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Mesocosm trials reveal the potential toxic risk of degrading bioplastics to marine life

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ABSTRACT

If biodegradable plastics tackle the marine plastic pollution problem sufficiently remains questionable. To gain more insight in degradability, performance, and the impact of degradation on the toxicity, commercial bags made from two biodegradable plastics and one conventional plastic (PE) were exposed for 120 days in a mesocosm featuring benthic, pelagic, and littoral habitat simulations. Degradability was assessed as weight loss, and specimens were tested for toxicity using *Paracentrotus lividus* sea-urchin larvae after different exposure times. Both biodegradable bags showed degradation within 120 days, with the littoral simulation showing the highest and the pelagic simulation the lowest decay. Disregarding habitat, the home-compostable plastic showed higher marine degradation than the industrial-compostable material. The relevant initial toxicity of both biopolymers was lost within 7 days of exposure, pointing towards easily leachable chemical additives as its cause. Interestingly, littoral exposed specimens gained toxicity after 120 days, suggesting UV- induced modifications that increase biopolymer toxicity.

1. Introduction

Plastic pollution is one of the greatest emerging threats to the environment in our time. Plastic can enter marine habitats on different pathways, e.g. as lost material from the fishing and shipping industry as well as migrated from land-based trash (Geyer et al., 2017; Moore et al., 2005; Portman and Brennan, 2017). It is estimated that about 70–80% of the marine debris is plastic (Derraik, 2002; Gacutan et al., 2022; Selvam et al., 2021). Once it has entered the sea, most plastics initially stay afloat (Barnes et al., 2009; Cózar et al., 2014), and are transported by currents and tides (Coyle et al., 2020; Howell et al., 2012) often leading to accumulation zones in ocean subtropical gyres (Law et al., 2014; Lebreton et al., 2018; Moore, 2008; Yamashita and Tanimura, 2007). Biofouling, water logging and swelling can lead to sinking and accumulation on the sea floor (Fazey and Ryan, 2016; Peng et al., 2020; Schlining et al., 2013) In general, the different final marine environmental compartments can lead to different degradation rates (Briassoulis et al., 2019; Sekiguchi et al., 2011a), as degradation is highly influenced by abiotic factors (Ammala et al., 2011), especially UV light (Gewert et al., 2015; Masry et al., 2021; Råby, 1989), and microorganism composition (Oberbeckmann et al., 2014; Sekiguchi et al., 2011b; Shah et al., 2008; de Tender et al., 2015). The combination of biotic and abiotic degradation leads to alternation and fragmentation of plastic and often to the formation of micro- (MP) and nano- plastics (NP) (Lucas et al., 2008). Especially hydrolytic, mechanical and photo(*oxo*) degradation plays a major role in the formation of MPs (Jahnke et al., 2017; Lambert and Wagner, 2016; Song et al., 2017). The threat large and small plastic particles pose to marine life gained more and more attention during recent years (Avio et al., 2017; Balestri et al., 2017; Beiras and Schönemann, 2020; Tanaka et al., 2013) and thus the usage of so called bio- and biodegradable plastic has gained more attention (Andrady, 2011; Emadian et al., 2017; Krzan et al., 2006). However, whether biodegradable plastics are successfully tackling the problem is questionable as studies in laboratory (Bagheri et al., 2017; Tosin et al., 2012; Witt et al., 2001) and field conditions representing different marine zones (Lott et al., 2020, 2021; O'Brine and Thompson, 2010; Volova et al., 2011) showed contrasting outcomes. Today, it remains unclear whether biodegradable formulations are advantageous to reduce marine litter compared to conventional polymers (Napper and Thompson, 2019), and bio labelled plastic is under suspicion for greenwashing commercial strategies (Nazareth et al., 2019; Viera et al., 2021).

On the other hand, polymer degradation processes are suspected to alter the toxicity exhibited by plastic particles (Jahnke et al., 2017;

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Abbreviations

BEN	benthic exposure
BIO1	home compostable bag
BIO2	industrial compostable bag
CRT	classification and regression tree
ISO	International Organization for Standardization
LIT	littoral exposure
LOI	loss on ignition
MP	micro- plastics
NP	nano- plastics
PAR	photosynthetic active radiation
PBAT	poly(butylene adipate-*co*-terephthalate)
PE	polyethylene bag
PEL	pelagic exposure
PLA	polylactide
PVC	Polyvinyl chloride
SET	sea urchin embryo test
T (air)	surrounding air temperature
T(aq)	water temperature inside the mesocosm
T (mar)	marine water temperature
TOC	total organic carbon
TU	toxic unit
ΔLc	control corrected length of *Paracentrotus lividus larvae*

