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Research Paper

Terrestrial characterization factors for bio- and fossil-based plastics: microplastics ingestion and additives release

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ABSTRACT

Only a few works have contributed to quantifying the potential impacts of mismanaged plastics at the end-of-life stage. The MarILCA working group has developed characterization factors (CFs) to include the aquatic compartment, however, the terrestrial compartment remains a methodological gap. This work contributes to the quantification of the potential impacts of polypropylene (PP) and low-density polyethylene (LDPE) as well as their potential market substitutes plastic biopolymers (BPs) (PHA- and PLA-based) in the terrestrial compartment. Emission-based CFs have been developed to quantify their impacts through physical effects on biota related to microplastic ingestion, and ecotoxicological effects due to additives release. Fate factors (FFs) were derived from Plastic Footprint Network data and studies on accelerated photooxidation, the primary degradation pathway in the terrestrial compartment. Effect factors (EFs) were developed by the USEtox recommendations based on literature data on the physical and ecotoxicological impacts related to microplastics ingestion and additives release. An exposure factor (XF) of 1 was applied, as the CFs integrate potential impacts without distinguishing between short- and long-term effects. The study found that additives pose a greater environmental risk than microplastics ingestion, with CFs 3 to 4 orders of magnitude higher in the terrestrial compartment and even higher in the aquatic compartment. It is, therefore, essential to consider both the terrestrial and aquatic compartments to understand the impact of plastic pollution comprehensively. Finally, the study also found that the CFs of BPs are close to petrochemical plastics, underling the importance of proper waste management for the environmental performance of BPs.

1. Introduction

Plastic litter has become a significant global environmental concern (Davis et al., 2022; Napper and Thompson, 2020; Roy Chowdhury et al., 2023), and its production is expected to keep increasing in the coming years (OECD, 2022). Fossil-based plastics have high demand due to their versatile properties, e.g., lightness, moldability, stability, and resistance to chemicals and light (Shen et al., 2020; Woods et al., 2021), which also leads to plastic waste accumulation in the environment mainly due to poor end-of-life (EoL) management practices (Lavoie et al., 2022; Law and Narayan, 2021).

Polyhydroxyalkanoate (PHA) and polylactic acid (PLA) are plastic biopolymers (BPs) (i.e., bio-origin polymers with plastic properties) that can be combined to produce biobased and biodegradable items (European Commission, 2022; Mai et al., 2024). These materials offer a potential substitute for fossil-based plastics, provided their quality and

Abbreviations: AF, accelerated factor; ATR, attenuated total reflection; BP, plastic biopolymer; CF, characterization factor; COCO, coconut oil; DSC, differential scanning calorimetry; EC50, effect concentration 50; EF, effect factor; EoL, end of life; FF, fate factor; FTIR, fourier transform infrared; GLAM, Global Guidance for Life Cycle Impact Assessment Indicators and Methods; HC20, hazard concentration killing 20% of the exposed population; IS, impact score; LCA, life cycle assessment; LCI, life cycle inventory; LCIA, life cycle impact assessment; LDPE, low density polyethylene; MCT, mercury cadmium telluride; MNP, micro- and nano plastics; NOEC, no observed effect concentration; OCPs, organochlorine pesticides; PAF, potentially affected fraction; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PDF, potentially disappeared fraction; PFAs, polyfluoroalkyl substances; PHA, polyhydroxyalkanoate; PLA, polylactic acid; PFN, plastic footprint network; PP, polypropylene; SA, surface area; TC, triethyl citrate; Tg, glass transition temperature; Tm, melting temperature; XF, exposure factor.

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environmental performance meet certain standards (European Commission, 2021; Pizzol et al., 2023). In this sense, Life Cycle Assessment (LCA) is the appropriate tool to assess and quantify their performance accurately (Roibás-Rozas et al., 2022) and several guidelines exist for quantifying the environmental impacts of plastics (Owsianiak et al., 2023). However, up to now, most LCA of conventional plastics have ignored mismanaged plastics, underestimating their long-term effects (Pellengahr et al., 2023). This is primarily due to the lack of data at the life cycle inventory (LCI) stage, which compiles all inputs and outputs after the plastic use phase, and the ongoing development of the life cycle impact assessment (LCIA) models, which assess the potential environmental impacts of those inputs and outputs (International Organization for Standardization, 2006). In terms of LCI data, the Plastic Footprint Network (PFN)[1] has provided an estimation of plastic leakage from different sources (based on plastic size) into different environmental compartments, including freshwater, ocean, air, soil, and other terrestrial compartments (Quantis and EA, 2020). However, to the best of our knowledge, few studies have included mismanaged plastics so far (Corella-Puertas et al., 2023; Jakrawatana et al., 2023; Saavedra del Oso et al., 2023; Zhao and You, 2022). In relation to LCIA models, the development of characterization factors (CF), which are coefficients used to convert LCI data into environmental impacts, is crucial. The MarILCA[2] project has made a huge effort in developing CFs in the marine compartment, considering plastic size and emission compartments (Woods et al., 2021).

