

SOIL Discuss., author comment AC1
<https://doi.org/10.5194/soil-2021-70-AC1>, 2021
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Reply on RC1

Zacharias Steinmetz et al.

Author comment on "Are agricultural plastic covers a source of plastic debris in soil? A first screening study" by Zacharias Steinmetz et al., SOIL Discuss.,
<https://doi.org/10.5194/soil-2021-70-AC1>, 2021

Thank you very much for your time and the rigorous evaluation of our manuscript. We highly appreciate your constructive comments and questions that we believe will help to further improve our work.

In the following, we address all comments point by point and suggest changes for a future manuscript revision (highlighted in bold face).

Method

1. The authors have not included any information on laboratory quality control measures which are a must for microplastics studies. Were laboratory and field blanks analysed and how? What were concentrations in the blank samples? Were deposition blanks conducted during the FTIR analysis? Were samples extracted in a fume hood, were lab coats (what sort) worn during extraction? Were duplicates conducted to assess heterogeneity in the sample? What were your internal standard recoveries, were polymer concentrations recovery corrected? Please include a section for QA/QC in the manuscript.

> Our response: In the submitted version of our manuscript, we intended to keep QA/QC brief and combined it with our method validation (Section 2.6: Method validation and quality control). Therein, we stated that "The soil cores were immediately transferred to uncoated paper bags and air-dried therein to reduce the risk of contamination." (Lines 83f) and "All measurements were monitored with procedural blanks." (Line 164).

We will expand this to a more comprehensive QA/QC section which could read as follows:

"To prevent the risk of contamination, all laboratory equipment coming into direct contact with the sample or the extract solution was made of glass, metal, paper, or PTFE. PE, PP, or PS equipment was completely avoided. The worn laboratory coats were of 100% cotton. In addition, all samples and extracts were kept in closed vessels or covered with aluminum foil. The vessels were only opened under a fume hood.

The sample extraction was monitored with weekly procedural blanks that underwent the complete extraction procedure as the samples but without soil addition. Plastic contents in our procedural blanks were exclusively below the LOD."

Please note that we did not take field blanks because we could hardly treat them in the same way a sampled soil is. But we analyzed all our equipment, including the used paper bags, for their contamination potential and found them not interfering our analysis. In addition, it remains worth noticing that the majority of our soil samples did not contain any plastics (<LOD) which suggests negligible sample contamination.

Furthermore, we did not run FTIR deposition blanks for the particles >2mm since our FTIR-ATR analysis only aimed at the qualitative identification of single suspect particles. In this case, the FTIR signal of the sample surface was expected to significantly exceed that of dust traces on the particle.

Since we designed our study to be a first screening, we ran single measurements only. We suggest to further clarify this in the methods section (Line 136f):

"Each sample was measured once as described in Section 2.3."

We further did not assess the recovery of our internal standard, namely deuterated PS (PS-d5). This is because PS-d5 was only added after sample extraction and served as a quality control measure for internal instrumental repeatability during measurement sequences.

We suggest to put this more clearly by adding (Line 152f):

"The internal standard PS-d5 was added after sample extraction and used for continuous repeatability checks of sample measurements."

2. More information is needed on the Py-GC-MS quantification. Why were the dienes chosen for quantification of the polyethylene (PE), was this from a previous published method? Were the samples analysed in full scan or SIM mode?

> Our response: Our solvent-based Py-GC/MS approach was originally published in Steinmetz et al. (2020). In order to avoid extensive repetitions, we tried to keep this short. Yet, we assessed the Py-GC/MS method performance once more in the present manuscript. In Section 3.4, Line 230ff, we stated that "The pyrolysates chosen for PE, PP, and PS quantification were 22:2(1,21), 2,4Me9:1(1), and Sty, respectively, as they performed the best in terms of signal linearity (adj. R2 > 0.995), instrumental LODs (<10 ng), and measurement repeatability (RSD <10 %, Table 2).".

To make this clearer, we suggest to add:

"The n-alkadiene 22:2(1,21) was preferred over the respective n-alkene or n-alkane because of its higher selectivity for PE (Steinmetz et al., 2020)."

Furthermore, our Py-GC/MS measurements were ran in SIM mode, which we report in Line 140ff: "The MS selectively monitored m/zs 70 and 126 for the PP pyrolysate 2,4-dimethyl-1-heptene (2,4Me9:1(1), RI 841), m/zs 104 and 118 for the PS pyrolysates styrene (Sty, RI 895) and α -methylstyrene (α MeSty, RI 981), respectively, and m/zs 82 and 95 for PE n-alkadienes like 1,21-docosadiene (22:2(1,21), RI 2187).".

