



Short Communication

Evaluating additive release from conventional and biodegradable mulch films

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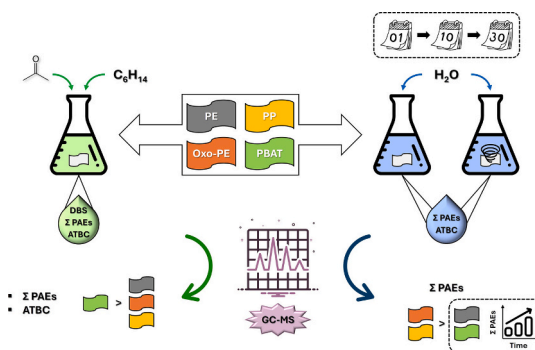
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HIGHLIGHTS

- Phthalates in plastic mulches vary in release levels, depending on the film type.
- PBAT had the highest additive release in organic solvent extractions.
- Additive release increased over time, especially in PBAT and PE films.
- PP and Oxo-PE showed higher phthalate release in aqueous conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

The rising demand for food and the effects of climate change necessitate improved agricultural practices. Mulching enhances soil conditions and reduces water use, with plastic films often favoured for their durability and cost-effectiveness. However, these films contain additives, which may pose environmental and health risks by leaching into soil and crops. This study evaluated the release of seven phthalates and three other common plasticizers from four types of films: polyethylene (PE), oxo-degradable polyethylene (Oxo-PE), polypropylene (PP), and biodegradable polybutylene adipate terephthalate (PBAT).

The additives were extracted using both acetone-hexane mixture and aqueous solutions. The results revealed that PP and Oxo-PE released significantly higher amounts of phthalates ($6,17 \pm 1,06$ mg/kg and $7,40 \pm 1,65$ mg/kg respectively under static conditions) and acetyl-tributyl-citrate ($2,75 \times 10^{-02} \pm 2,21 \times 10^{-03}$ mg/kg and $2,37 \times 10^{-02} \pm 2,62 \times 10^{-03}$ mg/kg, respectively under static conditions) in aqueous environments compared to PBAT ($5,01 \times 10^{-02} \pm 7,73 \times 10^{-03}$ and $3,66 \times 10^{-03} \pm 8,47 \times 10^{-04}$ phthalates and ATBC respectively, under static conditions) and PE ($1,73 \times 10^{-02} \pm 4,91 \times 10^{-03}$ mg/kg and $3,40 \times 10^{-03} \pm 1,50 \times 10^{-03}$ mg/kg phthalates and ATBC respectively, under static conditions). In contrast, PBAT exhibited the highest release of

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these compounds when extracted with organic solvents ($47,19 \pm 4,28$ mg/kg and $2,03 \pm 0,18$ mg/kg respectively). Time-dependent correlation analyses showed a significant positive correlation between exposure time and additive release, particularly for PBAT ($r = 0.90$, $p = 0.0023$ for phthalates, $r = 0.90$, $p = 0.0026$ for ATBC), and PE ($r = 0.96$, $p = 0.00003$ for phthalates, $r = 0.82$, $p = 0.007$ for ATBC), highlighting a growing release pattern over time.

The findings highlight the need to consider both the immediate and long-term impacts of mulch film contamination in soil. The results also provide insights into the comparative release behaviour of additives from biodegradable and conventional films, necessary for assessing their environmental safety.

1. Introduction

Improving crop productivity is crucial to meeting the food demands of our rapidly growing world population. As demand increases, so does the strain on our resources. Climate change worsens this issue, with water scarcity becoming more severe, limiting crops, and causing significant economic damage. Considering this, traditional farming methods should be integrated and improved, not only to meet food needs but also to better preserve natural resources, while respecting the environment (Somanathan et al., 2022), thus assuring a high quality of food in terms of safety, together with plant health according to the Food Safety policy in the EU (Food safety in the EU).

Mulching is a well-known agricultural practice which can improve the soil microenvironment and positively influence crop growth. It consists of covering the soil with a specific layer of material that can be made of different materials, such as conventional plastic, biodegradable plastic, straw, grass, maize starch, paper, sawdust, or gravel; however, mulch films are generally composed of polyethylene (PE), including high-density, low-density and linear low-density PE (Bläsing and Ame-lung, 2018; Somanathan et al., 2022). With this technique, soil water retention can be increased, consequently reducing the need for irrigation. Indeed, mulching was proven to increase yield per unit of water, with plastic mulches performing better than straw mulches (Qin et al., 2015).

Plastic mulching sheets are often preferred over non-synthetic materials because of their lower production costs, flexibility, durability, and ease of handling. These properties are enhanced by using additives, such as plasticizers, colour pigments, ultraviolet stabilizers, and so on.

Among these additives, the most typically used are phthalates, often addressed also as phthalic acid esters (PAEs), which are lipophilic chemicals added during the plastic production process to increase the malleability of the material (Zhou et al., 2023; Steinmetz et al., 2016). Phthalates are not chemically bonded to the polymer, so they can easily migrate from plastics and come into contact with food and plants (Vinod and Harathi, 2022). For this reason, PAEs present in mulch films can be released into the soil and crops, compromising food safety (Scopetani et al., 2023; Scopetani et al., 2024; S. Wang et al., 2021c). Indeed, PAEs are toxic organic compounds, even at low concentrations, and for this reason, they are considered a significant hazard to humans and the environment (Vinod and Harathi, 2022). Their use is regulated by the European Commission Regulation 2018/2005, which stipulates that di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and diisobutyl phthalate (DIBP) cannot be used as pure substances or in mixtures at concentrations equal to or >0.1 % by weight of those items intended for mucous membrane contact or prolonged skin contact ("EUR-Lex - 32018R2005 - IT - EUR-Lex", n.d.). Phthalates are considered a priority pollutant by the European Union and the United States Environmental Protection Agency due to their status as endocrine disruptors, capable of mimicking or blocking hormonal actions that normally regulate the metabolic activities of living organisms. These substances can accumulate in the body, causing chronic liver intoxication, and impair the proper functioning of the reproductive system (Viljoen et al., 2023; P s, Vinod and Harathi, 2022; Hlisenkova et al., 2020).

The issue of PAEs in mulching films, with potential environmental

and health impacts, is further exacerbated by the complexities associated with the disposal of these films once their use is over. Despite the benefits in terms of yield and crop quality, the difficulty of removing and managing them as waste can sometimes lead to their inappropriate removal. Anyway, even when the films are properly removed, some fragments remain in the soil, persisting after harvest and slow degrading. This process contributes to soil pollution and, more broadly, to the growing global problem of plastic pollution (El-Beltagi et al., 2022; Salama and Geyer, 2023).

