min in a horizontal shaker at 150 rpm. Afterwards, the extracts were centrifuged (1500 rcf, 15 min) and the supernatant was discarded. The remaining methanol was evaporated at 60 °C under a gentle N_2 stream. The Fenton digestion was performed by adding 10 mL of aqueous $FeSO_4 \cdot 7\ H_2O$ solution (CAS 7782-63-0, 20 g L^{-1}, pH 2, Carl Roth, Karlsruhe, Germany) and 10 mL of H_2O_2 (CAS 7722-84-1, 30 %, Carl Roth, Karlsruhe, Germany) to the spiked soil in accordance with Hurley et al. (2018). The reaction mixture was left for 60 min in an ice bath before slowly heating it to 60 °C to dry the sample and decompose remaining H_2O_2. Humic substances were flocculated by

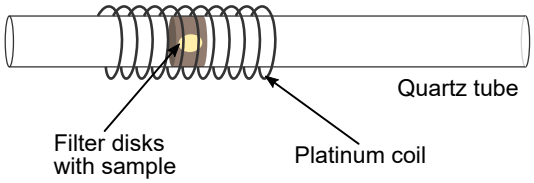

Figure 1. Schematic of a pyrolyzer quartz tube equipped with filter disks to absorb the liquid sample

mixing 4 mL of a 500 mg L^{-1} aqueous $KAl(SO_4)_2 \cdot 12\ H_2O$ solution (CAS 7784-24-9, ≥98 %, Carl Roth, Karlsruhe, Germany) with the soil (Mandalakis et al., 2018). The mixture was shaken for 60 min at 150 rpm and evaporated under N_2 at 105 °C.

Finally, all soil samples were extracted with 8 mL TCB at 120 °C for 60 min. After having cooled down, the extracts were allowed to sediment before transferring the supernatant into ND9 vials using glass Pasteur pipettes. Procedural blanks and control soil without any plastic added followed all extraction steps to quantify a potential contamination.

2.3 Py-GC/MS analysis

Instrumental analyses were performed using a Pyroprobe 6150 filament pyrolyzer (CDS Analytical, Oxford, United States) coupled with a Trace GC Ultra with DSQII mass spectrometer (MS; Thermo Fisher Scientific, Bremen, Germany). The pyrolyzer probe consists of a resistively heated platinum coil that holds an open ended quartz tube. The quartz tubes were filled with two quartz filter disks punched out of a Whatman QM-A microfiber filter (Kent, United Kingdom) using a 2 mm biopsy punch with plunger (Miltex, Rietheim-Weilheim, Germany). The filter disks were positioned inside the quartz tube so that they align with the center of the platinum coil when placed into the pyrolyzer probe (Figure 1).

Prior to Py-GC/MS analysis, a sample aliquot of 2 µL was applied onto the filter disk inside the quartz tube using a gastight 10 µL syringe with PTFE plunger (Hamilton 1701 N with 26s gauge, Bonaduz, Switzerland). The quartz tube was transferred into the pyrolyzer using stainless steal tweezers to avoid any contamination, for instance, from nitrile or latex gloves. The pyrolyzer interface was held at 300 °C and continuously flushed with 20 mL min^{-1} He to evaporate remaining TCB and volatiles. After 3 min, the sample was flash pyrolyzed (10 K ms^{-1} to 750 °C with a 15 s hold) and transferred to the GC/MS system via a passivated transfer line (350 °C). The split/splitless injector was operated at 300 °C with a split ratio of 1:10. The pyrolysates were separated on a 30 m × 0.25 mm capillary column (5 % phenyl-arylene, 95 % dimethylpolysiloxane, 0.25 µm film thickness, ZB-5MS) connected to a 2 m deactivated fused silica guard column (both Phenomenex, Aschaffenburg, Germany). The He carrier gas flow was set at 1.3 mL min^{-1}. The gas chromatograph (GC) oven was programmed from 40 °C (2 min hold) to 300 °C at 8 K min^{-1} (50 min run time). The transfer line connecting the GC with the MS was kept at 280 °C, and the MS ion source (electron ionization, 70 eV) was heated to 230 °C. The fore pressure of the MS was checked to be <0.07 mbar. The background intensity of 28 *m/z* (atmospheric N_2) was supposed to be $<5 \times 10^7$ and the total ion current (TIC) $<10^8$. Values exceeding these criteria indicated a leak in the system.

2.4 Pyrolysate identification and calibration

Pyrolysates were first screened in scan mode (50–300 *m/z*) before switching to selected ion monitoring of specific *m/z* ratios (100 ms dwell time) as indicated in Table 2 and reported in previous research (Tsuge et al., 2011; Fischer and Scholz-Böttcher, 2017; Dümichen et al., 2015). TIC pyrograms were evaluated using OpenChrom (Community Edition version 1.4.0; Wenig, 2011) with NIST08 database for peak identification. Identified pyrolysates (Table 2) were abbreviated based on a modified "lipid number" notation in the form of *b*C:D(p_1, p_2, …, $p_{D/2}$), in which C is the total number of carbon atoms of the compound, D denotes the number of double bonds, and their respective position p is given in parentheses (Zelles, 1999). The prefix *b* specifies additional functional groups and their position in the carbon backbone, for example, 2Me for a methyl group or 2Ph for a phenyl moiety at the second carbon atom.