To further clarify this, we suggest to add **"SIM mode"** in parentheses.

3. Styrene is not an ideal pyrolysis product for monitoring polystyrene (PS) as it is not selective. It can originate from organic material (although this may have been removed in your TD analysis) as well as being a pyrolysis product of many other polymers. Typically, the dimer or trimer or polystyrene is monitored. This will increase the MDLs but improve your selectivity. Also, how can you be certain the PS isn't a sampling/analysis artefact without any blank information? Combined with the poor matrix spike recoveries of PS in the reference soil, your method is not optimised or validated for analysis of PS and you cannot confidently report these results.

> Our response: Our blank chromatograms, these were the weekly procedural blanks (see item 1 above), did not contain styrene at intensities exceeding the LOD; nor did the analyses of our reference soils. In this regard, the selectivity of our method for PS does not originate from choosing styrene as a marker but (1) from the density separation excluding plastics with a density $>1.2 \text{ g cm}^{-3}$ and (2) the subsequent selective dissolution of our target polymers with trichlorobenzene/xylene. We think that this is also the reason why tire wear added to our reference soil at a level twice as high as our highest standard did not induce styrene signals that exceeded the LOD.

Our approach is further in line with Fabbri et al. (2020, doi: 10.1016/j.jaap.2020.104836) who similarly used styrene as a marker compound after polymer dissolution with toluene. The authors argued that dimers may also originate from secondary reactions of monomers with one another, which would challenge their selectivity in general. Such secondary reactions are, however, disfavored when PS is spread on a thin layer or on quartz filters after the solvent has dried. After polymer dissolution, the peak intensities of the PS oligomers are thus considerably lower than those obtained after the pyrolysis of solids. Although this is a very interesting observation, we are reluctant to add it to our discussion (Section 3.4) as it deviates from the common theme of the manuscript and was already addressed by Fabbri et al. (2020). If you and the editor prefer to have this added, we will be happy to do so.

We rather suspect the poor PS recoveries from clay soil to originate from aromatic PS domains interacting with soil particles during the density separation. This is currently discussed in Section 3.4, Line 256ff: "The dramatic decrease in PS recovery may be attributed to interactions forming between the delocalized π -electrons of the aromatic PS ring and SOM, iron and aluminum oxides, or cations bound to the negatively charged surface of clay particles (Newcomb et al., 2017).".

In line with your suggestion, we should interpret the PS results more carefully. This would include the following additions/modifications in our discussion.

This specifically applies to

Section 3.4 (Line 251):

"Irrespective of the spiking level though, our PS recoveries from the clayey RefeSol 06-A were particularly low (<12 %)."

Section 3.4 (Line 263):

"The 50 % PE and 62 % PP we recovered from RefeSol 06-A suggest a rather semi-quantitative evaluation of soils with a clay content >47 % and a Corg content >2.5 %. PS is evaluated qualitatively for its low recoveries."

Section 3.5 (Line 286):

“Due to the poor PS recoveries, these findings are most likely underestimated.”

Conclusions (Line 321):

“The combination of soil aggregate dispersion and density separation with solvent-based Py-GC/MS enabled the simple, yet selective quantification of PE and PP debris in agricultural soil. Analyzing a sample amount of 50 g better accounted for the heterogeneous distribution of discrete plastic particles in the soil matrix. The additional dispersion step further made plastic debris occluded in soil aggregates amenable to quantification. By contrast, poor PS recoveries potentially induced by that additional separation step challenged a reliable PS quantification.”

4. Details on PET, PMMA and PVC standards need to be included. What were your tyre wear debris? Were these obtained from a chemical standards company, were they prepared in house and from what type of tyres? Did you really not see a styrene peak from pyrolysis of PVC or from the styrene-butadiene rubber in tyre tread? This suggests your analysis or extraction method is not optimised.

> Our response: We used the same polymers in Steinmetz et al. (2020) and thus refrained from explaining them in detail.

We will add the following explanation to the revised version of our manuscript (Line 162ff):

“The PET came from a cryomilled bottle recyclate (PETKA CZ, Brno, Czech Republic) as detailed in David et al. (2018). The PMMA was ground from a commercial plexiglass provided by Bundesanstalt für Materialforschung und -prüfung (Berlin, Germany). The PVC was purchased from Aldrich Chemistry (Taufkirchen, Germany), and TWD was from a test rig at Bundesanstalt für Straßenwesen (Bergisch Gladbach, Germany).”