Ouyang et al., 2021), especially those containing functional additives (Barrick et al., 2021). It was shown that toxic effects of plastic leachates are enhanced upon exposure to UV light (Almeda et al., 2016) and weathering (Gewert et al., 2021). Furthermore, NPs potentially produced by fragmentation of plastic objects exhibit a higher toxicological risk. Beiras and Schönemann (2020) showed that the deleterious effects of plastic particles on aquatic organisms increase as particle size decreases. NP and small MP are known to cross biological membranes leading to accumulation in tissues and inducing toxic effects (Bhattacharjee et al., 2014; Della Torre et al., 2014; Gambardella et al., 2013; Pinsino et al., 2017; Stapleton, 2019).

Durability during the operational life of polymeric materials is a desirable property, and multiple techniques and standards have been developed to assess durability of plastics under different laboratory conditions. However, the complexities of the polymer degradation processes limit the predictive value of modelling environmental behaviour on the basis of laboratory tests, and relating accelerated laboratory tests with outdoor service behaviour is difficult (Harrison et al., 2018; White and Turnbull, 1994). To close the gap between laboratory and field scenarios, a mesocosm study in environmentally relevant conditions was conducted with three commercially available plastic bags. One conventional polymer made of polyethylene (PE) and two polymers labelled as biodegradable were exposed to simulated pelagic, benthic, and littoral conditions. Degradability was assessed as weight loss and compared for each marine zone and polymer type. To monitor toxicity during the degradation process, the *Paracentrotus lividus* sea-urchin embryo test (SET) was performed with lixiviates of the new and degraded specimens.

2. Materials and methods

2.1. Test materials

Commercially available plastic bags with similar thickness were purchased from Green Maker China (BIO1), Eco Pac Spain (BIO2), and Pampols Spain (PE). The characteristics of these materials are reflected in table S1.

BIO1 is a green bag made from a polylactide (PLA), poly(butylene adipate-*co*-terephthalate) (PBAT) and maize starch-based polymer and labelled OK compost HOME – TÜV Austria. BIO2 is a translucent-beige t-shirt bag, claiming compostability in industrial conditions (OK compost INDUSTRIAL- TÜV Austria). According to the producer, it is a maize starch-based polymer. PE is a white, low-density polyethylene bag, and it was used as a non-biodegradable negative control in compliance with International Organization for Standardization (2020).

Rectangular (2 × 15 cm) specimens were cut from each bag using a scalpel, avoiding edges and folds (ASTM Standard D3826-18, 2018). Samples (n = 18) were taken before and after 7, 14, 28, 60, 90 and 120 days of exposure in randomized fashion from each tank, rinsed with distilled water, and carefully cleaned with a cotton swamp to remove any biofilm and dirt without damaging the surface (International Organization for Standardization, 2020). Specimens were then left to dry in dark conditions at ambient temperature until constant weight was reached (ASTM Standard D7473M-21, 2021).

2.2. Test system and settings

Degradation of polymers in simulated pelagic (PEL), benthic (BEN) and littoral (LIT) habitats was conducted in the mesocosm facilities of ECIMAT-CIM (University of Vigo, Galicia, Spain), belonging to the European mesocosms network AQUACOSM-plus. PEL and BEN exposures were set up inside 400 l fiberglass tanks (100x100x50 cm; Fiberglass S. A.), whereas 80x40x38 cm plastic boxes were used for LIT treatment. PEL and BEN are flow-through-systems (144 l/h) with passive drainage, using natural 60 μm- filtered seawater from the Ria de Vigo (NW Iberian Peninsula). LIT is a sand system with no seawater, influenced by precipitation and natural humidity and air salt content. Specimens were individually hold in frames made from high pressure PVC pipes and glued with Loctite Super Glue-3 (Henkel Iberica). All materials introduced into the test systems (holding devices, drainage systems) were previously weathered in the mesocosm water system (International Organization for Standardization, 2018). In addition, all system components were flushed with running seawater for at least 5–10 days before starting the experiment.

2.2.1. Pelagic system

The samples were mounted to frames (75 × 75 cm and 45 × 45 cm) consisting of PVC Pipes (Fig. 1). PVC clamps were glued to the sides and one frame of each size introduced in every tank. Total water depth was set to 40 cm. The frames were mounted at a distance of 12 cm from the bottom, leaving at least 11 cm water column above every specimen. The system allows full contact with the surrounding water and exposure to sunlight. Each plastic material was tested in a separate tank.