Peaks were automatically integrated from the valley between the peaks to the horizontal baseline using a sliding window size of 3 scans and a minimum signal-to-noise ratio of 7. Further data analysis was performed using R (version 3.6.1).

Table 2. Polyethylene (PE), polypropylene (PP), and polystyrene (PS) pyrolysates analyzed for method development

Polymer	Pyrolysate	Full name	CAS	RI†	*m/z*
PE	14:2(1,13)	1,13-Tetradecadiene	021964-49-8	1385	82, 95
	14:1(1)	1-Tetradecene	001120-36-1	1392	55, 69, 83‡
	14:0	Tetradecane	000629-59-4	1400	55, 69, 83‡
	15:2(1,14)	1,14-Pentadecadiene	021964-50-1	1485	82, 95
	15:1(1)	1-Pentadecene	013360-61-7	1493	55, 69, 83‡
	15:0	Pentadecane	000629-62-9	1500	55, 69, 83‡
	16:2(1,15)	1,15-Hexadecadiene	021964-51-2	1585	82, 95
	16:1(1)	1-Hexadecene	113032-42-1	1593	55, 69, 83‡
	16:0	Hexadecane	000544-76-3	1600	55, 69, 83‡
	17:2(1,16)	1,16-Heptadecadiene	021964-52-3	1686	82, 95
	17:1(1)	1-Heptadecene	006765-39-5	1693	55, 69, 83‡
	17:0	Heptadecane	000629-78-7	1700	55, 69, 83‡
	18:2(1,17)	1,17-Octadecadiene	013560-93-5	1787	82, 95
	18:1(1)	1-Octadecene	000112-88-9	1793	55, 69, 83‡
	18:0	Octadecane	000593-45-3	1800	55, 69, 83‡
PP	2,4Me9:1(1)	2,4-Dimethyl-1-heptene	19549-87-2	841	70, 126
	2,4,6Me12:1(1)*i*	2,4,6-Trimethyl-1-nonene (isotactic)	55771-40-9	1307	69, 111
	2,4,6Me12:1(1)*h*	2,4,6-Trimethyl-1-nonene (heterotactic)	55771-40-9	1316	69, 111
PS	Sty	Styrene	100-42-5	895	78, 104
	αMeSty	α-Methylstyrene	98-83-9	981	103, 118
	2,4Ph16:1(1)	2,4-Diphenyl-1-butene	16606-47-6	1721	91, 208
	2,4,6Ph24:1(1)	2,4,6-Triphenyl-1-hexene	18964-53-9	2438	91, 207

†RI = retention index; ‡used for screening only

Calibration series of 5–150 µg mL^{-1} mixed PE, PP, and PS standards were pyrolyzed together with 3–5 blanks (0 µg mL^{-1} in TCB). LODs and LOQs were calculated using Equations 1 and 2, respectively, in accordance with the German standard DIN 32645 (2008) as implemented in the R package "envalysis" (version 0.3.3, code publicly available from `https://doi.org/cn74`).

$$\mathrm{LOD} = \frac{\sigma_{\mathrm{blank}}}{a} \cdot t_{n-1;0.01} \sqrt{n^{-1} + m^{-1}} \tag{1}$$

$$\mathrm{LOQ} = k \cdot \frac{\sigma_{xy}}{a} \cdot t_{n-2;0.01} \sqrt{n^{-1} + m^{-1} + \frac{(\mathrm{LOQ} - \bar{x})^2}{S_{xx}}} \tag{2}$$

Therein, σ_{blank} is the standard deviation of integrated peak areas from blanks, σ_{xy} is the residual standard deviation, and a is the slope of the calibration curve. t is the 99 % percentile of the Student's t distribution with $n-1$ and $n-2$ degrees of freedom, n as the total number of measurements, and m as the number of replicates. $k = 3$ is the recommended certainty factor for the LOQ; $\bar{x}$ is the arithmetic mean of all standard concentrations, and S_{xx} is the sum of squares of x. Note that calculating the LOQ is an iterative process with $\mathrm{LOQ} = k \cdot \mathrm{LOD}$ as initial value. Instrumental detection limits were calculated by multiplication of the respective LODs with the injection volume of 2 µL. Method detection limits were estimated by dividing LODs by the extraction volume of 8 mL and multiplying it with the extracted soil mass (4 g).

2.5 Method validation

At the beginning of each week, a fresh calibration series was prepared. Sample measurements of the following days were bracketed with 100 µg mL^{-1} standards to correct for inter-day variations in peak intensities. Corrected peak areas were then used for quantification.

In line with IUPAC recommendations (Currie, 1995), the intra-day repeatability of the Py-GC/MS method was verified by measuring a sequence of 150 µg mL^{-1} standards ($n = 10$) and determining relative standard deviations (RSDs) of peak areas. A linear model was fitted to the data to check if the peak areas changed significantly during the day. Inter-day variability was estimated from two 150 µg mL^{-1} standard samples repeatedly measured for eight days.

