Quantitative methodology for poly (butylene adipate-co-terephthalate) (PBAT) microplastic detection in soil

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Keywords: Micro-plastics, PBAT, GCMS
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Agricultural mulch films (AMFs) are inexpensive, easy to use, increase crop yield, and reduce the use of pesticides and herbicides. The conventional plastic used for AMFs is low-density polyethylene (LDPE), due to its low price and excellent mechanical performance. During this collection, small amounts of the plastic are left behind, fragmenting and leading to microplastics (MPs) production, size <5mm (Jin et al., 2022; UNEP, 2022; Uwamungu et al., 2022). LDPE does not degrade, leading to an accumulation of the MPs, which can hinder soil health (UNEP, 2022; Yu et al., 2021). Poly (butylene adipate-co-terephthalate) (PBAT) is a biodegradable polymer that has attracted commercial and academic attention due to its ductility and good processability (Kyrikou and Briassoulis 2007; Sintim et al. 2020; Tan et al. 2016; Lawson and Taber 2011; Bhagwat et al. 2020; Nunes, de Souza, and Rosa 2020). Additionally, due to its low glass transition temperature, it has a relatively high rate of soil degradability, making it a promising alternative to conventional plastics in AMF applications (Zumstein et al. 2018; Touchaleaume et al. 2016)

The effects of biodegradable, PBAT-based AMFs on soil systems have been described as indirect and direct by Bandopadhyay and collaborators (Bandopadhyay et al. 2018). The indirect effects, via microclimate modification, are somewhat similar to the LDPE based films; however, the direct effects, via incorporation in soil, of the MP are different. Astner and collaborators reviewed the interactions of MPs coming from the increasing AMF industry with agricultural soil ecosystems(Astner et al. 2023). Conventional films' MPs accumulate with time, are 'easily' detectable and their lack of degradability leads to a continuous increase in their impact (Zhang et al. 2018; Jin et al. 2022; Uwamungu et al. 2022; He et al. 2018; Astner et al. 2023). Uwamungu and collaborators, described their impacts on the different soil cycles such as bacterial, fungal and plant growth cycles (Uwamungu et al. 2022; Astner et al. 2023). PBAT based films degrade with time, leading to a stabilization of their MP concentration (Yu et al. 2021). Even though their impact is lesser than MP's coming from conventional films, it is important to monitor and study how microbial, fungi and plant cycles react to them (Bandopadhyay et al. 2018; Astner et al. 2023).

The quantification of PBAT at various stages of degradation and from different environments is a challenge. However, it is greatest when the plastic is too small to be detected by any sieving process (MPs), but the depolymerization is just starting. Cho and collaborators developed an effective gas chromatography coupled with mass spectroscopy (GC-MS) method to quantify degraded PBAT in wastewater (Choet al., 2022a; 2022b). The method dissolves the PBAT in chloroform ($CHCl_3$) and performs a fatty acid methyl ester (FAME) derivatization to break down the polymer chains and thus allow quantification of PBAT in $CHCl_3$ (Cho et al., 2022a). However, the limit of detection (LOD) and limit of quantification (LOQ) were reported to be 0.26 g/L (260 ppm) and 0.80 g/L (800 ppm), respectively, which are uncommonly high for a GCMS methodology (Wollein and Schramek 2012). Nelson and collaborators developed an analytical methodology to quantify microplastics from PBAT in soils (Nelson et al. 2019). Using proton nuclear magnetic resonance (^{1}H-NMR) they extracted PBAT in $CHCl_3$ and compared it with 1,4 dimethoxybenzene in deuterated-$CHCl_3$ ($CDCl_3$), allowing them to quantify very effectively the PBAT. Their LOD and LOQ were determined to be 1.3 µg/ml $CDCl_3$ (1.3 ppm) and 4.4 µg/ml $CDCl_3$ (4.4 ppm), respectively. However, this methodology uses deuterated chloroform for the analysis, which is an expensive solvent, and their LOD and LOQ depend on the PBAT extraction from soil (Nelson et al. 2019). The presented work will therefore detail and test in a real-world application an accessible and reliable methodology that combines the ultrasonication methodology reported by Astner et al. and Nelson et al. (Astner et al. 2023; Nelson et al. 2019) with the FAME and GCMS analysis presented by Cho and collaborators (Cho et al., 2022a; 2022b).