2.2.2. Benthic system

For BEN exposures (Fig. 1) tanks were filled with 110 l sterile artificial sand (ASTRALPOOL Silica Sand 0.4–0.8 mm), introduced slowly under constant stirring. The tank outflow was covered with a nylon mesh (250 μm). A natural inoculum (ASTM Standard D6691-17, 2017) consisting of 2000 ml solid and 1300 ml liquid phase was introduced into the BEN system to establish microorganism consortium. Inoculum was collected at Vao beach (42°11′49.7″N 8°47′45.2″W) in three places, one close to a sewer containing freshwater at the border between supralittoral and eulittoral zone, one directly on the low tide line, and one close to a rock formation on the south-west end of the beach (low tide line) (Trujillo, 2017). A hole was dug until inflow of water was observed. This pore water was taken and sieved through 20 μm. Solid phase was taken from the same depth as the ground water and particles exceeding 1 mm and all megafauna were removed using metallic sieves. Inoculums from all spots were mixed before introducing them into the

Fig. 1. From left to right: PEL- Samples (beige) are mounted on the PVC test frame, leaving the complete surface area exposed to environmental influences. BEN- Samples (white) are introduced in alterning groups into the system. Three layers of mesh underneath and three layers of mesh on top of the samples secure sample position and contact with the sediment. A frame is used to tighten the mesh. The outflow diameter is extended to 0.196 m^2 surface to prevent clogging. LIT - Four rows of samples are introduced onto the natural beach sand. Samples are mounted to the holding device on one side, allowing movement due to wind.

tanks with low flow applied for 24 h. Sediment height was 11 cm and water level adjusted to 40 cm. Samples were covered with a monofilament nylon net (filament = 0.3 mm, mesh size = 4 cm) to ensure sediment contact (Fig. 1). Each plastic material was tested in a separate tank.

2.2.3. Littoral system

For LIT exposures 120 l boxes were filled to the top with natural beach sand (Fig. 1). For each plastic material two boxes were used. To avoid waterlogging due to rain, two drainage holes were drilled and covered with 250 μm nylon mesh, preventing loss of sand. No water was introduced to the system otherwise. Samples were attached to PVC clamps and introduced in rows to the boxes. The system was covered with two layers of monofilament nylon net (filament = 0.3 mm, mesh size = 4 cm) to prevent access to birds or sample loss due to wind.

Radiation, precipitation, wind speed and direction, air temperature and humidity were measured by the ECIMAT weather station. Dissolved oxygen and pH were weekly measured in the water inside the tanks with an OD LDO10103, a PHC10103 probe and a Hach HQ40d. Water temperature was tracked every 30 min with a SBE 39 (Seabird).

2.3. Chemical analyses and characterization

2.3.1. Water

Measurements of NH_4^+, NO_2^-, NO_3^- and PO_4^{3-} and total organic carbon (TOC) were done by the *Centro de Apoio Científico-Tecnolóxico á Investigación* (C.A.C.T.I) with a continuous- flow analyzer (AutoAnalyzer AA3 Bran+Luebbe) and a high-performance TOC analyzer (Analytik Jena multi N/C 3100®). Samples were stored in amber glass bottles on dry ice until processing.

2.3.2. Sediment

The solid inoculum as well as sediment from the benthic simulations were screened for hydrocarbon content and analysed for NH_4^+, NO_2^-, NO_3^- and PO_4^{3-}. Tank sediment was taken as columns (d = 2 cm) and frozen at −80 °C. Freeze drying was performed with a Telstar LyoAlfa6. For hydrocarbon analyses, 15 g of the dry matter was extracted with Hexane:Acetone (1:1) in FOSS Soxtec ST 243 and GC–MS analyses used an Agilent GC 7820A-Agilent 5975 MSD. For nutrient analyses, sediment samples and a 1 mol/l potassium chloride solution (1:10) was stirred for one hour and afterwards centrifuged. Thereafter, the extracted was analysed with continuous- flow analyzer (AutoAnalyzer AA3 Bran+Luebbe) (International Organization for Standardization, 2005).

Organic content of the solid inoculum and the sediment at day 8 was estimated with loss on ignition (LOI) with 30 g dry sediment at 450 °C for 2.5 h.

Particle size distribution of the sediments used in the BEN and LIT exposures was analysed by using a CISA BA 200 N using 1000 μm, 500 μm, 250 μm, 150 μm, 63 μm and 20 μm stainless steel sieves. Shaking time was set to 10 min with an amplitude of 2 mm.