To overcome these issues, the replacement of conventional plastic sheets with biodegradable mulch films, which may not require removal, has been proposed as one possible alternative. However, a crucial consideration in using biodegradable mulches is the release of plastic additives during the degradation processes; these films have a shorter degradation period at a faster rate compared to conventional mulches and do not necessarily need to be removed from the soil, leading to a potential higher release and number of additives into the agricultural soil. Currently, there is not much data in the literature regarding the additives used in the production of biodegradable mulch films, but some authors argue that the issue related to the presence of PAEs used in the production of biodegradable mulches should not be overlooked (Uzamurera et al., 2023).

The present study fills this knowledge gap by evaluating the release of additives from both biodegradable and conventional plastic sheets. The additives were selected based on previous screening analyses conducted on mulch films in our laboratory and their toxicity to the environment and human health (Cruz, 2013).

This research stands out from existing studies in the literature for several reasons. Unlike prior studies that relied exclusively on a single extraction method — either organic solvents or aqueous solutions — this work investigates and contrasts the extraction of additives from mulch films using both techniques. By adopting this dual-method approach, it provides a more thorough insight into the potential additive release across varying conditions. Additionally, while earlier research has typically examined only two or three types of mulch films, this study evaluates all four of the most commonly used types (polyethylene, oxo-degradable polyethylene, corn starch and polybutylene adipate terephthalate, and polypropylene).

While the shift toward biodegradable mulch films is often seen as a step toward sustainability, the potential unintended consequences of their degradation remain poorly understood. The release of plastic additives which could accumulate in agricultural soils and impact both crop safety and environmental health is a critical aspect that has received limited attention. As these additives accumulate in the food chain, they can enter animal and human bodies, leading to long-term health risks. Persistent chemicals, such as phthalates, may bioaccumulate in organisms over time, resulting in harmful effects on human health, including endocrine disruption, developmental issues (Viljoen et al., 2023; P s, Vinod and Harathi, 2022; Hlisenkova et al., 2020). The lack of comprehensive data on the specific additives used in biodegradable films makes it difficult to assess their true ecological footprint. Given that biodegradable films degrade more rapidly, understanding their additive release profile under different environmental conditions is essential. By incorporating a dual extraction method and analysing multiple mulch film types, this study provides a more

complete picture of how these materials interact with their surroundings, helping to bridge existing knowledge gaps and inform future agricultural practices.

2. Materials and methods

2.1. Experimental design and test materials

Conventional mulch films and films made of biodegradable material were both extracted with organic solvents (hexane and acetone) and placed in contact with an aqueous solution, allowing the release of the additives to be compared. These additives include seven phthalates and three other plastic additives, not belonging to the phthalate family but commonly used in the plastic industry: dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, DEHP, BBP, di-n-octyl phthalate (DnOP), di-n-butyl sebacate (DBS), tri-2-ethylhexyl phosphate (TEHP), and acetyl tributyl citrate (ATBC).

The extraction with organic solvents was conducted first, as these solvents are stronger and helped to identify which additives were present in the films, allowing to focus on the most relevant ones. Additionally, because the organic solvent extraction is more thorough, it provides a clearer understanding of the films' total additive content. Last but not least, this extraction could mimic the long-term release of additives into water, potentially over the course of years, especially in the case of biodegradable films that may be left in the fields and not removed, gradually breaking down and releasing additives into the environment. The aqueous extraction was performed to simulate the release of additives from the films in contact with soil, water run-off, or rain, providing insights into the amount of additives that could be released under real environmental conditions in a short time (up to 30 days).

Four types of mulch films were used as test materials:

- Polyethylene mulch film (PE);
- Oxo-degradable polyethylene mulch film (Oxo-PE);
- Biodegradable mulch film, consisting of corn starch and polybutylene adipate terephthalate (PBAT);
- Polypropylene mulch films (PP).

These materials were purchased from agricultural suppliers and selected based on their prevalence, choosing those most used by farmers. Fourier-transform infrared (FTIR) spectra of all the films were recorded in the range of 400–4000 cm^{-1} using a IRAffinity-1S (Shimadzu Corporation, Kyoto, Japan) equipped with the attenuated total reflectance (ATR) sampling accessory (MIRacle™ PIKE Technologies).

2.2. Chemicals

The standard chemicals for the calibration curves comprised phthalates (phthalate mix, O2Si smart solutions, North Charleston, South Carolina, USA), acetyl tributyl citrate (ATBC), tetrabromobisphenol A (TBPA), DBS and TEHP (Chiron, Trondheim, Norway). Deuterated solutions of DEHP (Chiron Trondheim, Norway) and ATBC (Toronto Research Chemicals, Toronto, Canada) were used as internal standards. Hexane and acetone were purchased from Honeywell Research Chemicals.

Columns of anhydrous sodium sulphate (Chem-lab) were used for sample clean-up.

2.3. Experimental set-up

2.3.1. Test with organic solvents

Four mulch films were cut into pieces of $2 \times 1.5 \text{ cm} \times 2.5 \text{ cm}$ size, placed in an amber glass bottle with 20 mL of a mixture of hexane and acetone (1:1) and stirred for 1 min with a Vortex (220 rpm), followed by 30 min of sonication and 5 min of centrifugation (3000 rpm). The same

steps were repeated three times, except for the sonication, following the slightly modified method described by Zhong et al. (2023) and Scopetani et al. (2023). Deuterated internal standards (DEHP-d4 and ATBC-d3) were added, and the samples were cleaned up with an anhydrous sodium sulphate column, evaporated down to 1 mL with ultra-pure nitrogen, and analyzed by gas chromatography–mass spectrometry (GC–MS) technique.

2.3.2. Release test in aqueous solution

The four mulch film materials (cut into pieces of $1.5 \text{ cm} \times 2.5 \text{ cm}$) were immersed in water at pH 6.20. This pH level was chosen to reflect the acidic conditions that are generally compatible for the growth of most crops.

Following the method described by Zhong et al. (2023), to gain a more comprehensive understanding, release tests were conducted under both static and dynamic (i.e., stirring at 180 rpm) conditions, for 24 h, 10 days, and 30 days. For each treatment (static and dynamic conditions) and time point, three replicates and four blanks were included, for a total of 96 samples.