While the marine compartment has attracted attention as major sink for plastic waste, the impacts on terrestrial compartment must not be overlooked, as most of the plastic waste is firstly disposed (and a significant fraction stays there) on land (Quantis and EA, 2020). In this context, the ECOPOLYVER project[3] aims to materialize circular strategies by transforming lipid-rich effluents into BPs, particularly PHAs, that can then be converted into plastic materials for the food industry. This project highlight the importance of developing the necessary methodologies to compare the entire life cycle of these BPs with PP and LDPE. The objective of this work is to develop the required characterization factors to include the potential impacts of mismanaged BPs (PHA/PLA based) and fossil-based plastics (low-density polyethylene (LDPE) and polypropylene (PP) in the terrestrial compartment, considering both the physical impacts of microplastics ingestion and the ecotoxicological impacts associated with their additives. This paper is organized as follows: firstly, the case study evaluated is described (2.1), the inventory data and literature sources reviewed (2.2), and the development of the characterization factors presented (2.3). Section 3 summarizes the results from the photooxidation experiments (3.1.) and the fate (3.2) and effect (3.3) factors calculations. Section 4 discusses the results presented in section 3, integrates the factors developed for the terrestrial compartment with the aquatic compartment (4.1), and presents the main future outlooks (4.2).

2. Materials and methods

2.1. Case study: Plastic packaging materials

Two items commonly used for packaging purposes were selected by the Spanish National Association of canned fish and Seafood Manufacturers (ANFACO CECOPESCA):

- a LDPE film, with bis(2-ethylhexyl) phthalate (CAS: 117–81-7) as additive;
- and a PP tray with dibutyl phthalate (CAS: 84–74-2) as additive;
- as bio-based alternatives, BPs based on a combination of two biopolymers, i.e., PHA (in the form of PHBV, 88:12 butyrate: valerate, which allows properties similar to PP and LDPE); and PLA (for its final consistency) were selected with the additional incorporation of triethyl citrate (TC) (CAS: 77–93-0) or coconut oil (COCO) (CAS: 8001–31-8) as plasticizers. The samples used were: sample 1, PHA:PLA (50:50); sample 2, PHA:PLA (30:70); sample 3, PHA:PLA:TC (27:63:10); and, sample 4, PHA:PLA:COCO (27:63:10); all stated as percentual weight ratio.

2.2. End of life modelling and inventory

Once the packaging materials have been used by the final consumers, waste management has been modelled based on Spanish statistics and information provided by MITECO (2021) (see Section 1.01 in Supplementary Material 1).

Leakage during the production and moulding process is generally low, estimated at 0.005 % according to Ryberg et al. (2018), and during their EoL, it is estimated that around 4.5 % of generated plastic is deposited on terrestrial or aquatic compartments (Jambeck et al., 2015). The PFN guidelines (Quantis and EA, 2020) have been followed to estimate the amount of mismanaged plastics that end up in both terrestrial and aquatic compartments (Fig. 1). So, the allocation was made according to the recyclability of the plastics, if 85 % (m/m) of PP and 75 % (m/m) of LDPE and bioplastic items end up in the terrestrial compartment due to the better recyclability of the PP. It has been assumed that all mismanaged plastics have suffered photooxidation (the main degradation pathway (Bacha et al., 2023) and then transformed into micro- and nanoplastics. After the photooxidation process, only 70 % of the disposed macroplastics (Quantis and EA, 2020) remain in the form of microplastics in the terrestrial compartment.

2.3. Characterization factors

The impact score (IS) is quantified according to equation (1) (Jolliet et al., 2006), where M represents the mass of the pollutant in the considered environment, and CF is the emission-based characterization factor, a coefficient used to convert LCI data into environmental impacts. The CF is composed of three subfactors: fate factor (FF), effect factor (EF), and exposure factor (XF).

$$IS = M\left[kg_{plastic/additive}\right]\cdot CF\left[\frac{PAF\cdot m^3\cdot days}{kg_{plastic/additive}}\right] = \\ = M\left[kg_{plastic/additive}\right]\cdot\left(FF\left[\frac{kg_{in\ compartment}\cdot \text{days}}{kg_{emmited}}\right]\cdot EF\left[\frac{PAF\cdot m^3}{kg_{plastic/additive}}\right]\cdot XF\left[\frac{kg_{bioavailable}}{kg_{compartment}}\right]\right) \quad (1)$$

The FF represents the pollutants' residence time in the environment as well as the mass accumulation in a specific compartment following its release from the emission compartment (Maga et al., 2022), the EF the

[1] https://www.plasticfootprint.earth/
[2] https://marilca.org/
[3] https://biogroup.usc.es/ecopolyver