As detailed in our response to item 3, our solvent-based Py-GC/MS approach was selective not only because of choosing specific pyrolysis markers but also due to the density separation (1.2 g cm^{-3}) and selective dissolution with trichlorobenzene and xylene that specifically targeted PE, PP, and PS. PVC and tire wear did not interfere with our analysis because they have a higher density and do not dissolve in the applied extraction mixture.

5. Your samples are filtered at 4 μm . Can you comment on possibility of micro/nanoplastics in the smaller size range that may have been missed.

> Our response: Thank you for this important remark. This is a common challenge of current sample preparation methods for the analysis of microplastics in complex matrices. Particles smaller than 4 μm cannot be assessed quantitatively as they will partly flush through the filter but may at a certain stage be retained when the filter becomes increasingly clogged with clay particles. Furthermore, aggregated or coated nanoplastics may be retained more efficiently than virgin ones. Although quite speculative, we would be happy to add these thoughts to our discussion.

At least, we should highlight this drawback in our discussion (Line 248):

“The required filtration step, however, systematically excluded particles $<4 \mu\text{m}$

that were not retained by the used cellulose filter.”

Validation

1. You cannot state your method is validated for plastics in soils when one of your two soil reference materials returned unacceptably low recoveries. Further, your LODs (MDLs) are the concentration where you have acceptable method extraction and analysis recoveries. Considering you have <30% recovery for a 2 ug/g spike in the second reference soil, the method LODs certainly are not 0.3-0.8 ug/g. The extraction method needs further assessment to determine which types of soils are applicable and what the actual MDLs are. I also suggest removing PS from the analysis due to the above mentioned issues.

> Our response: We agree that this needs further clarification. In the current version of our manuscript, we highlighted that the “.. extrapolation of these validity criteria to field samples with a different texture and Corg composition remains difficult and requires careful interpretation.” (Line 249ff). This is a general shortcoming of soil analyses since reference soils will always differ from real soil samples.

For the calculation of LODs, we adhered to the German standard DIN 32645 (2008) and the EURACHEM guideline (Magnusson and Örnemark, 2014) which define the LOD as the minimum amount qualitatively detectable in a blank soil. In this sense, a low recovery close to the LOD (2 µg/g) is not surprising nor contradictory.

We thus suggest to add LOQs to Table 3 and critically discuss this data throughout the manuscript. Note that, according to DIN 32645, the calculation of LOQs is an iterative process that uses the LOD as an initial value but optimizes mostly toward the calibration standards. This is why the LOQs are quite similar in both soils:

Polymer	Pyrolysate	LOD* [mg kg ⁻¹]	LOQ* [mg kg ⁻¹]	Interference [†] [mg kg ⁻¹]	Recovery	
					at 2 mg kg ⁻¹ [%]	at 20 mg kg ⁻¹ [%]
<i>LUFA 2.2</i>						
PE	22:2(1,21)	1.9	9.5	0.9±0.3	133±9	105±3
PP	2,4Me9:1(1)	2.9	2.9	0±0	70±10	93±5
PS	Sty	3.3	6.2	0±0	52±2	86±4
<i>RefeSoil 06-A</i>						
PE	22:2(1,21)	1.2	9.5		30±20	50±10
PP	2,4Me9:1(1)	0.8	2.5		30±20	62±1
PS	Sty	0.7	6.2		0±0	12±5

*method limits of detection and quantification; [†]introduced from 40 mg kg⁻¹ non-target polymers.

Line 233:

“The respective method LOQs ranged from 2.5 to 9.5 mg kg⁻¹ (Table 3).”

Line 237ff:

“Recovering plastic debris at levels close to the method LOD (2 mg kg⁻¹) and below the respective method LOQs led to an overestimation of recovered PE (133±9 %) while underestimating PP (70 %) and PS (50 %).”

We further recalculated method LODs directly from the peak intensities of the blank soil.

In the first version of our manuscript, we estimated them from averaged soil contents. This now leads to about 1.5 times higher method LODs than before. The slightly elevated LODs reduce the total number of positive detections to 15 which, however, does not affect the outcome of our study.