All cut mulch films were weighted before and after the treatment. The data are reported in Table 1S of the Supplementary material.

2.4. GC–MS analysis

An Agilent Technologies 6890N (G1530N) gas chromatograph with an Agilent Technologies 5973 inert mass spectrometer and a DB-5MS 30 m, 0.250 mm, 0.25 μm internal diameter gas chromatograph column was used for the analysis of the plastic additives. The MS system was operated in the selected ion monitoring (SIM) mode.

The ion source was set at 230 °C, quadrupole temperatures at 150 °C and the temperature program was 50 °C, 30 °C/min to 280 °C, 15 °C/min to 310 °C, with a total run time of 14.67 min. The injection was performed with 1 μL in splitless mode; helium was used as the carrier gas at a constant flow rate of 1 mL/min.

To prevent laboratory contamination from the target compounds, all equipment and glassware were meticulously cleaned, starting with milliQ water, followed by acetone and hexane. Sources of contamination and interferences were tracked by performing procedural blanks at each stage of the analysis, with necessary corrections applied accordingly.

The target compounds exhibited a recovery rate ranging from 80 % to 110 %. The instrumental limits of quantification (LOQ) and detection (LOD) were determined based on the signal-to-noise ratio of the lowest standard concentrations with the LOD corresponding to a signal-to-noise ratio of 3:1 and the LOQ corresponding to a signal-to-noise ratio of 10:1. These values are detailed in Table 2S in the Supplementary material, as well as the information about the primary and secondary ions and the retention times of the analytes (Table 3S).

2.5. Statistical analysis

The collected data were analyzed using the R and Origin 2024 (OriginLab) software. The Shapiro-Wilks and Levene tests were performed to verify normality and homogeneity. Since the data did not follow a normal distribution, the various treatments were compared using non-parametric tests, specifically the Kruskal-Wallis test followed by Dunn's test and the Mann Whitney test. Correlation analyses were performed to identify possible patterns in the release of additives from the four different mulch films over time. Differences between treatments were considered significant when the results showed a p -value ≤ 0.05 .

3. Results and discussion

3.1. FTIR spectra analysis

The FTIR spectra of the four mulch films are reported in Fig. 1, with the spectrum of the PE film shown in Fig. 1a. Intense absorption peaks

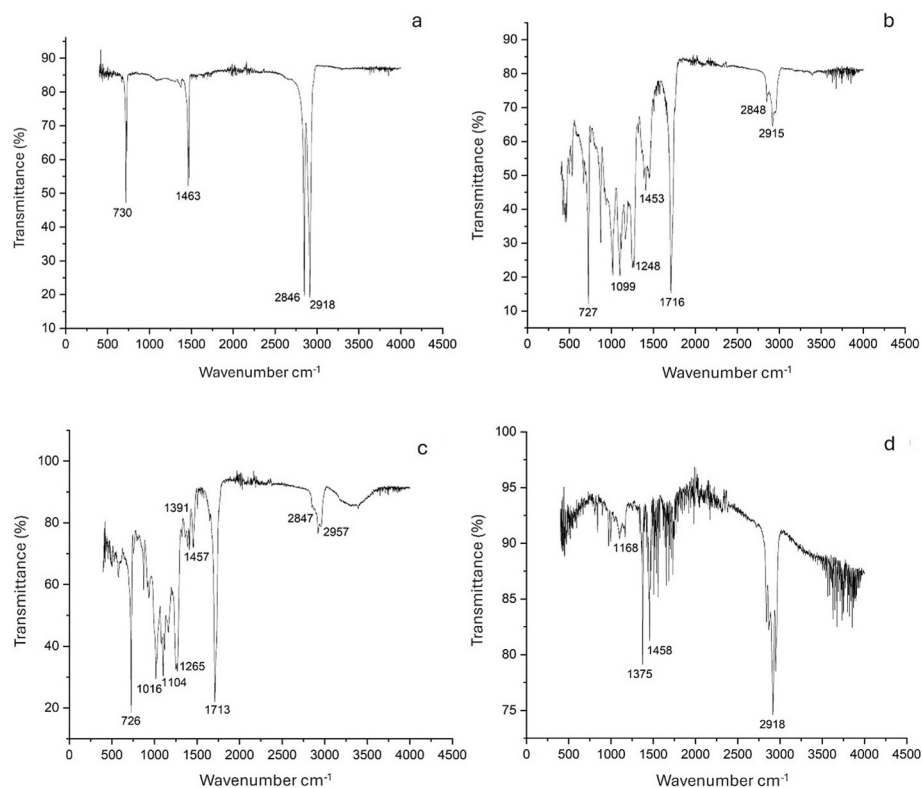


Fig. 1. ATR-FTIR spectrum of PE (a), Oxo-PE (b), PBAT (c) and PP (d). Characteristic peaks of PE: 2913 and 2846 cm^{-1} (CH stretching region), at 1463 (CH_2 bending), and 730 cm^{-1} (CH_2 rocking). Characteristic peaks of Oxo-PE: 2917 and 2848 cm^{-1} (CH stretching region), at 1716 cm^{-1} (C=O stretch), 1453 cm^{-1} (CH_2 bending), 1248 cm^{-1} (C–O stretch), 1099 cm^{-1} (C–O stretch) and 727 cm^{-1} (CH_2 rocking). Characteristic peaks of PBAT: 2957, 2925 and 2847 cm^{-1} (CH stretching region), 1713 cm^{-1} (C=O stretch), at 1457 (CH_2 bending), 1391 (CH_2 plane bending), 1265 and 1104 cm^{-1} (C–O stretching), 1016 cm^{-1} (aromatic CH in-plane bend) and 726 cm^{-1} (CH_2 rocking). Characteristic peaks of PP: 2977, 2918 and 2803 cm^{-1} (CH stretching region), at 1458 (CH_2 bending), 1375 (CH_3 bending) and 1168 cm^{-1} (CH bending, CH_3 rocking, CC stretching).

can be seen at 2913 and 2846 cm^{-1} (CH stretching region), at 1463 (CH_2 bending), and 730 cm^{-1} (CH_2 rocking) (Gulmine et al., 2002; Jung et al., 2018; Krimm et al., 1956).

The ATR-FTIR spectrum of Oxo-PE (Fig. 1b) shows absorption peaks at 2917 and 2848 cm^{-1} (CH stretching region), at 1716 cm^{-1} (C=O stretch), 1453 cm^{-1} (CH_2 bending), 1248 cm^{-1} (C–O stretch), 1099 cm^{-1} (C–O stretch) and 727 cm^{-1} (CH_2 rocking).