To test whether PE, PP, and PS selectively decompose into their respective pyrolysates without interfering with each other, successive measurements of 150 µg mL^{-1} mixed polymer standards were compared with standards containing each individual polymer. Furthermore, potential interferences from soil matrix and non-target plastics (PET, PMMA, PVC, and TWP) were assessed. Differences in peak areas of pyrolysates were statistically evaluated using analyses of variance (ANOVAs) with Bonferroni-adjusted Tukey tests for post-hoc multiple comparisons. ANOVAs were checked for normality and homoscedasticity of residuals using quantile–quantile and residual vs. fitted plots. The same statistical tools were applied to compare the various extraction and cleanup methods for PE, PP, and PS from different soil types with one another. Results are given as mean ± standard deviation (SD).

3 RESULTS AND DISCUSSION

3.1 Polymer quantification

From the initial screening set of 22 pyrolysates (Table 2), six compounds performed best in terms of linearity (adj. R^2 >0.996) within the calibration range, LODs, and LOQs (Figure 2 and Table 3). LODs were below the lowest standard of 5 µg mL^{-1} for the PE *n*-alkadienes 15:2(1,14) and 17:2(1,16) detected via 82 and 95 *m/z*. 18:2(1,17) produced an LOD of 11.3 µg mL^{-1}. The LOQs ranged between 25 and 54 µg mL^{-1}. For PP, only 2,4Me9:1(1) was quantifiable (70 and 126 *m/z*) with an LOD and LOQ of 43.2 and 46.7 µg mL^{-1}, respectively. Sty and αMeSty were the most indicative pyrolysates for PS and detected via 78 and 104 *m/z* and 103 and 118 *m/z*, respectively. Their adj. R^2s, LODs, and LOQs were similar to PE pyrolysates.

Taking into account the 2 µL injection volume, instrumental detection limits were 1–86 ng. This is at least 2.5 times lower than most recent advances in PE, PP, and PS method developments with TED-GC/MS and microfurnace Py-GC/MS (Duemichen et al., 2019; Fischer and Scholz-Böttcher, 2019; Dierkes et al.,

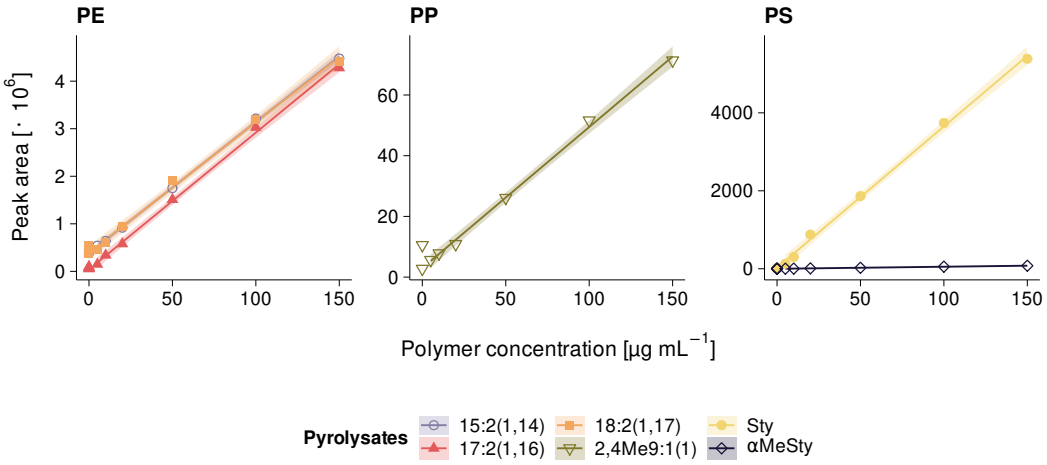

Figure 2. Calibration curves of PE, PP, and PS standards in 1,2,4-trichlorobenzene (TCB); see Table 3 for parameters

Table 3. Calibration parameters of pyrolysates selected for quantification

Polymer	Pyrolysate	Intercept	Slope	adj. R^2	LOD [µg mL^{-1}]	LOQ [µg mL^{-1}]
PE	15:2(1,14)	384 440	27 563	0.9992	4.8	25.7
	17:2(1,16)	40 501	28 782	0.998	2.5	38.6
	18:2(1,17)	391 786	27 423	0.9962	11.3	53.4
PP	2,4Me9:1(1)	2 987 986	464 559	0.9971	43.2	46.7
PS	Sty	26 306 594	36 246 576	0.9975	0.5	43.3
	αMeSty	−860 185	527 700	0.9986	1.6	33.1

2019). Note that Dierkes et al. (2019) reported LOQs calculated from blanks, which is usually defined as LOD (Equation 1). While Duemichen et al. (2019) and Dierkes et al. (2019) used the same indicator pyrolysates for quantification as we did but on different *m/z* ratios, Fischer and Scholz-Böttcher (2019) chose *n*-alkanes, *n*-alkenes, and the PS trimer 2,4,6Ph24:1(1).