We suggest to discuss LODs and LOQs in Line 251f:

“Inconsistent recoveries at a spiking level below the method LOQs of 2.5–9.5 mg kg⁻¹ challenged the sensitivity and robustness of our solvent-based approach.”

Line 263f:

“Based on the two reference soils tested and on previous work (Steinmetz et al., 2020), we considered our method sufficiently sensitive and quantitative for environmentally-relevant PE and PP levels exceeding the respective method LOQs. The 50 % PE and 62 % PP we recovered from RefeSol 06-A suggest a rather semi-quantitative evaluation of soils with a clay content >47 % and a Corg content >2.5 %. PS is evaluated qualitatively for its low recoveries.”

We believe that these changes will facilitate the interpretation of our data.

Since the primary aim of our study was to conduct a first screening of agricultural soil, we also limited our reference soils to those of agricultural origin.

2. Line 248 needs to be rewritten, as highlighted above, your method is not sensitive, robust or selective. Similarly, Lines 252-254 needs to be rewritten as I would argue your MDLs are definitely not 1-100 times lower than previously published studies.

> **Our response:** We agree that we used “robust” in a wrong context since the performance of our method depends on the analyzed soil.

We thus suggest to modify the mentioned lines accordingly and move the text passage to the end of the paragraph (Line 263f):

“Based on the two reference soils tested, we considered our method sufficiently sensitive and quantitative for environmentally-relevant PE and PP levels exceeding the respective method LOQs. The 50 % PE and 62 % PP we recovered from RefeSol 06-A suggest a rather semi-quantitative evaluation of soils with a clay content >47 % and a Corg content >2.5 %. PS is evaluated qualitatively for its low recoveries. These findings once more highlight the importance of specifically testing and evaluating analytical methods for plastic analysis with various soil types (Thomas et al., 2020). The extrapolation of specific validity criteria to field samples with a different texture and Corg composition thus remains difficult and requires careful interpretation.”

Results

1. If you didn't find any evidence of the plastic covers in the >2mm size fraction, how can you know the PE and PP detected in the <2mm size fraction are from the covers? There is not enough data to make the conclusion that the edge of the sheets are the source of the PE and PS detected on the edges of the field. Are there other common farming sources of the three plastics analysed e.g. tractors/farming equipment? Fertiliser bags? Can these

sources be discounted from the study areas?

> Our response: This study aimed at screening commercially managed agricultural fields for plastic debris. With this, we depended on the reports made by the respective farmers. To our knowledge, fertilizer bags were not used. However, we cannot exclude other potential sources. To address this uncertainty, we already discussed that "... this suggests an external source of plastic debris, for instance from adjacent streets or other fields, or residues from previous land use (Harms et al., 2021)." (Line 226ff). In Line 301, we further reason: "Even at larger scales though, it remained unresolved to what extent the PE debris in the field periphery (mainly sites 7 and 8) originated from the covered field centers or whether it came from an external source via wind drift. Due to ubiquity of products made from PE, such an external source cannot be excluded."

Yet, we will communicate the uncertainty of our results in a clearer way in the revised version of our manuscript. We suggest the following amendment (Line 312f):

"In the past, beads made from expanded PS were used for the conditioning and stabilization of horticultural soils (Maghchiche et al., 2010). However, it remained unresolved whether this was the case for the agricultural field investigated in this study."

2. I would suggest the low detection and variable PS results are due to the extraction method not performing for clay type soils (which are most of the sites). Did the soil type differ between the field and the periphery where the PS was detected? Again, it would be good to have field blank information here and confirmation from another PS pyrolysis product.

> Our response: The screened soils have a clay content of 15–36 % which ranges between that the two reference soils (8 and 47 % clay). For that reason, we expected that the method will perform within this range. Please see also our response further above addressing PS pyrolysis products and blanks.

We suggest to add the following to

Section 3.4, Line 270:

"The 50 % PE and 62 % PP we recovered from RefeSol 06-A suggest a rather semi-quantitative evaluation of soils with a clay content >47 % and a Corg content >2.5 %. PS is evaluated qualitatively for its low recoveries."

Section 3.5, Line 314:

"Given that our investigated soils had a clay content of 15–36%, the obtained PE, PP, and PS contents were potentially underestimated by a factor of 1.5–2."

3. There is not enough data to state that PE detected at sites 1,7,8 are from the perforated foils and there is not enough data to make the conclusion that application of a foil for 4 months results in detectible PE microplastics in the soil (Line 289).