Fig. 1c shows the ATR-FTIR spectrum of PBAT film with intense absorption at 2957, 2925 and 2847 cm^{-1} (CH stretching region), 1713 cm^{-1} (C=O stretch), at 1457 (CH_2 bending), 1391 (CH_2 plane bending), 1265 and 1104 cm^{-1} (C–O stretching), 1016 cm^{-1} (aromatic CH in-plane bend) and 726 cm^{-1} (CH_2 rocking) (De Matos Costa et al., 2020; Jung et al., 2018).

Fig. 1d represents ATR-FTIR spectrum of PP films, with the characteristic absorptions at 2977, 2918 and 2803 cm^{-1} (CH stretching region), at 1458 (CH_2 bending), 1375 (CH_3 bending) and 1168 cm^{-1} (CH bending, CH_3 rocking, CC stretching) (Chércoles Asensio et al., 2009; Jung et al., 2018; Noda et al., 2007; Verleye et al., 2001).

3.2. Additives in mulch films extracted with organic solvents

The data provided present the concentrations of the various plastic

additives detected in the four different types of mulch films: PE, PBAT, Oxo-PE and PP. The concentrations are reported in milligrams per kilogram (mg/kg), along with their standard errors in Table 1, while Fig. 2a and b shows the amount of each contaminant and the total phthalates content in the mulches, respectively. DnOP and TEHP were not detected in any of the samples. The total PAEs concentration was the highest in PBAT (47.19 ± 4.28 mg/kg), followed by PP (23.74 ± 1.23 mg/kg), PE (16.84 ± 1.58 mg/kg), and Oxo-PE (12.88 ± 0.94 mg/kg). These results are in line with the PAEs contents found in literature, where phthalates concentrations in PE, PP, Oxo-degradable, and biodegradable films varied in the ranges 0.23–359 mg/kg, 0.35–6.13 mg/kg, 9.62–32 mg/kg, and 0.19–73.63 mg/kg respectively (Cui et al., 2024; Y. Wang et al., 2021a; Y. Xu et al., 2023; D. Wang et al., 2021b).

However, as previously stated, this study differs from the aforementioned research in several ways. First, while those studies performed only one type of extraction — either with organic solvents or with aqueous solutions — this work evaluates and compares the extraction of additives from mulch films using both methods. This dual approach provides a more comprehensive understanding of the potential release of additives under different conditions. Moreover, each one of the cited studies focused on only two or three types of mulch films, whereas this study examines all four of the most used types (PE, PP, Oxo-PE, PBAT),

Table 1

Concentration of additives extracted with acetone and hexane from mulch films (mg/kg) - Mean \pm Standard Error ($n = 3$). LOD stands for limit of detection.

	DMP	DEP	DBP	BBP	DEHP	Σ PAEs	ATBC	DBS
PE	0.03 ± 0.00	0.87 ± 0.05	4.15 ± 0.13	<LOD	11.79 ± 1.44	16.84 ± 1.58	0.13 ± 0.01	<LOD
PBAT	0.13 ± 0.01	3.76 ± 0.19	9.40 ± 0.74	<LOD	33.91 ± 3.49	47.19 ± 4.28	2.03 ± 0.18	16.14 ± 3.12
Oxo PE	0.07 ± 0.00	1.97 ± 0.15	3.07 ± 0.40	<LOD	7.76 ± 0.52	12.88 ± 0.94	0.10 ± 0.02	45.84 ± 12.43
PP	0.03 ± 0.00	1.23 ± 0.07	3.89 ± 0.15	2.02 ± 0.05	16.57 ± 1.37	23.74 ± 1.23	0.32 ± 0.15	43.97 ± 5.70

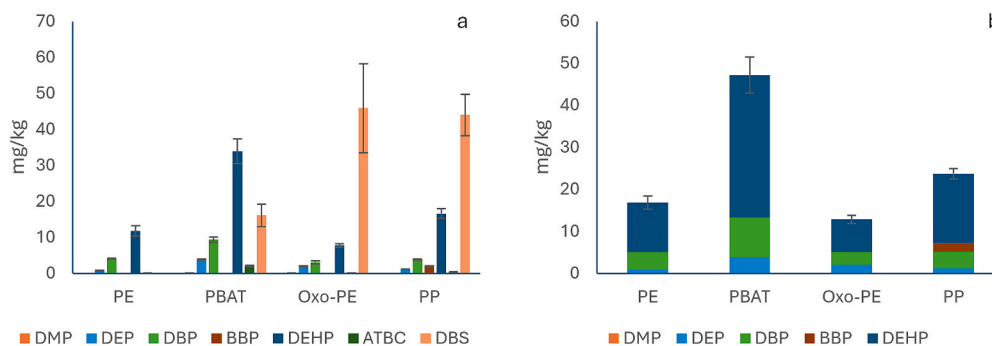


Fig. 2. a: Additives extracted from mulch films. Mean \pm Standard Error ($n = 3$). b: Σ PAEs extracted from mulch films. Mean \pm Standard Error ($n = 3$).

offering a broader comparative analysis.

The Kruskal-Wallis test was utilized to determine whether there were statistically significant differences in the release of additives among the different mulch films. The results showed significant differences ($p < 0.05$) for the overall sum of phthalates, as well as for specific phthalates and other additives such as DMP, DEP, DBP, DEHP and ATBC. Specifically, Dunn's test revealed a significant difference in total phthalate concentration between PBAT and Oxo-PE film, with a p -value of 0.019. PBAT exhibited also the highest DMP, DEP, DBP, DEHP and ATBC concentrations (0.13 ± 0.01 mg/kg, 3.76 ± 0.19 mg/kg, 9.40 ± 0.74 mg/kg, 33.91 ± 3.49 mg/kg, and 2.03 ± 0.18 mg/kg, respectively).

Interestingly, DBS was detected at the highest level in Oxo-PE (45.84 ± 12.43 mg/kg) followed by PP (43.97 ± 5.70 mg/kg), and PBAT (16.14 ± 3.12 mg/kg), while it was not detected in PE films and no significant differences were highlighted by the Kruskal-Wallis test. The high concentrations of DBS in Oxo-PE and PP could indicate that these materials rely heavily on DBS to maintain flexibility and durability. DBS is a versatile plasticizer used to enhance flexibility and softness of plastic materials, such as polyvinylchloride (PVC), coatings, and films, and is commonly found in plastics, pharmaceuticals, cosmetics, and food packaging because it is considered non-toxic (Carlisle et al., 2019). DBS also functions as a lubricant in industrial applications and helps in controlling the release of active ingredients in tablet coatings and capsules (Chaudhary et al., 2019).