All these studies have in common that they relied on a very sensitive microscale to weigh several nanograms of solid polymer directly into pyrolyzer sample cups or to quantitatively transfer a representative aliquot of solid mixture. To facilitate the heat transfer of the pyrolyzer filament or microfurnace into the sample, the lowest sample amount possible is typically aimed for. However, the lower the amount to be weighed, the higher the relative weighing error becomes and the more challenging it is to obtain a homogeneous mixture. So far, this has been one of the major drawbacks of Py-GC/MS (Fischer and Scholz-Böttcher, 2019). When combining Py-GC/MS with prior dissolution of polymers in an appropriate solvent such as TCB, stock solutions can be easily handled, quantitatively diluted or preconcentrated, and transferred directly into the pyrolyzer quartz tubes. Dissolution in TCB therefore allows for constantly pyrolyzing the same but low amount of sample. Absorbing the TCB solution into the quartz filter disks inside the quartz tube further ensures the optimal alignment of the sample with the pyrolyzer filament and thereby enabling more accurate and reproducible pyrolyses down to the nanogram range.

3.2 Repeatability

The RSDs of PE indicator pyrolysates were 3.4–4.5 % without showing any trend of systematically increasing or decreasing peak intensities during a one-day series of $n = 10$ standard measurements (Figure 3, $p > 0.529$, linear model); this is intra-day variability. By contrast, inter-day variability was 15.2–17.9 %. The PP pyrolysate 2,4Me9:1(1) produced a stable ($p = 0.728$, linear model) intra-day RSD of 7.2 %, and an inter-day RSD of 10.4 %. With 3.2 and 4.2 % of intra-day variability, the RSDs of PS pyrolysates Sty and αMeSty were in the same range as PE. However, Sty showed a statistically significant tendency to decrease in signal intensity by 0.88 % per measurement ($p = 0.002$, linear model), while

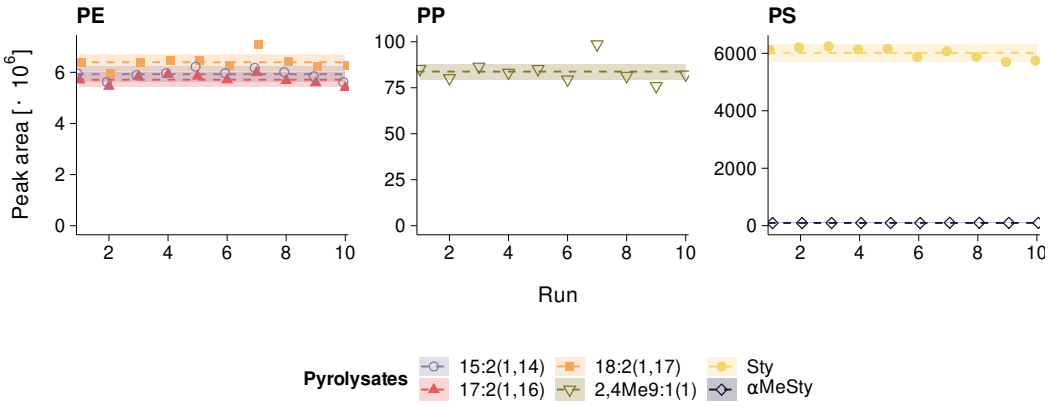

Figure 3. Repeatability of Py-GC/MS measurements ($n = 10$) with means (dashed lines) and ± 5 % RSD bands

αMeSty increased by 1.05 % ($p = 0.020$, linear model). With respect to the RSDs of the measurement series, these changes are deemed negligible if peak intensities are corrected with bracketing standards measured in the beginning and at the end of each day. This also applies to the inter-day variability of Sty and αMeSty which were 13.9 and 16.5 %.

Measurement repeatability was in line with comparable studies. PS analysis via liquid chromatography/mass spectrometry with an atmospheric pressure photoionization source, for instance, resulted in an intra- and inter-day repeatability of 1.8–2.4 % and 15.5–25.6 %, respectively ($n = 5$; Schirinzi et al., 2019). With TED-GC/MS, Duemichen et al. (2019) achieved RSDs ranging from 6 to 12 % for various PP pyrolysates. The authors suggested using an internal standard to further optimize RSDs. Fischer and Scholz-Böttcher (2019) used androstane, deuterated anthracene, 9-dodecyl-1,2,3,4,5,6,7,8-octahydro anthracene, and cholanic acid for internal standardization of PE, PET, polycaprolactam, and PS. Since those internal standards are not polymers, they probably behave differently than the polymer analytes when heated to typical pyrolysis temperatures of 600–800 °C. Particularly polycyclic aromatic hydrocarbons such as anthracene are thermally stable and more likely to evaporate instead of thermally decomposing along with the polymer analytes. Accordingly, Fischer and Scholz-Böttcher (2019) reported that the deuterated anthracene might have interacted with the inner surface of the pyrolyzer which eventually decreased repeatability. Though expensive, deuterated plastics (Dierkes et al., 2019) or specialized polymers like poly(3,4-ethylenedioxythiophene) typically used in semiconductor industry could be promising alternatives since they decompose in the same temperature range as the polymer analytes (Jin et al., 2013). The use of an appropriate internal standards for routine Py-GC/MS analyses will be evaluated in future studies.