2.3.3. Weight

Weight of the plastic specimens was measured with a Sartorius LE225D balance with a 0.00001 g precision, and weight loss calculated by the difference of means of n = 40 specimens (for t_0), or n = 18 otherwise, respect to $t = 0$ was used as endpoint.

Eq. (1) calculation of control corrected weight, used for statistical analyses. t_i refers to the measured weight at the point in time, while t_0 refers to the original weight of the sample.

$$\Delta\text{weight} = \frac{weight\ t_i}{mean\ weight\ t_0} \tag{1}$$

2.4. Toxicity assays

The SET using *P. lividus* was conducted as described in Beiras et al. tier I (Beiras et al., 2019). Eight samples were grinded with dry ice to 250 μm (Retsch Ultra Centrifugal Mill ZM 200) and dried for 24 h at 20 °C in dark conditions. One g/l lixiviates were obtained in 50 ml glass bottles (Lorenzo et al., 2002) by stirring the plastic powder in artificial sea water in an overhead rotator at 1 rpm for 24 h in the dark. Lixiviate is filtered through glass microfiber filters (Whatman®, Grade GF/F 0.7 μm) and tested after x1 (undiluted), x1/3, x1/10 and x1/30 dilutions in FSW. Sea-urchins were provided by the ECIMAT stock, originally collected from natural habitats in the Ria de Vigo (NW Iberian Peninsula). Size recordings were done with Leica analysis software LAS V4.12 and a Leica DMI 4000 B microscope with a 2.5× objective for larvae and a 5.0× objective for the eggs. Size increase, calculated as mean (n = 35) maximum dimension minus mean egg size at $t = 0$, was used as endpoint (Beiras et al., 2012).

2.5. Statistical analyses

All statistical analyses were done with IMB SPSS Statistics 25.

Normal distribution of data was verified with the Shapiro-Wilk test, and homogeneity of variance with the Levene's test. If normally distributed, a one factor ANOVA was conducted to compare the means. For toxicity data, treatments significantly different from the control were identified by using the Dunnett's *t*-test if variances were homogeneous, and T3 test otherwise. If data were not normally distributed Mann-Whitney-*U* test was performed. For plastic specimen weight data, Bonferroni post hoc test was used to identify significant degradation.

EC50 values were calculated by fitting the data of the control corrected lengths (ΔLc) to Probit dose-response models. Toxic units (TU) were derived as TU = 1/EC50 (Beiras et al., 2012) and used for comparisons between experiments. In addition, Pearson correlations between time and ΔLc were conducted. The day 0 corrected weight was calculated for all data, to achieve comparability between plastic species (Eq. (1)). Decision tree classifications using a classification and regression tree (CRT) were conducted to find homogeneous groups inside the data. Homogenous groups was thereby calculated by the least-squared deviation of the variance and validated with cross validation (10 folds) (Krzywinski and Altman, 2017; Loh, 2011). Groups were afterwards confirmed on significance using a three factor ANOVA, including plastic type, time, and environment. If significant differences between groups was confirmed, data was reduced stepwise by removing homogeneous groups from the analysis until main drivers for heterogeneity were found.

3. Results

3.1. Test system

Biofouling was observed in both BEN and PEL tanks. By visual estimation, the degree and type of algae growth was similar in all tanks. No clogging was experienced, and turbulence was minimal. Detachment from the clips was only occasionally seen in the PEL treatment, and detached specimens were removed from the tank and not analysed. In the LIT treatment samples were frequently observed to experience mechanical stress caused by the wind.

3.2. Water

The average water temperature in the mesocosm (T(aq)) was 17.8 °C with an average temperature range of 5.5 °C between day and night throughout the experimental period. The highest total temperature range was 9.7 °C (08/07/2021). The temperature of the natural water in the sea showed a similar average temperature (17 °C), following a seasonal trend, with increasing mean values from April to July–August. Air temperature and UV radiation seasonally increased towards August also (Fig. 2, S2–S4). The nutrient analyses of the mesocosm water revealed remarkably higher concentrations of ammonia and nitrate at day 11 for the BIO1-BEN, at day 91 for BIO1-PEL and BIO2-BEN. Tanks containing PE showed levels similar to the concentrations measured in the inflowing water, except for the PE-BEN at day 120, where high nitrate concentrations were measured (S5). Interestingly, in both biodegradable bags, additives containing an amide group were confirmed (not published).