Our data revealed significant differences in phthalate and plasticizer concentrations depending on the type of film. For DMP, PBAT showed significantly higher concentrations than PP films ($p = 0.02787$), suggesting varying release patterns between the films.

PBAT had also significantly higher concentrations of DEP than PE films ($p = 0.01341$), raising concerns due to DEP's known health risks as an endocrine disruptor, as highlighted by Weaver et al. (2020). DEHP and DBP levels were also significantly higher in PBAT compared to Oxo-PE films ($p = 0.01879$, $p = 0.01341$, respectively). Given DEHP and DBP's role as endocrine disruptors, their presence in biodegradable films could have serious implications for soil health and crop safety. These findings align with Uzamurera et al. (2023), who showed that biodegradable mulches deteriorated quickly, resulting in higher soil phthalates pollution compared to PE mulches.

DEHP and DBP were detected in all samples and were the most abundant congeners. The same findings were highlighted in the review by Cui et al. (2024), which systematically evaluated the presence, release, migration, and transformation of PAEs, as well as their potential environmental risks. A significant difference was noted for ATBC as well, with PBAT showing higher concentrations than Oxo-PE films ($p = 0.02787$). ATBC is a plasticizer commonly used in biodegradable films, and its higher levels in PBAT suggest an increasingly heavier reliance on alternative additives.

These findings underscore that even biodegradable films can introduce substantial amounts of plasticizers into the environment, which could have unpredictable effects, as discussed by Salama and Geyer (2023), Uzamurera et al. (2023) and Zimmermann et al. (2019). Indeed,

the total phthalate content highlights that biodegradable films like PBAT could potentially release higher amounts of hazardous chemicals into the environment, challenging the perception of their entirely eco-friendliness (Zimmermann et al., 2019). These findings align with the concerns raised in literature, such as the review by Salama and Geyer (2023), which emphasized the need for a cautious approach when adopting biodegradable plastics in agriculture due to potential contaminant release. Because PBAT is designed to break down more rapidly in the environment, this accelerated degradation process could lead to a quicker and more substantial release of additives such as phthalates and other additives. This is in accordance with the findings from previous studies, such as those by Uzamurera et al. (2023), which highlight that biodegradable plastics can release higher quantities of additives as they degrade faster than traditional plastics.

However, other studies present conflicting findings. Y. Xu et al. (2023) reported higher concentrations of PAEs in PE mulch films compared to polylactic acid/PBAT and PP films, while Ding et al. (2021) and Li et al. (2020) observed greater PAEs concentrations in biodegradable, oxidative-biodegradable mulch films than in PE ones (Cui et al., 2024).

These contrasting findings can be explained by several factors, such as the variability in the composition and characteristics of the films themselves. Different brands may use varying formulations, including different types or amounts of additives, which can influence the release of substances like PAEs. Film thickness is another important factor; indeed, Y. Wang et al. (2021a) found that the release rate of DEHP was negatively related to the film thickness. It seems that thicker films may degrade more slowly, releasing additives at a different rate compared to thinner films. Additionally, the colour and other physical properties of the films could affect how they interact with environmental factors such as sunlight and temperature, further influencing their degradation rates and the release of additives.

The susceptibility to degradation of PBAT, while beneficial in reducing long-term plastic waste, may increase the immediate release of hazardous chemicals into the environment, thus potentially contributing to soil contamination and raising concerns about the safety and environmental impact of using biodegradable mulch films in agriculture.

In contrast, some mulch films like PP showed less significant differences in additive release, which might suggest a more stable profile in terms of additive leaching. However, the environmental persistence of these materials remains a significant issue, as noted by Salama and Geyer (2023).

The environmental and toxicity issues related to the use of phthalates are driving research toward finding alternative materials that are equally effective and cost-efficient (Jagarlapudi et al., 2023). This explains the presence in the analyzed films of DBS and ATBC, two plasticizers with properties similar to those of phthalates but which are considered non-toxic (Arrieta et al., 2014; Jagarlapudi et al., 2023). However, the literature presents conflicting opinions regarding the safety of ATBC. In fact, although the European Chemicals Agency (ECHA) does not classify it as a hazardous substance, Huang (2023)

highlighted potential risks associated with its exposure, and studies conducted by Horie et al. (2022) suggested that this substance can act as an endocrine disruptor, affecting hormonal activity and, at concentrations of 194.5 µg/L, causing abnormal development of fish embryos.

3.3. Additives concentrations in the aqueous phase

The concentration of the selected PAEs and the other plastic additives released from the four different types of mulch films into the aqueous solutions are reported in Table 2.

The data indicate significant differences in phthalate release between conventional PE, Oxo-PE, PP, and PBAT mulch films.

The Oxo-PE films, especially under shaking conditions, released the highest amounts of phthalates, with the total phthalate concentrations reaching up to 8.75 ± 2.90 mg/kg after 30 days. The highest individual phthalate released was DEHP, reaching 7.30 ± 2.62 mg/kg under shaking conditions after 30 days. In static conditions, the PAEs release was slightly lower, with a total of 7.40 ± 1.65 mg/kg after 30 days, still dominated by DEHP (6.96 ± 1.64 mg/kg). The high phthalate release from Oxo-PE films under both conditions suggests a significant risk of environmental contamination, especially when these films are left in the

soil after use.

PP films released phthalates as well, with the total phthalate concentration under shaking conditions reaching 5.00 ± 1.29 mg/kg after 30 days. The highest release was again observed for DEHP (4.36 ± 0.10 mg/kg), suggesting that also PP films can contribute to phthalate contamination over time.

The static condition showed a slightly higher release (ΣPAEs 6.17 ± 1.06 mg/kg) compared to the shaking one, with a notable peak in DBP amount (1.39 ± 0,36 mg/kg) after 30 days.

The PBAT films showed a much lower release of phthalates overall, with a total of 3.12 × 10⁻² ± 9.73 × 10⁻³ mg/kg and 5.01 × 10⁻² ± 7.73 × 10⁻³ mg/kg under dynamic and static conditions after 30 days. However, an interesting increase in DMP and DEP was observed under shaking conditions after 30 days, indicating that the degradation process might release different phthalates over time.