3.3 Selectivity of indicator pyrolysates

PE pyrolyzes into *n*-alkanes, *n*-alkenes, and *n*-alkadienes of decreasing chain length. In the pyrogram sections given in Figure 4, the first peaks of these triplets are the *n*-alkadienes used for quantification (RIs = 1486, 1686, and 1786; Table 2) followed by their respective *n*-alkenes (RIs + 7). Note that the *n*-alkanes (RIs = 1500, 1700, and 1800) were low in intensity due to *m/z* ratios optimized for *n*-alkadienes. Regardless of pyrolyzing a 150 µg mL^{-1} PE standard individually or in a mixture with PP and PS, the *n*-alkadiene peaks aligned accurately with one another, while signals from PP or PS were negligible particularly for 15:2(1,14) and 17:2(1,16). 18:2(1,17) was slightly interfered by PP and PS although this was not statistically significant (Figure 5; $p = 1$, Tukey). For 15:2(1,14), however, triplicate measurements of the polymer mixture were on average about 15 % lower than pure PE ($p < 0.001$, Tukey). In general, 17:2(1,16) showed the least interferences with background signals from pure PP and PS being comparable to blank measurements ($p = 1$, Tukey). The PP indicator pyrolysate 2,4Me9:1(1) at RI 841 was about 10 % lower in intensity when pure PP was pyrolyzed compared to the polymer mixture ($p = 0.057$, Tukey). This suggests a minor interference from PE that may have originated from the peak shoulder at RI 845 and a slightly higher but statistically insignificant background noise from PE and PS ($p = 1$, Tukey). In comparison to that, Sty and αMeSty from PS pyrolysis were both selective in terms of showing no

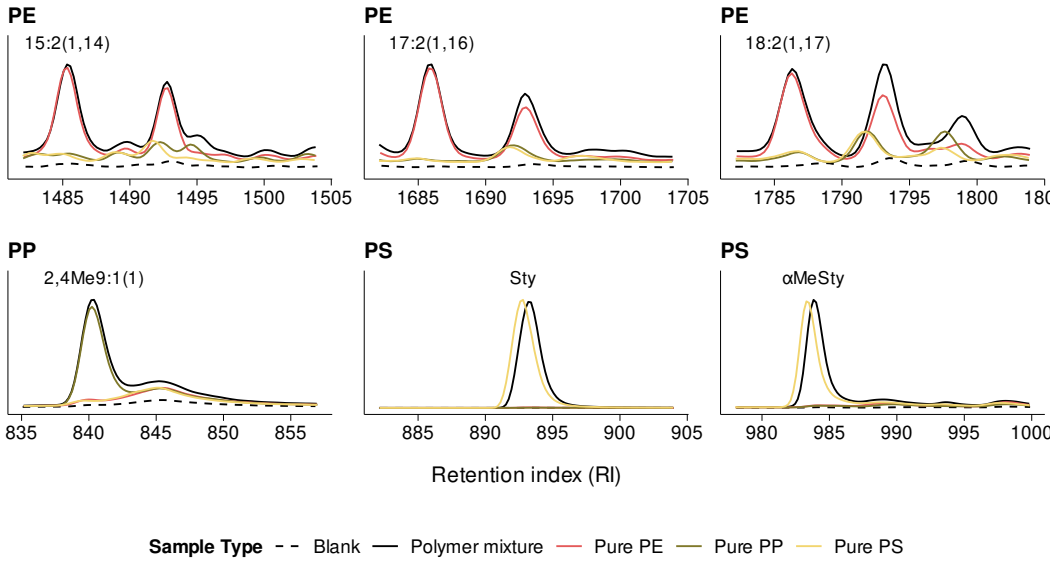

Figure 4. Pyrogram sections of PE, PP, and PS pyrolysates obtained by analyzing each individual polymer or a mixture of all three polymers (150 µg mL^{-1})

interference from PE and PP ($p < 0.001$, Tukey). For its lower variation compared to Sty, αMeSty may be favorably used for PS quantification.

To our knowledge, the possibility of polymers analyzed together and interfering with each other by formation of identical or chromatographically inseparable pyrolysates has so far only been described by Fischer and Scholz-Böttcher (2017). However, the authors neither tested potential interferences in their Py-GC/MS setup nor suggested a certain approach to counteract them. With our experimental design, we were able to show that PE, PP, and PS can be selectively analyzed in a polymer mixture without interfering with each other by more than 10 % at equal concentrations. Especially PP quantified via 2,4Me9:1(1) may be slightly overestimated when PE is present in large quantities. But since the PE pyrolysate 17:2(1,16) was particularly robust against background signals from PP or PS, it would be possible to correct the overestimated PP content for its PE share.