> Our response: We agree that we should more clearly address the uncertainty of our results. We suggest the following addition to Line 291:

“On the one hand, this is remarkable because the agricultural films were on site for four months only. On the other hand, the elevated plastic contents may have originated from another, potentially diffuse input source prior to plastic coverage.”

Conclusions

1. The method is not robust, as it does not have high recoveries for different soil types. Also, the method is not successfully validated as described above.

> **Our response:** We used “robust” in the wrong context here and suggest to remove it from this sentence. In a future revised version, it would read:

“The combination of soil aggregate dispersion and density separation with solvent-based Py-GC/MS enabled the simple, yet selective quantification of PE and PP debris in agricultural soil. Analyzing a sample amount of 50 g better accounted for the heterogeneous distribution of discrete plastic particles in the soil matrix. The additional dispersion step further made plastic debris occluded in soil aggregates amenable to quantification. By contrast, poor PS recoveries potentially induced by that additional separation step challenged a reliable PS quantification.”

2. As discussed above I disagree with the statement that 4 months of covering with thinner perforated foils is associated with elevated PE content as there is no evidence that the PE originated from the foil and not other sources.

> **Our response:** We would like to emphasize that this linkage does not indicate a causal relationship. To clarify this, we suggest the following addition:

“Due to the ubiquitous use of plastic covers and potentially interfering external plastic sources, a causal relationship between the use of plastic covers and elevated plastic levels in soil needs yet to be shown, for instance, by conducting more controlled and systematic experiments.”

Specific comments

Line 90: thermodesorption should be thermal desorption

> **Our response:** Thank you for this remark. We will correct this throughout the manuscript

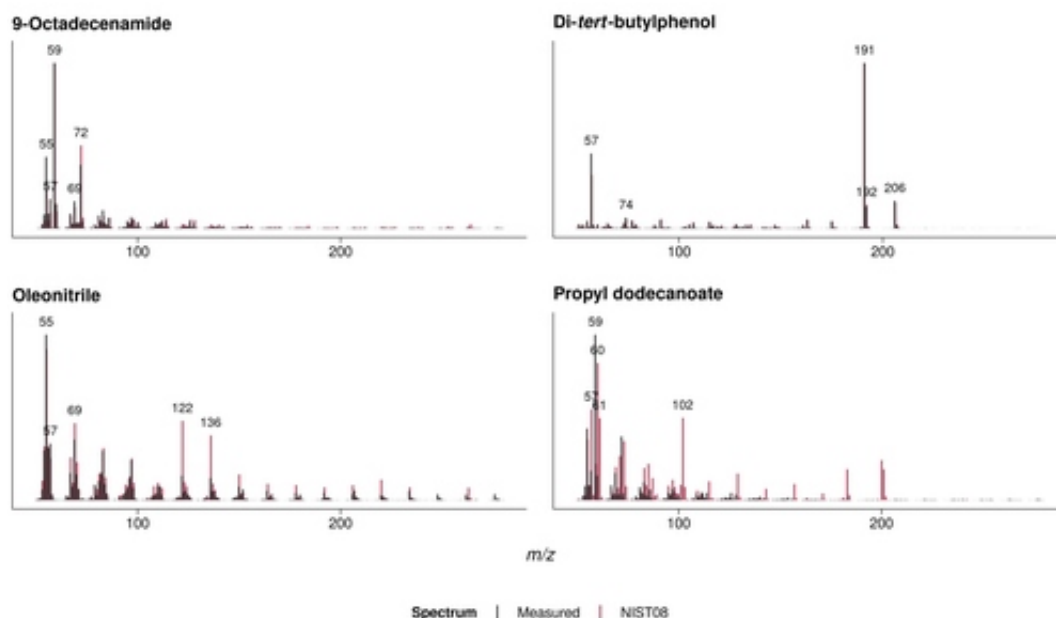
Line 113: How were the soil cores homogenised?

> **Our response:** The soil cores were sieved as a whole and homogenized manually directly after. We suggest to add this information as follows (Line 113):

“All soil cores were sieved to fine soil (≤ 2 mm) and homogenized manually as suggested by Thomas et al. (2020).”

Line 199: Please expand BHT and please include the spectral matches as a Figure for all the NIST library identified compounds from the TD analysis.

> **Our response:** We wrote out BHT throughout the manuscript. We further suggest to add the following figure for the comparison of spectral matches to the appendix:



Line 200: Do you have any reference for propyl dodecanoate and oleonitrile being added to agricultural plastic covers?