Two calibration curves were made with different chloroforms are shown in Figure 1. This data allows us to define a confidence interval of the GCMS sensitivity to slight concentrations changes. Therefore, combining both calibration curves allowed the determination of LOD and LOQ, significantly lower than those reported in reviewed literature (Table 1).

Table 1. Limits of detection and limits of quantification of PBAT concentration

Method	LOD	LOQ	Slope	R^2
GCMS (This work)	77 ppb	255 ppb	238	0.908
GCMS (Cho et al., 2022a; 2022b)	260 ppm	800 ppm	2884100	0.996
NMR (Nelson et al., 2019)	1.3 ppm	4.4 ppm	NA	1.00

Based on these results, an experimental method was developed to detect and quantify PBAT microplastic content produced by its biodegradation in an industrial compost setting. PBAT films were packed with soil at a local industrial composting (IC) facility. Weight loss and PBAT microplastic quantification in the soil around the samples were assessed simultaneously. Figure 2 depicts the evolution of both weight loss and PBAT in soil during the 80-day experiment. It becomes clear that even thought there is total weight loss after 53 days in the IC, PBAT is still detected in the soil until the end of the experiment. However, after peaking around the 60th day, the amount of PBAT detected in the soil diminishes, showing the MPs degradation. The detected monomer corresponds to the adipic acid dimethyl-ester, a PBAT monomer separated through FAME. This method cannot assess degradation products beyond this monomer formation of PBAT. Based on this data, it is not unreasonable to think that after 160 days of IC, no remaining PBAT films residue will be detectable. This works presents an accessible methodology to accurately detect small amounts of PBAT, including in complex and heterogeneous environments like soil or compost.

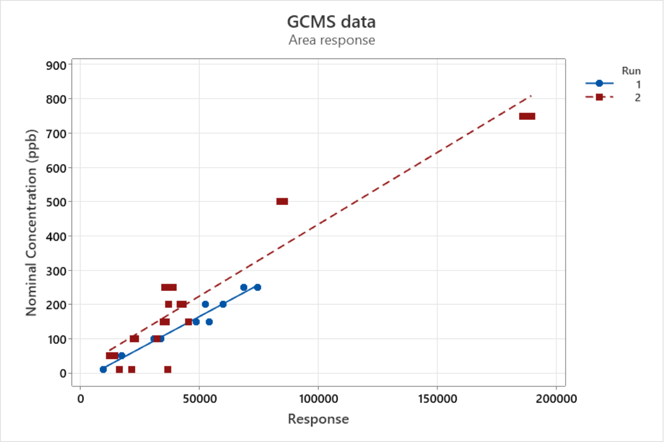

Figure 1. Calibration curves to relate GCMS response with adipic acid dimethyl ester concentration in $CHCl_3$

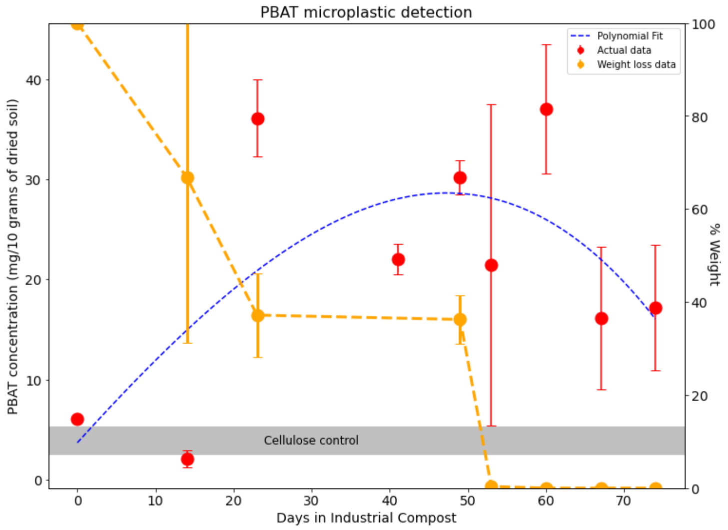

Figure 2. Evolution of PBAT concentration in soil and sample weight in an industrial compost environment.

Acknowledgments

The authors want to thank Sabit Nadhvee for his help in the initial measurement protocol development. Thanks also to Dr. Nathan Eddingsaas for his advice and knowledge on GCMS protocols, and to Tom Allston for his help with the GCMS runs. This work was possible through the support of the Foundation for Food and Agriculture Research (FFAR) grant #CA19-SS-0000000013.

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