3.4 Matrix interferences

Extracting LUFA 2.2 and RefeSol 06-A with TCB, but without adding plastic, resulted in background signals equivalent to 70 ± 10 and 31 ± 4 µg g^{-1} PE, respectively (Table 4). Interestingly, addition of the non-target plastics PET, PVC, PMMA, and TWP to LUFA 2.2 soil did not increase matrix interferences. With 700 ± 200 µg g^{-1}, the matrix-induced background signal in WR soil was about 10–20 times higher than in LUFA 2.2. For soils with a C_{org} content exceeding 2 %, namely RefeSol 06-A and WR, a prior cleanup step with methanol doubled PE background levels. Similarly, Fenton digestion of WR soil resulted in matrix interferences equivalent to 1000 ± 200 µg g^{-1} PE. Only flocculation with $KAl(SO_4)_2$ considerably reduced background levels to 400 ± 200 µg g^{-1}. Regardless of the extraction method and pretreatment, procedural blanks were below the estimated method detection limit of 5 µg g^{-1}. The PP background extracted with TCB was not detectable except for WR soil (100 ± 100 µg g^{-1}). Similar to PE, PP levels doubled when applying a prior methanol cleanup step. However, $KAl(SO_4)_2$ flocculation and Fenton digestion were able to reduce matrix interferences below the LOD. PS background levels in LUFA 2.2 soil were below the method detection limit of 3.2 µg g^{-1}. In line with PE and PP, PS contents slightly increased with the C_{org} content of the soil. With respect to SDs, neither the methanol cleanup nor Fenton digestion changed the matrix-induced background considerably while $KAl(SO_4)_2$ decreased matrix interferences to non-detectable levels.

The matrix interferences identified in our study were generally comparable to those reported in previous research: Dierkes et al. (2019) detected matrix interferences equivalent to 140, 210, and 50 µg g^{-1} PE in an artificial, inert matrix spiked with 3 % of wood, leafs, or humic acids, respectively. The authors applied ASE with methanol and THF prior to Py-GC/MS quantification via 15:2(1,14). Similarly,

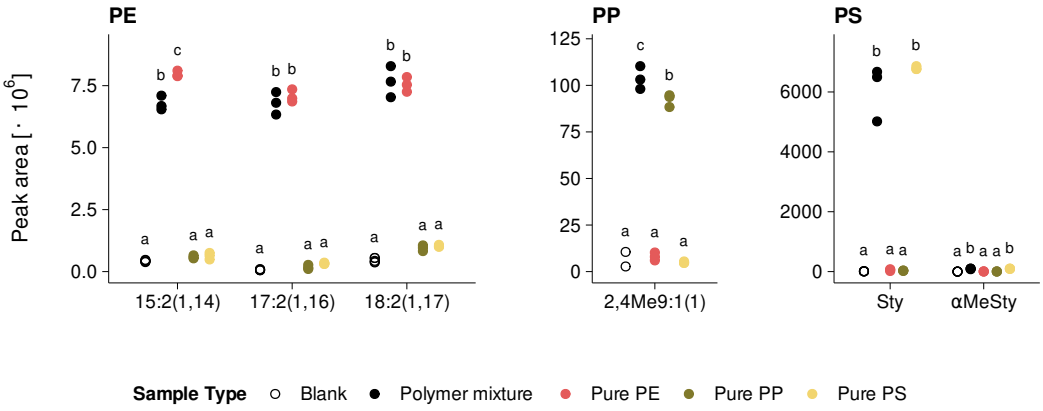

Figure 5. Peak areas of PE, PP, and PS pyrolysates measured individually or in a mixture of all three polymers (150 µg mL^{-1}); different letters indicate significant differences between sample types for each pyrolysate ($p < 0.05$, Tukey)

Table 4. Matrix interferences of different soil types (mean ± SD)

Polymer	**Soil**	**Extraction procedure** [µg g^{-1}]			
		TCB only	Methanol cleanup	$KAl(SO_4)_2$ flocculation	Fenton digestion
PE	LUFA 2.2	70 ± 10			
	LUFA 2.2*	70 ± 7			
	RefeSol 06-A	31 ± 4	70 ± 20		
	WR	700 ± 200	1300 ± 100	400 ± 200	1000 ± 200
PP	LUFA 2.2	0 ± 200			
	LUFA 2.2*	0 ± 100			
	RefeSol 06-A	0 ± 0	32 ± 100		
	WR	100 ± 100	200 ± 100	0 ± 0	0 ± 0
PS	LUFA 2.2	2 ± 4			
	LUFA 2.2*	4 ± 3			
	RefeSol 06-A	20 ± 30	1 ± 1		
	WR	7 ± 3	12 ± 4	0 ± 4	8 ± 3

*with 50 µg g^{-1} non-target polymers (19 % PET, 11 % PMMA, 41 % PVC, and 29 % TWP); indicator pyrolysates were 17:2(1,16) for PE, 2,4Me9:1(1) for PP, and αMeSty for PS

Fischer and Scholz-Böttcher (2017) found their PE and PS pyrolyses affected by chitin, wood, wool, and cellulose, however, without quantifying potential interferences. For two natural soils with unreported C_{org}, 790–850 µg g^{-1} PE, 40 µg g^{-1} PP, and 40–50 µg g^{-1} PS were detected (Dierkes et al., 2019). The question whether these levels came from matrix interferences or a contamination with plastic debris remained unresolved. By contrast, Dümichen et al. (2015) applied TED-GC/MS and found that soil matrix with an unspecified C_{org} did not induce any interferences. Since Dümichen et al. (2015) and Dümichen et al. (2017) determined PE in a concentration range approximately three orders of magnitudes higher than we did, contrasting findings are most likely attributed to the higher sensitivity of our Py-GC/MS setup.