> **Our response:** The cited reference (Hahladakis et al., 2018) only provides general information on common polymer additives. Polymer additives of specific commercial products like agricultural covers are typically a trade secret and have to our knowledge not been published yet. If you have more detailed insights, we would be happy to have your support.

Line 206: The lower melting temperatures of PP covers (than virgin PP) may indicate addition of additives or impurities to the PP covers.

> **Our response:** This is interesting. We will modify the following sentence (Line 208) accordingly:

“Decreasing melting temperatures may indicate the presence of additives or other impurities but could also be a first sign of polymer aging as similarly observed after 5–20 months of temperate weathering (Tocháček et al., 2019)”

Line 310: Have these PS beads been used in Germany? Do you know if they were applied to these sites?

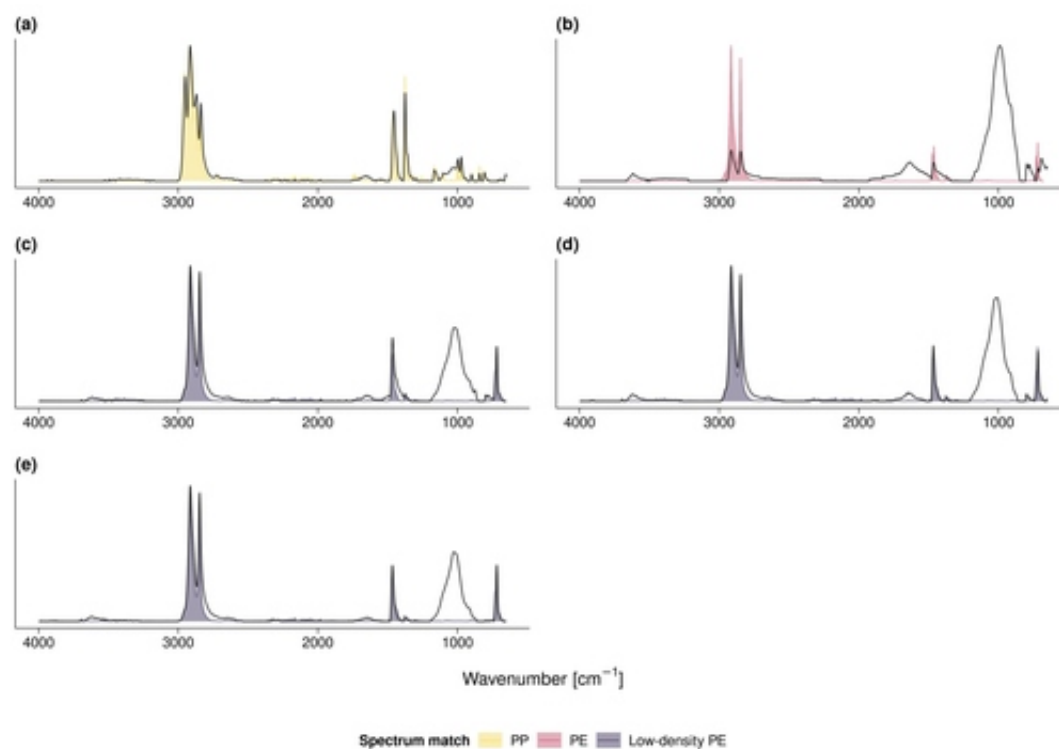
> **Our response:** We do not know for sure. This is why we discuss different possibilities here.

Line 315: What size range did the previous studies use and how do they compare to your study (4µm-2mm).

> Our response: Solvent-based Py-GC/MS methods are still a new and emerging field. To our knowledge, other solvent-based approaches have not yet been combined with density separation. While density separation allows for higher sample amounts to be analyzed (50 g), it requires subsequent filtration which may systematically exclude smaller particles. Dierkes et al. (2019) directly extracted 1 g of soil with ASE. The soil was not sieved and no lower size cutoff was reported for the used ASE filters/membranes. Primpke et al. (2020) used filters with a pore size of 1 µm for the quantification of microplastics in sediment and water. The authors, however, directly analyzed the crushed filters without dissolving the polymers. For these reasons, detailed comparisons are difficult to draw at the current stage.

Figure A1: Please overlay the reference spectra with the samples for comparison

> Our response: We modified the Figure A1 as suggested:



We further applied the same modifications to Figure A3 (now A4):