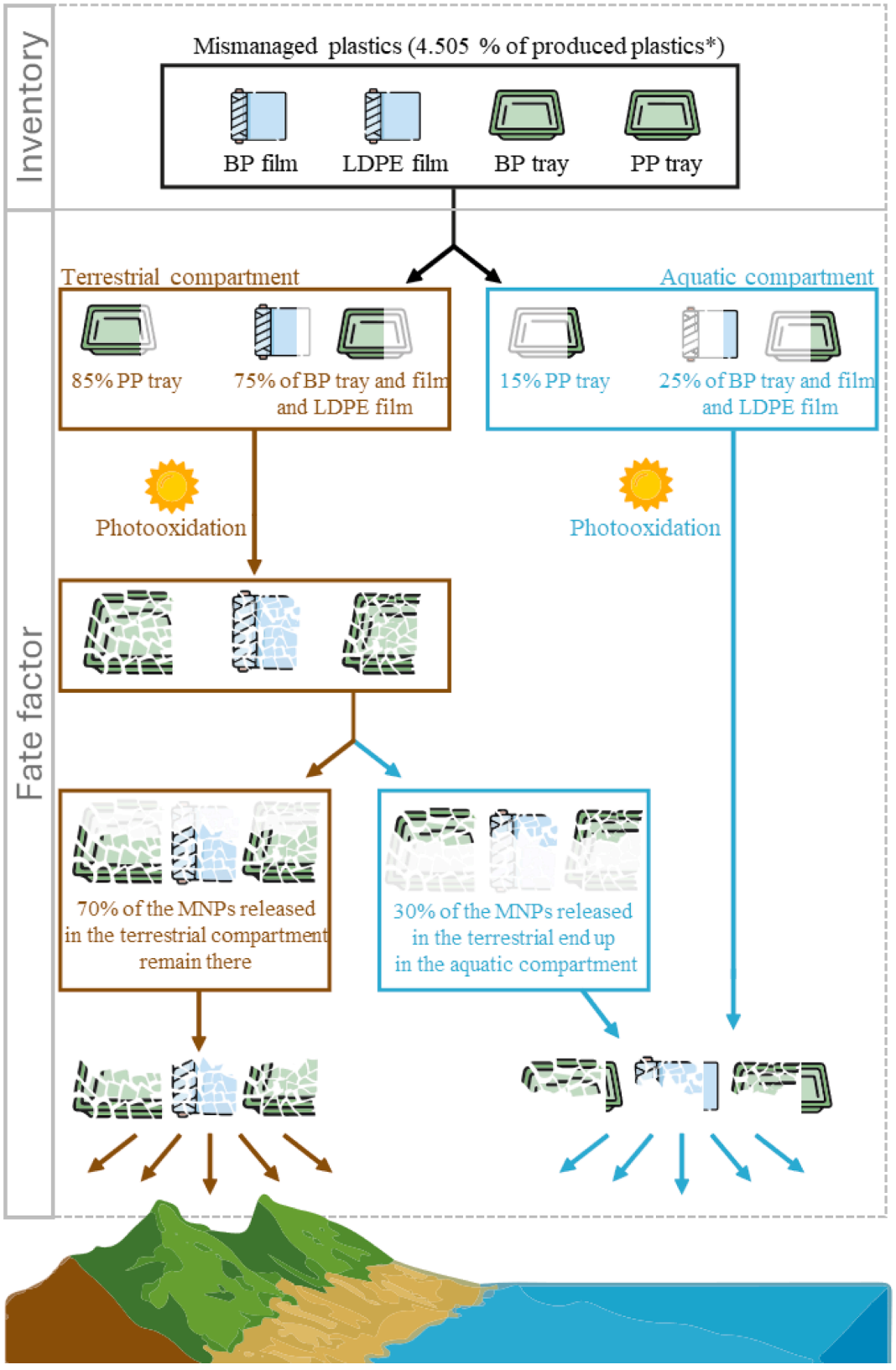

Fig. 1. Pathways and final destination of mismanaged plastics. *4.505 % = 0.005 % (production and moulding stage) + 4.5 % (EoL stage).

potentially affected fraction (PAF) of species in an ecosystem (Rosenbaum et al., 2007) per volume and mass of the emitted pollutant in the compartment, and the XF the bioavailability of the released pollutant to the exposed ecosystem. Thus, IS represents the impact score in PAF, for midpoint, and Potentially Disappeared Fraction (PDF) for endpoint over unit of volume and time, as further described in section 3. In the case of microplastic ingestion, the impacts refer to physical effects on biota in the terrestrial compartment. The midpoint reflects ecosystems disruption through ingestion and physical damage to organisms, potentially harming biological functions; while the endpoint captures the long-term consequences for ecosystem health, such as biodiversity loss and species decline. For plastic additives, the impacts are associated with terrestrial ecotoxicity. At the midpoint, this represents the potential for toxicity due to chemicals release into the soil, while the endpoint translates this into broader ecological impacts, such as reduced species populations and overall ecosystem function.

In this case, as CFs integrate potential impacts over time window without differentiating between short- and long-term, XF has been assumed to be 1 for both microplastics and additives.

2.3.1. Accelerated photooxidation studies

Fate factors will depend on the behaviour of the materials once they reach the terrestrial compartment, with photooxidation (degradation via UV light) as the main degradation pathway in the terrestrial compartment (Bacha et al., 2023), and therefore the first mechanism that should be evaluated. While studies on the photooxidative behaviour of PP and LDPE under UV light have been well documented (Song et al., 2022), there is a lack of experimental research on BPs based on the combination of PHA and PLA.