Besides a facilitated sample handling, dissolution of PE, PP, and PS in TCB offers the advantage of restricting the amount of other polymers and interfering matrix being dissolved along with the analytes and transferred into the Py-GC/MS system. Apart from our three target polymers, TCB is recommended as SEC solvent only for poly(ethylene-vinyl acetate), polythiophene, and other polyolefins (Bivens, 2016). In addition, only compounds thermally decomposing between 300 and 750 °C were passed to our GC/MS, which may have further reduced the potential for interferences.

In spite of that, we found particularly high matrix interferences for PE in WR soil, a pristine forest soil with 5.16 % C_{org}. The two agricultural soils with <2.5 % C_{org} showed considerably less background signals. This is not surprising since up to 9 % of soil C_{org} consists of $(CH_2)_n$ chains of 25–30 units (Hu et al., 2000) as, for example, present in suberins, cutins, or microbial cell membranes. Based on the C_{org} of our reference soils, this fraction could potentially induce interferences equivalent to 1500–4500 µg g^{-1} PE. Just by using TCB as an extraction agent, we were able to reduce potential interferences by a factor of 5–20. In comparison with that, prior Fenton digestion or methanol cleanup might have rather mobilized than removed certain fractions of interfering matrix as indicated by elevated PE background levels from both pretreatments. Here, existing ASE applications with three rinsing cycles of 15 mL methanol per 1 g of sample at 100 °C (Fuller and Gautam, 2016; Dierkes et al., 2019) may be superior to our simplified batch setup. But matrix interferences from such extraction setups have not been quantified for organic rich soils yet. Besides that, it cannot be excluded that reference soils may have been contaminated with plastic debris on-site or during packaging and shipping, thereby, mistaking a potential plastic contamination for matrix interferences. This could only be assessed by characterizing soil organic matter fractions from soil databases dating back to times before the introduction of today's consumer plastics. Based on these findings, further efforts should be made to reduce interferences from specific soil constituents, for instance by using an advanced flotation and filtration apparatus (Han et al., 2019), selective enzymes (Löder et al., 2017), dispersive solid phase extraction, or on-line transesterification and evaporation of lipid-like substances with BF_3 or trimethylsulfonium hydroxide prior pyrolysis. Moreover, further research will need to test alternative solvent mixtures to extend the applicability of our Py-GC/MS approach to a wider range of polymer types.

3.5 Plastic recovery from soil

As outlined above, matrix interferences equivalent to >400 µg g^{-1} exceeded the spiked polymer content by a factor of 2–4. In those cases, the calculation of matrix-corrected recoveries was not meaningful and data were thus excluded from further examination (Figure 6). PE recovered from LUFA 2.2 with TCB only ranged from 80 to 110 %. The recoveries were independent of the spiking level, and the addition of non-target polymers did not influence the recovery of PE. For RefeSol 06-A, recoveries with TCB were slightly lower than in LUFA 2.2 (61 and 70 %). The methanol cleanup decreased the recovery to 26 and 55 %. Due to high matrix interferences, PE recoveries from WR soil could only be evaluated for samples flocculated with $KAl(SO_4)_2$ prior to TCB extraction, and the recovery was very low (10 ± 10 %). Extracting PP from LUFA 2.2 and RefeSol 06-A soil using TCB yielded recoveries of 100–160 %. At 50 µg g^{-1} spiking level, recoveries were higher and varied more than at 250 µg g^{-1}. In line with PE, the methanol pretreatment decreased recoveries to 63 and 80 %. In WR soil, only 30 ± 20 % of PP were recovered after $KAl(SO_4)_2$ flocculation. Prior Fenton digestion increased recoveries to 110 and 140 %. PS recoveries ranged from 77 to 119 %, except for the Fenton digestion of WR soil (130 ± 10 %) and TCB extraction of RefeSol 06-A at the lower spiking level of 50 µg g^{-1} (46 ± 7 %).

In summary, TCB extractions without any pretreatment performed best (70–128 % recovery), particularly at 250 µg g^{-1} spiking level from soils with less than 2.5 % C_{org}. PP contents were slightly overestimated due to the interference with PE as discussed before. Although $KAl(SO_4)_2$ effectively removed interfering matrix constituents, it concomitantly reduced PE and PP recoveries. Interestingly,