The relatively lower release suggests that biodegradable films could be a safer alternative in terms of phthalates pollution, though their overall environmental impact still needs further investigation, especially considering the potential for accelerated release due to their biodegradability and the fact that under harsher conditions, when extracted with hexane and acetone, they released higher amounts of PAEs than all

Table 2
Concentration of additives released from mulch films into aqueous solutions (mg/kg) - Mean ± Standard Error (n = 3). LOD stands for limit of detection.

		Σ PAEs	DMP	DEP	DBP	BBP	DEHP	ATBC
Shaking Oxo-PE	24 h	6,58E+00 ± 3,97E-01	8,68E-04 ± 7,86E-05	5,05E-01 ± 1,93E-01	6,56E-01 ± 1,72E-01	<LOD	5,42E+00 ± 2,02E-01	4,51E-02 ± 9,70E-03
	10d	4,84E+00 ± 1,69E+00	7,80E-04 ± 6,38E-05	6,66E-01 ± 2,99E-01	1,79E-01 ± 5,56E-02	<LOD	3,99E+00 ± 1,33E+00	2,76E-02 ± 1,88E-03
	30d	8,75E+00 ± 2,90E+00	8,58E-04 ± 9,75E-05	1,14E+00 ± 2,21E-01	3,04E-01 ± 1,50E-01	<LOD	7,30E+00 ± 2,62E+00	1,99E-02 ± 3,46E-03
Static Oxo-PE	24 h	4,69E+00 ± 8,05E-01	8,03E-04 ± 4,45E-05	3,06E-01 ± 1,13E-01	6,39E-01 ± 3,38E-01	<LOD	3,75E+00 ± 9,69E-01	5,08E-02 ± 7,61E-03
	10d	4,64E+00 ± 1,13E+00	1,38E-02 ± 4,87E-03	3,98E-01 ± 7,17E-02	1,76E-01 ± 8,24E-02	<LOD	4,06E+00 ± 9,81E-01	4,19E-02 ± 1,45E-02
	30d	7,40E+00 ± 1,65E+00	1,12E-02 ± 5,35E-03	4,15E-01 ± 2,91E-02	1,41E-02 ± 8,57E-04	<LOD	6,96E+00 ± 1,64E+00	2,37E-02 ± 2,62E-03
Shaking PP	24 h	3,52E+00 ± 4,70E-01	5,22E-04 ± 4,48E-05	2,38E-01 ± 1,41E-02	2,63E-01 ± 3,72E-02	<LOD	3,02E+00 ± 4,53E-01	5,04E-02 ± 3,46E-03
	10d	4,75E+00 ± 2,00E+00	4,61E-04 ± 1,01E-04	3,16E-01 ± 8,19E-02	2,12E-01 ± 6,48E-02	<LOD	4,22E+00 ± 1,86E+00	6,30E-02 ± 5,86E-03
	30d	5,00E+00 ± 1,29E+00	5,29E-04 ± 3,20E-05	2,12E-01 ± 6,61E-02	4,35E-01 ± 3,51E-01	<LOD	4,36E+00 ± 9,97E-01	2,75E-02 ± 2,21E-03
Static PP	24 h	4,25E+00 ± 3,49E-01	4,89E-04 ± 4,97E-05	5,61E-01 ± 4,23E-01	1,97E-01 ± 1,54E-02	<LOD	3,49E+00 ± 2,28E-01	5,94E-02 ± 1,92E-03
	10d	3,58E+00 ± 6,76E-01	4,67E-04 ± 1,12E-05	6,98E-02 ± 3,18E-02	1,16E-02 ± 3,78E-03	<LOD	3,49E+00 ± 7,11E-01	6,23E-02 ± 1,39E-02
	30d	6,17E+00 ± 1,06E+00	5,50E-04 ± 3,63E-05	6,40E-01 ± 5,41E-01	1,39E+00 ± 3,56E-01	<LOD	4,13E+00 ± 1,42E+00	4,55E-02 ± 1,85E-02
Shaking PBAT	24 h	1,72E-04 ± 8,89E-05	<LOD	7,78E-05 ± 6,11E-05	4,44E-05 ± 2,78E-05	<LOD	5,00E-05 ± 2,83E-05	2,92E-04 ± 1,37E-04
	10d	8,33E-05 ± 0,00E+00	<LOD	1,67E-05 ± 0,00E+00	1,67E-05 ± 0,00E+00	<LOD	5,00E-05 ± 0,00E+00	1,05E-03 ± 2,61E-04
	30d	3,12E-02 ± 9,73E-03	<LOD	1,73E-02 ± 5,00E-03	7,21E-04 ± 6,72E-04	3,79E-03 ± 4,96E-04	9,43E-03 ± 3,78E-03	1,07E-03 ± 7,85E-04
Static PBAT	24 h	2,11E-03 ± 1,09E-03	<LOD	1,78E-05 ± 1,11E-06	1,78E-05 ± 1,11E-06	<LOD	2,07E-03 ± 1,09E-03	4,30E-04 ± 4,54E-05
	10d	8,44E-05 ± 1,11E-06	<LOD	1,67E-05 ± 0,00E+00	1,78E-05 ± 1,11E-06	<LOD	5,00E-05 ± 2,83E-05	1,88E-03 ± 7,79E-04
	30d	5,01E-02 ± 7,73E-03	<LOD	1,10E-02 ± 1,63E-03	7,76E-03 ± 5,58E-03	<LOD	3,14E-02 ± 5,24E-04	3,66E-03 ± 8,47E-04
Shaking PE	24 h	3,17E-04 ± 1,70E-04	<LOD	2,05E-04 ± 1,88E-04	6,18E-05 ± 4,51E-05	<LOD	5,00E-05 ± 2,83E-05	5,00E-05 ± 4,91E-21
	10d	4,88E-03 ± 6,77E-04	<LOD	1,67E-05 ± 0,00E+00	1,67E-05 ± 0,00E+00	3,74E-03 ± 1,11E-03	1,11E-03 ± 1,06E-03	9,60E-04 ± 4,66E-04
	30d	2,99E-02 ± 3,48E-03	<LOD	1,37E-02 ± 1,81E-03	5,60E-03 ± 4,91E-03	5,27E-03 ± 5,38E-04	5,36E-03 ± 1,85E-04	2,63E-03 ± 7,86E-04
Static PE	24 h	8,33E-05 ± 5,67E-21	<LOD	1,67E-05 ± 0,00E+00	1,67E-05 ± 0,00E+00	<LOD	5,00E-05 ± 2,83E-05	5,00E-05 ± 4,91E-21
	10d	1,56E-02 ± 7,76E-03	<LOD	3,18E-03 ± 1,59E-03	5,72E-03 ± 3,14E-03	<LOD	6,64E-03 ± 3,34E-03	5,88E-03 ± 1,45E-03
	30d	1,73E-02 ± 4,91E-03	<LOD	3,89E-03 ± 1,34E-03	1,67E-05 ± 0,00E+00	<LOD	1,34E-02 ± 4,56E-03	3,40E-03 ± 1,50E-03

the other films.