In this study, BPs films (samples 1, 2, 3, and 4 presented in Section 2.1.) with a surface area of 20 cm^2 and a thickness of 0.08 mm were subjected to accelerated photooxidation using a Suntest XLS + high-speed exposure unit equipped with a xenon light source, with an irradiation power of 765 $W{\cdot}m^{-2}$ (see sections 3.1, 3.2, 3.3 and 3.4 of the Supplementary Material 2 for more information on the BPs chemical properties). A glass filter with a cut-off at λ less than 295 nm was used to simulate outdoor daylight conditions, ensuring realistic degradation pathways. The samples' temperature was fixed at 30 °C and black standard temperature of 50 °C. Accelerated photoaging of BPs samples was carried out for up to 3 000 h, and changes were monitored at intervals of 250 h. The mass changes were followed until 2 000 h treatment, as longer times induced extensive embrittlement of films (for more details, see the Table 2 in the Supplementary Material 2), which broke up in small fragments, making it difficult to attribute the mass loss to the release of volatile compounds or to the loss of sample. Accelerated photoaging conditions were followed by the measure of mass, by gravimetrical measurements; functional groups, by Attenuated Total Reflection (ATR) – Fourier Transform Infrared (FTIR); thermal properties, by Differential Scanning Calorimetry (DSC); and color, by spectrophotometry. The experiment was carried out until the complete photooxidation of the BPs. i.e. from macroplastics to microplastics (Ø<5mm) (for more details see Section 2 in Supplementary Material 2).

2.3.2. Fate factors

Once the photooxidation times under accelerated conditions were measured for BPs (current study) and PP and LDPE (Song et al., 2022) they needed to be converted to natural time for FF calculation. To achieve this, accelerated factors (AFs) were calculated following equation (2) and represent the comparison between the time of 1 calendar year (8 760 h) versus the time t_y [h] required in the photoaging chamber to simulate 1 calendar year (for more details, see Section 1.03 in Supplementary Material 1).

$$AF = \frac{8\,760\left[\frac{h}{year}\right]}{t_y\left[\frac{h\ in\ chamber}{year\ outdoors}\right]} = \frac{8\,760\left[\frac{h}{year}\right]}{\frac{H\left[\frac{kW{\cdot}h}{m^2{\cdot}d}\right]}{E\left[\frac{W}{m^2}\right]}\cdot 3.65{\cdot}10^5\left[\frac{d{\cdot}W}{yr{\cdot}kW}\right]} \tag{2}$$

t_y was reported by Van De Ven et al. (2010) and includes the average daily solar irradiation per unit area of the selected location H [$kW{\cdot}h{\cdot}d^{-1}{\cdot}m^{-2}$] as well as the power of the photoaging chamber per unit area [$W{\cdot}m^{-2}$]. AFs are related to the average solar radiation so they will differ according to the selected location. To estimate the time of photooxidation (t) for a specific location, the experiment photooxidation time (t_a) will be multiplied by the AF of the selected location, as follows in equation (3):

$$t\,[h] = t_a[h]{\cdot}AF \tag{3}$$

FFs can be calculated as the inversion of the specific surface degradation rate constant matrix $K_{degradation}$ (4) (Frantke et al., 2017; Rosenbaum et al., 2007). Since the terrestrial is both the emission and receiving compartment, only this specific element within the matrix is considered (Frantke et al., 2017) (for more details see Section 1.02 in Supplementary Material 1):

$$FF[days] = -\left(K_{degradation}\left[days^{-1}\right]\right)^{-1} \tag{4}$$

The $K_{degradation}$ represents the rate at which the polymer photooxidation occurs in the terrestrial compartment. It was calculated following the methodology outlined by Chamas et al. (2020), where K_{SSDR} is the specific surface degradation rate calculated according to equation (7), and r_{max} is half the thickness of the studied film and tray (5):

$$K_{degradation}\left[days^{-1}\right] = \frac{2K_{SSDR}\left[\frac{m}{days}\right]}{r_{max}[m]} \tag{5}$$

K_{SSDR} is also related to the mass loss per unit time according to the surface area (SA), and the polymer density (ρ):

$$-\frac{dm\,[kg]}{dt[days]} = SA\left[m^2\right]{\cdot}K_{SSDR}\left[\frac{m}{days}\right]{\cdot}\rho\left[\frac{kg}{m^3}\right] \tag{6}$$

After the integration of equation (6) between time zero and the time required for its complete photooxidation (t calculated in (3)):

$$K_{SSDR}\left[\frac{m}{days}\right] = \frac{m_0[kg] - m_t[kg]}{\rho\left[\frac{kg}{m^3}\right]{\cdot}SA[m^2]{\cdot}t[days]} \tag{7}$$

Where m_o and m_t are the initial and final mass of the polymers [kg], respectively, assuming that the final mass (m_t) equals zero due to the complete degradation of the virgin polymer into micro- and nanoplastics.

Furthermore, a factor of 0.7 is needed for the FF calculation due to only 70 % of the macroplastics (Fig. 1) released in the terrestrial compartment remaining there in the form of micro- and nanoplastics, according to PFN data.

2.3.3. Effect factors

This study addresses the physical effects associated to the ingestion of microplastics (i.e. growth rates, intestinal damage, hindering, etc), as other authors did for the aquatic compartment (Corella-Puertas et al., 2023; Lavoie et al., 2022; Woods et al., 2021), as well as the ecotoxicological effects (reproductive malformations, apoptosis, head malformation, etc.) due to the ingestion of the additives contained in MNPs (Logan et al., 2024).