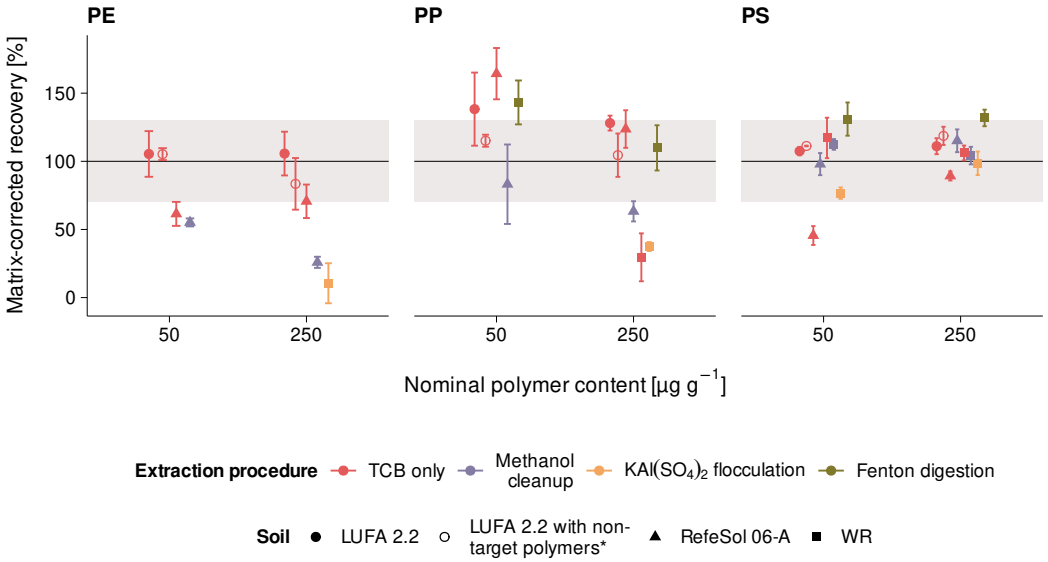

Figure 6. Recoveries of PE, PP, and PS from different soil types (mean ± SD) corrected for matrix interferences (Table 4); the gray band marks the 70–130 % range typically acceptable for recovery experiments; *50 µg g^{-1} consisting of 19 % PET, 11 % PMMA, 41 % PVC, and 29 % TWP

prior Fenton digestion led to elevated recoveries, which contrasts Hurley et al. (2018) who found Fenton reagent performing best in terms of organic matter removal and preservation of plastic particles prior to FTIR imaging. However, our findings are in line with previous thermoanalytical studies that obtained recoveries of 80–130 % when extracting PE, PP, and PS with dichloromethane and THF from solid matrices after an initial methanol cleanup (Fuller and Gautam, 2016; Dierkes et al., 2019). In contrast to our study, Fuller and Gautam (2016) used about 20–100 times higher spiking levels (5 mg g^{-1}) and Dierkes et al. (2019) extracted 50 and 750 µg g^{-1} microplastics from an artificial sample containing 3 % humic acids in sea sand. In such an artificial matrix, interferences are less likely to occur than in natural soil with its large variety of substance classes like natural polymers, lipids, or proteins.

4 CONCLUSIONS

Dissolution of plastic debris in an appropriate solvent prior thermoanalysis facilitates the preparation of calibration curves, simplifies sample handling, reduces the risk of contamination, and allows for the extraction of plastic debris from several grams of solid matrix. By dissolving the three most environmentally relevant polymers PE, PP, and PS in TCB for direct quantification of sample solutions via Py-GC/MS, we obtained instrumental detection limits ranging from 1 to 86 ng which is equivalent to 1–86 µg g^{-1} for the method. Furthermore, TCB was successfully tested for the selective extraction of PE, PP, and PS from up to 4 g soil. This enabled us to account for the heterogeneity of soil while keeping interferences from non-target polymers and soil matrix at a minimum. The lowest interferences and the best recoveries were obtained at spiking levels of 250 µg g^{-1} in agricultural soil with less than 2.5 % C_{org}. Therefore, further method development is necessary to reduce matrix interferences for soils with higher C_{org} contents to eventually comply, for example, with 2002/657/EC criteria for residual analysis by the European Commission (2002).

With less than 2 h needed for the batch preparation of 12 or more samples and 50 min analysis time per sample, our new Py-GC/MS method has the potential to be used for routine analyses and screening studies of agricultural soil. Py-GC/MS analyses may be complemented by FTIR or Raman microspectroscopy of selected samples if additional information on particles sizes and shape is needed. Follow-up studies to further improve and apply the new method are planned to better understand the occurrence and fate of plastic debris in agricultural systems, and more specifically, whether agricultural plastic films may function as source for plastic debris in soil.

ABBREVIATIONS

ANOVA	analysis of variance
ASE	accelerated solvent extraction
C_{org}	organic carbon
FTIR	Fourier transformed infrared spectroscopy
GC	gas chromatograph
GC/MS	gas chromatography/mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
MS	mass spectrometer
PE	polyethylene
PET	polyethylene terephthalate
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
RI	retention index
RSD	relative standard deviation
SD	standard deviation
SEC	size exclusion chromatography
TCB	1,2,4-trichlorobenzene
TED-GC/MS	thermal desorption-gas chromatography/mass spectrometry
THF	tetrahydrofuran
TIC	total ion current
TWP	tire wear particles

CONFLICT OF INTERESTS

The authors declare no competing conflicts of interest.

AUTHOR CONTRIBUTIONS

ZS conceived the idea, designed the study, performed the experiments, and took the lead in writing the manuscript. AK assisted with measurements. KM and GS supervised the project. The manuscript was finalized through contributions of all authors.

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