Conventional PE films released minimal amounts of phthalates, with the total concentration reaching only $2.99 \times 10^{-2} \pm 3.48 \times 10^{-3}$ mg/kg after 30 days under shaking conditions. This suggests that PE films might be less of a concern in terms of phthalate release, although they still contribute to long-term plastic pollution.

The Mann-Whitney test revealed no significant difference between static and dynamic conditions for any of the mulch films at any of the tested time points ($p \geq 0.1$). This suggests that the mode of agitation (static versus dynamic) does not significantly influence the release of phthalates from the mulch films. This also indicates that the release mechanism may be more closely tied to the intrinsic properties of the mulch materials rather than to the external physical conditions simulated in the experiment.

3.3.1. PAEs content comparison among the mulch films

The Kruskal-Wallis test indicated significant differences among the various mulch films under both static and dynamic conditions ($p \leq 0.05$). This suggests that the material composition of the mulch films plays a critical role in the release of phthalates. The observed differences are in line with the findings of Zimmermann et al. (2019), who noted that the chemical structure and additives used in different types of plastic mulches result in varied degradation behaviours and potential environmental impacts.

The Dunn test was used to identify which specific mulch films showed significant differences after 30 days of exposure. For both the experiment conditions (dynamic and static), significant differences were found between Oxo-PE and PBAT, Oxo-PE and PE, PP and PBAT, and PP and PE (all $p < 0.05$), indicating that Oxo-PE and PP mulches released phthalates at a higher rate compared to PBAT and PE films. The consistency of these results across both static and dynamic conditions reinforces the hypothesis that material composition is a major determinant of phthalates release. The lack of significant difference between Oxo-PE and PP ($p = 0.27523$ and $p = 0.51269$ for dynamic and static conditions respectively) supports the idea that these materials might share similar degradation and additive release profiles under the conditions of our experiment.

The statistical significance between PBAT and PE films differs under dynamic ($p = 0.82726$, no significance) and static ($p = 0.04953$, significant) conditions, with PE showing higher phthalate concentrations. This suggests PBAT's behaviour might depend on exposure type. PBAT may be more affected by agitation, leading to uniform exposure in dynamic conditions, reducing differences with PE and resulting in a non-significant Dunn test outcome. PBAT may degrade faster, disperse additives more efficiently, or interact differently with its surroundings under agitation, reducing differences with PE. In dynamic conditions, agitation likely promotes uniform water diffusion and exposure, leading to more consistent degradation. In contrast, under static conditions, slower or uneven diffusion may create distinct degradation patterns, increasing the differences between PBAT and PE.

The significant higher release of additives from Oxo-PE and PP films, compared to PBAT and PE, suggests that these materials could pose a greater risk of soil contamination. This observation is consistent with concerns in the scientific literature about the environmental persistence and potential toxicity of additives released from conventional and oxo-degradable plastics (El-Beltagi et al., 2022; Zhou et al., 2023).

Our results are consistent with those of Zimmermann et al. (2019), who analyzed eight major polymer types using in vitro bioassays. Their study found that HDPE had minimal toxic effects, while all PLA-based bioplastics showed significant baseline toxicity. Our study found that PBAT films released significantly lower amounts of PAEs into water compared to Oxo-PE films. However, in the test where mulch films were extracted with hexane and acetone, PBAT released a significantly higher concentration of PAEs compared to Oxo-PE. This discrepancy can be explained by the different extraction methods used in each test. The acetone and hexane solvents are much stronger and more efficient at

breaking down the materials, allowing for the release of more additives, especially from films like PBAT. In contrast, the water immersion test represents milder conditions and may not extract as many additives. Thus, biodegradable materials like PBAT may offer some environmental advantages, but their faster degradation rate could lead to a more rapid release of potentially harmful additives.

Although biodegradable films are increasingly used to enhance sustainability, PBAT films release slightly more additives than PE films (Table 2), though the difference is not significant. This suggests that their use may not effectively reduce environmental impact, as also observed by Qi et al. (2020) and Serrano-Ruiz et al. (2023). Furthermore, these findings support the argument that biodegradable films cannot be considered entirely a sustainable alternative (Mansoor et al., 2022) and highlight concerns regarding the presence of additives, which could pose potential food safety risks (Serrano-Ruiz et al., 2023). The same considerations can be made upon Oxo-PE films, with the aggravating factor that the concentrations of the additives released by them were significantly higher than the ones released by PBAT films.

The high release of phthalates, particularly from Oxo-PE and PP films, might pose significant risks to soil health and food safety. Given the well-documented endocrine-disrupting properties of phthalates (Panneel et al., 2024), their presence in agricultural soils could have far-reaching impacts on both human health and ecosystems, as also emphasized by Viljoen et al. (2023), that documented the persistence and harmful effects of phthalates, such as DEHP, in agricultural soils.

3.3.2. DBS, TEHP and ATBC concentrations into aqueous solutions

DBS and TEHP were not detected in any of the samples, while ATBC concentration ranged from 5.00×10^{-5} to 6.30×10^{-2} mg/kg.

As for phthalates, the Mann-Whitney test revealed no significant differences in ATBC release between static and dynamic conditions for any of the mulch films across all time points ($p \geq 0.1$). This outcome suggests that agitation does not significantly impact the release rate of ATBC from the mulch films.

The Kruskal-Wallis test showed significant differences in ATBC release among the different mulch films under both static and dynamic conditions. This implies that the type of material, again, significantly influences the release of ATBC, a pattern already observed with phthalates in our study and with different plasticizers in other literature studies (Y. Xu et al., 2023; Aliotta et al., 2020). The Dunn test provided detailed insights into the comparisons of mulch films after 30 days of exposure showing mirroring trends as for the phthalates release with significant differences for both the dynamic and static conditions between Oxo-PE and PBAT, Oxo-PE and PE, PP and PBAT, and PP and PE (all $p = 0.04953$). The higher release from Oxo-PE and PP compared to PBAT and PE suggests that the chemical composition and physico-chemical properties of Oxo-PE and PP films may lead to greater environmental release of ATBC.