Typical physical effects of macroplastics such as entanglement were not considered due to the morphology of the materials examined. To develop the effect factors, literature research was conducted to collect data on physical and ecotoxicological effects of the studied microplastics and additives on biota. The search focused on EC10 (effect concentration in mg/L for 10 % of organisms) values to align with the USEtox methodology (Owsianiak et al., 2023) However, due to the scarcity of EC10 values data in the literature, acute-chronic, NOEC (No observed effect concentration) and EC50 (effect concentration for 50 % of organisms) values were also included and extrapolated to EC10 for their use in calculating the effect factors (Aurisano et al., 2019), see Sections 1.04 and 1.05 in Supplementary Material 1). Data have been collected for a minimum of five species that belong to at least three trophic levels of taxonomic groups to ensure representativeness as suggested by Askham et al. (2023) and Owsianiak et al. (2023).

The EF is correlated with the concentration of the released pollutant in relation to the variation of the affected species studied (Rosenbaum et al., 2007) and was calculated following the USEtox recommendations (Owsianiak et al., 2023) as follows:

$$\log HC20_{EC10^{eq}} = SSD\mu_{\log EC10^{eq}} + z_{0.2} \cdot SSD\sigma_{\log EC10^{eq}} \quad (8)$$

$$SSD\mu_{\log EC10^{eq}} = \frac{1}{n} \times \sum_{i=1}^{n} (\log EC10_i^{eq}) \quad (9)$$

$$SSD\sigma_{\log EC10^{eq}} = \sqrt{\frac{1}{n} \times \sum_{i=1}^{n} (logEC10_i^{eq} - SSD\mu_{\log EC10^{eq}})^2} \quad (10)$$

$$z_{0.2} = \sqrt{2} \times erf^{-1}(2 \times P_{0.2} - 1) \quad (11)$$

$$EF\left[\frac{PAF \cdot m^3}{kg}\right] = \frac{0.2}{10^{HC20_{EC10^{eq}}}} = \frac{0.2}{HC20_{EC10^{eq}}\left[\frac{kg}{m^3}\right]} \quad (12)$$

where μ and σ denote the mean and standard deviation of a normal distribution applied to log-transformed EC10eq data. $Z_{0.2}$ represents the inverse of the standard normal distribution at the 0.2 probability level, i.e., −0.842, with *erf* indicating the error function. log $EC10^{eq}$ refers to the average log_{10}-transformed chronic $EC10^{eq}$ data points per species in cases where multiple data points are available. And the EF, derived from the slope of the Species Sensitivity Distribution at the $HC20^{eq}_{EC10}$, where HC20 is the hazard concentration causing effects to 20 % of the exposed population, illustrates the incremental change in the potentially affected fraction of species with incremental exposure to a chemical's bioavailable concentration at the HC20 level.

3. Results

3.1. Accelerated photooxidation of PHA/PLA-based BPS

All the samples showed negligible changes during the first 2 000 h of treatment, with the spectra and color changes remaining stable below the threshold of minimal detectable difference by the human eye, defined as $\Delta E_{12} = 2$. Only the last viable measurements at 2 250 h, before extensive embrittlement and pulverization of samples, revealed visually perceptible color changes, reaching $\Delta E_{12} = 31.2$ for sample 3 (for more details, see Table 3 in the Supplementary Material 2).

Prior to photoaging, all samples showed very similar DSC curves (for more details see the Fig. 8 in the Supplementary Material 2), with glass transition temperatures (Tg) and a complex endothermic peak due to the melting of crystallites. Tg of PLA is very close to 60 °C in all the samples except sample 4, where a little lower value is possibly due a plasticization of COCO. The expected Tg of PHA, close to 0 °C (Raunhan et al., 2023), is almost undetectable in all the samples except sample 1, having a higher PHA amount. Peaks corresponding to the melting of the crystalline phases of both polymers are visible in the range 150–190 °C. Although the contribution of the two components cannot be quantified, it is possible to distinguish between the main PLA peak, with a melting temperature (Tm) of 175–177 °C (Rasselet et al., 2014), and a shoulder due to PHA with a Tm at approximately 160°C (Raunhan et al., 2023) (for more details, see Table 4 in the Supplementary Material 2).

3.2. Fate factors of fossil and biobased polymers

Four FFs have been defined for four locations to calculate the FF for each type of plastic according to their photooxidation times (Table 1). The selection is based on the ECOPOLYVER project locations (i.e., Santiago de Compostela (NW Spain) and Granada (SE Spain)), and two more locations with extreme climatic conditions (i.e., Stockholm with low exposure to UV radiation and Cairo with high exposure to UV radiation).

The methodology for calculating FFs is detailed comprehensively, allowing any reader to apply the same procedure to develop FFs for any other desired location (for more details, see sections 1.02 and 1.03 in Supplementary Material 1).

3.3. Effect factors of fossil and biobased polymers

The calculated EFs (Table 2) were based on literature data for EC50 and NOEC of the additives used and the ingestion of microplastics (Sections 1.04 and 1.05 in Supplementary Material 1).