No significant difference was found between Oxo-PE and PP ($p = 0.12663$ in dynamic conditions, $p = 0.51269$ in static conditions) or between PBAT and PE ($p = 0.12663$ in dynamic conditions, $p = 0.82726$ in static conditions).

The significant release of ATBC from Oxo-PE and PP films compared to PBAT and PE under both static and dynamic conditions highlights potential environmental risks associated with the use of certain plastic films in agriculture. ATBC, a widely used plasticizer in biodegradable and conventional plastics, is known to be relatively less toxic than phthalates, but its release in large quantities could still pose risks to the environment and human health (Horie et al., 2022).

Our findings suggest that the choice of mulch material should consider not only the effectiveness of crop protection but also the potential environmental impact of plasticizers' release.

3.3.3. Correlation analyses

The correlation analysis data provided for the release of phthalates and ATBC from the four different mulch films under dynamic and static

conditions over time reveals several interesting patterns (Fig. 3). The analysis is based on the Pearson correlation coefficient (r) and p -values, where positive correlations are considered significant when $r > 0$ and $p \leq 0.05$.

Significant positive correlations were observed for PE under dynamic conditions with DMP ($r = 0.92$, $p = 0.0004$), DEHP ($r = 0.93$, $p = 0.0003$), BBP ($r = 0.82$, $p = 0.007$), ATBC ($r = 0.82$, $p = 0.007$), and the sum of phthalates ($r = 0.96$, $p = 0.00003$). Under static conditions, only DEHP exhibited a significant positive correlation ($r = 0.75$, $p = 0.021$), suggesting that even without agitation, this compound shows a time-dependent increase in release. The other additives did not show significant correlations, which suggests that static conditions are less effective at promoting additive release from PE film compared to shaking. PBAT films, under dynamic conditions showed significant positive correlations for DEP ($r = 0.85$, $p = 0.0037$), DEHP ($r = 0.78$, $p = 0.0129$), BBP ($r = 0.93$, $p = 0.0003$) and the sum of phthalates ($r = 0.84$, $p = 0.0049$), while under static conditions significant positive correlation were observed for DEP ($r = 0.92$, $p = 0.0013$), DEHP ($r = 0.91$, $p = 0.0016$), ATBC ($r = 0.90$, $p = 0.0026$), and sum of phthalates ($r = 0.90$, $p = 0.0023$). These data suggest that even in the absence of agitation, PBAT film releases these additives at an increasing rate over time.

The only significant positive correlation found within PP films was the one with DBP ($r = 0.82$, $p = 0.007$), under static conditions. This suggests that different additives might have variable responses to static versus dynamic conditions, and in this case, PP in static conditions favoured the release of DBP. No significant positive correlations were observed for Oxo-PE films in both conditions and for PP films in dynamic conditions.

The differences in correlation between the dynamic and static conditions suggest that the physical properties of the films and their interaction with the aqueous solution play a significant role in additive release. Oxo-PE and PP films seem less sensitive to time-dependent release under both static and dynamic conditions. PE and PBAT films show significant time-dependent release of additives under both conditions, with PE particularly sensitive to agitation, as indicated by the high correlation values under shaking. The data suggest that the additives are not immediately released but continue to migrate out of the polymer matrix over time, and that agitation might increase the release of additives, particularly for PE films. The varied responses between films and conditions highlight the complexity of additive release

mechanisms, which can be influenced by factors such as polymer composition, environmental conditions, and the physical properties of the films themselves. These analyses underscore the importance of considering both the material and the environmental context when evaluating the environmental impact of plastic mulch films.

4. Conclusions

In this study, the release of plastic additives from different mulch films (PBAT, PP, Oxo-PE, and PE) was examined using both aqueous extraction and organic solvents revealing significant differences based on film type and method.

Notably, the higher release of phthalates and ATBC from PP and Oxo-PE in aqueous environments suggests a greater risk of additive leaching into water systems from these films.

Additionally, while biodegradable films are marketed as eco-friendly, they do not consistently show lower additive leaching than conventional plastics under organic solvent extraction, challenging their perceived environmental benefits. The findings also indicate that additive release increases with prolonged water exposure, emphasizing a time-dependent release pattern.

These insights emphasize the need for an accurate evaluation of mulch film sustainability beyond degradability, considering additive release profiles over time and under various conditions. To better inform sustainable agricultural practices, further research should explore long-term environmental impacts, with respect to conventional and biodegradable films and their degradation products.

CRedit authorship contribution statement

Costanza Scopetani: Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Agnese Bellabarba:** Writing – review & editing, Funding acquisition, Conceptualization. **Giulia Selvolini:** Writing – review & editing, Funding acquisition, Conceptualization. **Tania Martellini:** Writing – review & editing, Supervision, Conceptualization. **Carlo Viti:** Writing – review & editing, Conceptualization. **Alessandra Cincinelli:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT in order to check the grammar. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

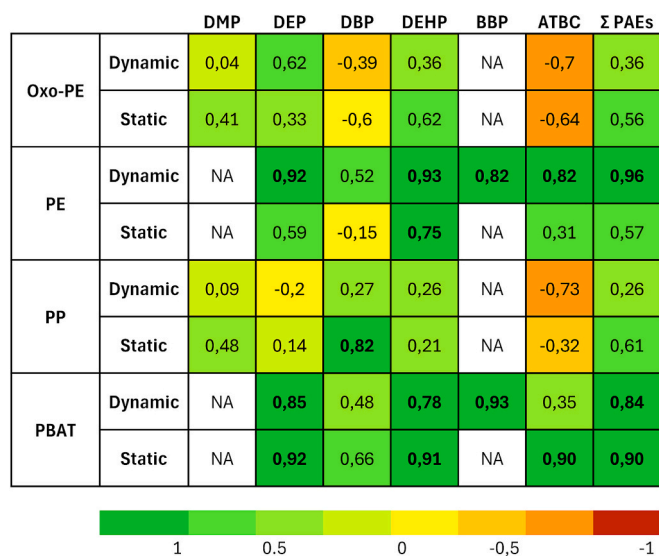


Fig. 3. Correlation analysis data of the release of phthalates and ATBC from the four different mulch films under dynamic and static conditions over time. The data corresponds to the r value and the bold type denotes a significant positive correlation with time ($r > 0$, and $p < 0,05$).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2025.179294>.

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