Table 1
FFs results for the BPs, PP and LDPE samples.

Polymer type	Location	FF (days)
BPs	Santiago de Compostela	32.20
BPs	Granada	25.25
BPs	Stockholm	44.41
BPs	Cairo	20.38
PP	Santiago de Compostela	11.69
PP	Granada	9.17
PP	Stockholm	16.12
PP	Cairo	7.40
LDPE	Santiago de Compostela	80.57
LDPE	Granada	63.19
LDPE	Stockholm	111.12
LDPE	Cairo	50.99

Table 2
EFs results for the additives in the BPs, PP, and LDPE samples and for microplastic ingestion.

Polymer type		Additive type	Effect factors [PAF·m^3·kg^{-1}]	
			Additives	Microplastics ingestion
BP	PHA:PLA (50:50)	–	0*	2.76E-03
BP	PHA:PLA (30:70)	–	0*	2.76E-03
BP	PHA:PLA:COCO (27:63:10)	COCO	0**	2.76E-03
BP	PHA:PLA:TC (27:63:10)	Triethyl citrate	25.28	2.76E-03
PP		Dibutyl phthalate	54.21	7.74E-03
LDPE		Bis(2-ethylhexyl) phthalate	9.48	5.61E-03

*No additives are present, so the EF is 0.
**Only one study on the ecotoxicological effect of coconut oil (on rodents) has been found (Cohen et al., 1986) and therefore considered not sufficiently representative.

3.4. Midpoint and endpoint CFs

CFs are developed to quantify both the physical impacts resulting from the ingestion of microplastics and the ecotoxicological impacts arising from the release of chemical additives in plastic items. These factors are defined at two levels: the midpoint level, which expresses impacts in terms of the potentially affected fraction (PAF·m^3·year·kg^{-1}), and at the endpoint level, which indicates damage in terms of potentially disappeared fraction (PDF·m^2·year·kg^{-1}) (Finnveden and Potting, 2014).

To transform midpoint to endpoint factors, the GLAM Phase 3 recommends a new severity factor of 0.025 PDF/PAF for the effect factor based on HC20(EC10eq) (Verones et al., in preparation as cited in the Supplementary Material of Corella-Puertas et al. (2023)). Midpoint and endpoint CFs were calculated (Table 3) for the terrestrial compartment for BPs, PP, and LPDE (for more details, see section 1.07 in Supplementary Material 1). In addition, a depth of 0.6 m was considered to transform m^3 at midpoint to m^2 at endpoint.

4. Discussion

4.1. Fate factors development from experimental data

Terrestrial FFs have been calculated as Corella-Puertas et al. (2023) did for the aquatic compartment. However, some of the assumptions required further clarification:

First, polymer mass loss here always refers to the loss of volatile compounds (Beltrán Sanahuja and Valdés García, 2021) (e.g. COCO in sample 4, consistent with DSC measurements in Fig. 8 of Supplementary Material 2). In contrast, the mass loss reported by Corella-Puertas et al. (2023) and Hoseini et al. (2023) does not indicate a true mass loss; rather, it represents the release of micro- and nanoplastics (MNPs) from the virgin polymer. This assumption is relevant as assuming total mass disappearance means that the associated impacts disappear, when in reality, the impacts change but do not disappear i.e. the mass remains constant while the size changes.

Photooxidation has been identified as the primary degradation pathway of mismanaged plastics in the environment (Sutkar et al., 2023) and can be divided into 3 steps (Yousif and Haddad, 2013): i) initialization, where chromophore groups absorb UV radiation, excite, and form free radicals; ii) propagation, where free radicals interact with oxygen and non-photoxidized polymers to form peroxyl and hydroperoxyl radicals; and iii) termination; where UV radiation fragments the polymers through β scission. So, the study of the impacts of polymers in a steady state based on their photooxidation will never have a single degradation rate (K_{SSDR} in eq (9)). It will have at least 2 phases, (i) and (ii and iii), with different K_{SSDR} and impacts, i.e., the necessary time to start the fragmentation with its macroplastic impacts and the time required to become MNPs with its impacts and those of the additives because it is when they are released.

In this study, it has been quantified the time needed to start fragmentation (initialization) and the time needed to turn into pulverized powder (propagation). Although it is not possible at present to link these times directly to their impacts due to the lack of ecotoxicological effects data, future works can link the calculated times to their impacts (i.e., macroplastics with their impacts and microplastics with their impacts). The impacts of additives are extremely greater (about 3 orders of magnitude) than the impacts of microplastic ingestion (Table 3), suggesting that either the ecotoxicological impacts of microplastic ingestion are poorly studied (Gomes et al., 2022) due to its high complexity, or that additives are responsible for the majority of the toxicological impacts of plastics but ignored so far due to its possible volatilization into the air.

4.2. Integration of environmental compartments

As presented in Fig. 1, when macroplastics are released into the terrestrial compartment, part of them remain there (75 % of BPs, LDPE, and 85 % of PP), while the remainder migrates to the aquatic compartment. Furthermore, 30 % of the microplastics generated

Table 4
Comparison of midpoint CFs on the physical impacts of microplastics on biota in the terrestrial compartment (this study) versus the aquatic compartment.

Polymer type	Midpoint CFs [PAF·m^3·year·kg^{-1}]		
	This study	Corella-Puertas et al. (2023)	
	Terrestrial	Marine	Freshwater
PHA	8.44E-02 ± 2.9E-02	3.70E + 01	3.70E + 00
PLA	8.44E-02 ± 2.9E-02	4.77E + 01	4.77E + 00
PP	8.59E-02 ± 2.94E-02	1.53E + 04	1.15E + 04
LDPE	4.29E-01 ± 1.46E-01	3.18E + 04	2.38E + 04

Table 3
Midpoint and endpoint CFs of the studied plastics for four different locations.

Polymer type		Location	Midpoint [PAF·m^3·year·kg^{-1}]		Endpoint [PDF·m^2·year·kg^{-1}]	
			Additives	Microplastics ingestion	Additives	Microplastics ingestion
BPs	Without additives	Santiago de Compostela	0	8.88E-02	0	3.70E-03
BPs	Without additives	Granada	0	6.97E-02	0	2.90E-03
BPs	Without additives	Stockholm	0	1.23E-01	0	5.11E-03
BPs	Without additives	Cairo	0	5.62E-02	0	2.34E-03
BPs	With additives (TC)	Santiago de Compostela	8.13E + 02	8.88E-02	3.39E + 01	3.70E-03
BPs	With additives (TC)	Granada	6.38E + 02	6.96E-02	2.66E + 01	2.90E-03
BPs	With additives (TC)	Stockholm	1.12E + 03	1.22E-01	4.67E + 01	5.10E-03
BPs	With additives (TC)	Cairo	5.15E + 02	5.62E-02	2.14E + 01	2.34E-03
PP		Santiago de Compostela	6.34E + 02	9.05E-02	2.64E + 01	3.77E-03
PP		Granada	4.97E + 02	7.09E-02	2.07E + 01	2.96E-03
PP		Stockholm	8.74E + 02	1.25E-01	3.64E + 01	5.20E-03
PP		Cairo	4.01E + 02	5.73E-02	1.67E + 01	2.39E-03
LDPE		Santiago de Compostela	7.63E + 02	4.52E-01	3.18E + 01	1.88E-02
LDPE		Granada	5.99E + 02	3.54E-01	2.49E + 01	1.48E-02
LDPE		Stockholm	1.05E + 03	6.23E-01	4.39E + 01	2.60E-02
LDPE		Cairo	4.83E + 02	2.86E-01	2.01E + 01	1.19E-02

through photodegradation in the terrestrial compartment are then transported to the aquatic compartment.

To accurately assess the environmental impacts of plastics, it is essential to consider both the terrestrial and aquatic compartments. For the 70 % of macroplastics that persist in the terrestrial environment, the CFs developed in this study for the physical impacts of microplastics should be applied. For those plastics that transition to the aquatic compartment (25 % of BPs and LDPE, 15 % of PP, and 30 % of the microplastics formed during terrestrial photodegradation) the CFs developed by Corella-Puertas et al. (2023) should be utilized.

The CFs developed by Corella-Puertas et al. (2023) for the aquatic compartment are several orders of magnitude higher than ours (3 for BPs (PHA and PLA), 5 for PP and 6 for LDPE) (Table 4). The reasons behind are related to FF and EF results, since the XF is equal to 1 in both cases.

On the one hand, the FFs [days] proposed by Corella-Puertas et al. (2023) for PHA (1.03E + 00 ± 5.14E + 00) and PLA (1.50E + 01 ± 1.85E + 00) differ significantly from PP (1.05E + 03 ± 5.22E + 03) and LDPE (2.78E + 03 ± 5.91E + 03). However, the calculated FFs [days] for BPs (PHA/PLA based) (2.93E + 01 ± 1.04E + 01) do not significantly differ from PP (1.06E + 01 ± 3.78E + 00) and LDPE (7.33E + 01 ± 2.61E + 01), as their photooxidation rates are similar.

So the compartment behaviour has also a significant role to play as the degradation rate of PHA and PLA (BPs in this study) are higher in the aquatic compartment than their fossil-based counterparts (PP and LDPE here) but all of them have a similar photooxidation rate in the terrestrial compartment.

On the other hand, the EF proposed by Corella-Puertas et al. (2023) for the physical impacts of microplastics in the aquatic compartment (1.07E + 03 PAF·m^3·kg^{-1}) is 6 orders of magnitude higher than the EFs calculated here, i.e. 2.76E-03 for BPs, 7.74E-03 for PP, and 5.61E-03 for LDPE (all expressed in PAF·m^3·kg^{-1}). The reason behind in now the EC10 values collected from the literature, which show that microplastics have a greater effect in the aquatic compartment than in terrestrial one probably due to the floatability of microplastics that makes them more accessible to aquatic species.

The CFs developed in this work on the ecotoxicity of the additives present in the polymers cannot be directly compared with similar factors for the aquatic compartment, as those factors have not yet been established. However, the recent work of MarILCA (Casagrande et al., 2024) has developed ecotoxicity effect factors for plastic additives in the aquatic compartment including two of the additives studied in this work. The effect factors are 1 (dibutyl phthalate) and 3 (bis(2-ethylhexyl) phthalate) orders of magnitude higher than ours (Table 5). This difference may be attributed to the EC10 literature data, which indicate that the potential effect of additives in the aquatic compartment is higher (Omidoyin and Jho, 2024). This is likely because additives in aquatic compartment have a larger surface area in contact with the organisms compared to their interaction in the terrestrial one.

Table 5
Comparison of Effect Factors of additives.

	EF [PAF·m^3·kg^{-1}]	
Additive type	This study	Casagrande et al. (2024)
Triethyl citrate	2.53E + 01	n/a
Dibutyl phthalate	5.42E + 01	2.23E + 02
Bis(2-ethylhexyl) phthalate	9.48E + 00	1.64E + 03

The high mobility and accessibility of microplastics in the aquatic compartment make the difference between CFs for the two compartments consistent. This further emphasizes the necessity of including both compartments in the environmental assessment of mismanaged plastics to avoid overestimating the impacts by focusing solely on one compartment.

The resultant CFs are presented in units of [PAF·m^3·year·kg^{-1}] at the midpoint level, and [PDF·m^2·year·kg^{-1}] at the endpoint level. To integrate these factors with those developed by Corella-Puertas et al. (2023), as recommended by the Global Guidance for Life Cycle Impact Assessment Indicators and Methods (GLAM), it is necessary to convert them into [PAF·year·kg^{-1}]. This is done by multiplying the midpoint CFs by a terrestrial volume, i.e. an area in [m^2] with a height of 0.6 m (0.3 m above and 0.3 m below ground level, the thickness at which are accessible the studied species), and the endpoint CFs by a terrestrial area [m^2] of study.

The EoL impacts of mismanaged plastics can now be assessed using the proposed characterization factors (Fig. 1). For the terrestrial compartment, the CFs developed in this work will be used to evaluate the physical impacts of microplastics on biota and the ecotoxicological impacts of additives. For the aquatic compartment, the CFs proposed by Corella-Puertas et al. (2023) will be applied to assess the physical impacts of microplastics, while those for the ecotoxicological impacts of additives, though not yet fully developed, will soon be available following the effects studies conducted by (Casagrande et al., 2024).

4.3. Future outlooks

Contributions to the photooxidation of BPs are key to understanding the complete picture of the impact of plastic materials on the environment. Besides, it will also be necessary to increase the available data on the ecotoxicological effects of MNPs as well as additives in the terrestrial and aquatic biota. It is estimated that each person could consume 5 g of microplastics per week (Senathirajah et al., 2021), and recent studies have demonstrated that polyethylene terephthalate (PET) microplastics could alter the human intestinal microbiota (Tamargo et al., 2022). So, studying the impacts of plastic and microplastics will be essential in the coming years. Not in our case (terrestrial compartment), but plastics could have more ecotoxicological effects than their additives and the ingestion of microplastics. In the aquatic compartment, they can adsorb organic pollutants present there as polyfluoroalkyl substances (PFAS), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), or heavy metals among others present in the compartment (Barboza et al., 2018; Costigan et al., 2022; Zhao et al., 2023).

Besides, the current level of methodology should be improved to reflect the behaviour of plastics closely to reality. This work has reflected that the photooxidation of plastics (in this case, BPs) never follows a first-order kinetic. Instead, it has at least three main steps, as stated in 3.2. Each stage has a different time and impacts, so it is necessary to integrate Eq. (10) between the times of each of the photooxidation stages to relate each of the stages with its different impacts.

The incorporation of EoL is also key to comparing BPs and fossil-based plastics properly. The environmental performance of BPs depends on the additives used, and only through proper waste management can a better environmental performance be obtained during their EoL.

5. Conclusions

As conclusion, valuable insights are extracted from the discussion carried out: i) the proportions of PHA and PLA in the BPs do not interfere in the developed fate factors; ii) BPs do not necessarily have a better environmental performance than fossil based plastics as can be seen in the CFs developed (Table 3); iii) additives have a high importance in the potential impacts of plastics so it is a must to take them into account; iv) all of the calculated impacts of this work could be avoided if plastic waste were properly managed.

Under this research, it is demonstrated that the incorporation of EoL is key for the proper comparative between BPs and fossil based plastics, the environmental performance of BPs does not have to be better since the additives have a high weight in the potential impacts and only through the proper waste management a better environmental performance of BPS can be obtained during its end of life.

CRediT authorship contribution statement

Brais Vázquez-Vázquez: Writing – original draft, Investigation, Formal analysis, Conceptualization. **Massimo Lazzari:** Writing – review & editing, Validation, Supervision, Conceptualization. **Almudena Hospido:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Brais Vazquez-Vazquez reports financial support was provided by Spanish Government. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary Material 1 (Excel) presents the calculations performed for the characterization factors developed in this work, divided into 7 sheets: 1.01 inventory, 1.02 fate factors, 1.03 accelerated factors, 1.04 and 1.05 effect factors, 1.06 exposure factor, and 1.07 characterization factors. Supplementary Material 2 describes the experimental work and the results obtained from the study of the accelerated photoaging of the plastic biopolymer samples in more detail. Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2025.02.008.

Data availability

Data will be made available on request.

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