3.3. Sediment

The analysis of the grain size of the sediment used in the BEN exposure resulted in a phi of 0.33, coarse sand with very low silt content (Wentworth, 1922), as commonly found in Ria de Vigo (NW Iberian Peninsula) (Garcia-Garcia et al., 2004).

Initially the artificial sand was of sterile nature and organic matter was only present in the natural inoculum. 8 days into the experiment organic content in the tanks had enriched to 3.7%, showing already a similar value as the natural sand used as solid inoculum: 4.7%. The nutrient development in the tank sediment also reached levels of nitrogen and phosphorus close to levels measured in the solid inoculum (S6).

The analyses of hydrocarbons in the solid inoculum and tank sediments after 8 days showed levels well below established threshold effect levels (Macdonald et al., 1996) (S8). Furthermore, no enrichment of hydrocarbons was observed after 120 days of experimental period, indicating no leaching from mesocosm components into the system (S8).

3.4. Plastic degradation

By visual and tactile evaluation both biodegradable bags showed surface alternations and lost colour in all three simulated environments after 120 days. Thereby BIO1 showed the greatest alterations in all environments followed by BIO2. The highest decay was seen in LIT conditions, which led to increased brittleness and fragmentation of all the specimens, including the PE also (Fig. 3). However, PE did not show any weight decrease over time, whereas the biodegradable labelled bags showed a significant weight loss ranging from 4.4% to 20% (Fig. 4). The

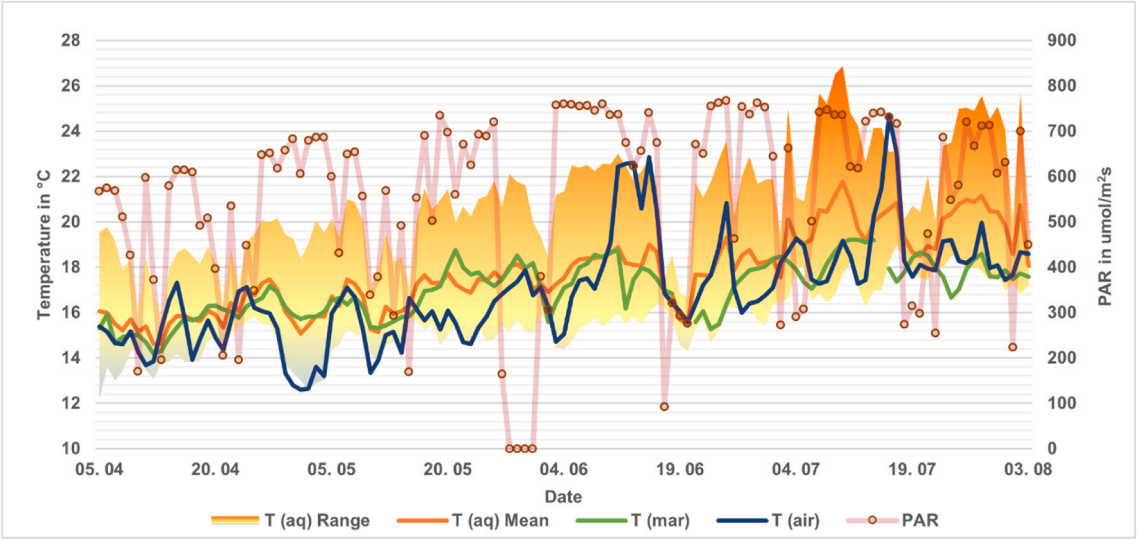

Fig. 2. Temperature and photosynthetic active radiation measured in the mesocosm facility. T(aq)- water temperature inside the mesocosm, PAR- photosynthetic active radiation, T (mar)- marine water temperature, T (air)- surrounding air temperature.

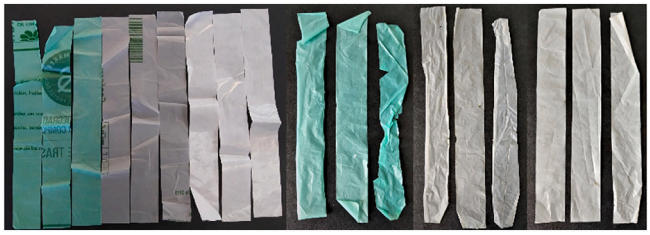

Fig. 3. Specimens of biodegradable (BIO1, green; BIO2, beige) and PE bags at day 0 (left) and after 120 days of degradation (right). For each bag from left to right: BEN, PEL, LIT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

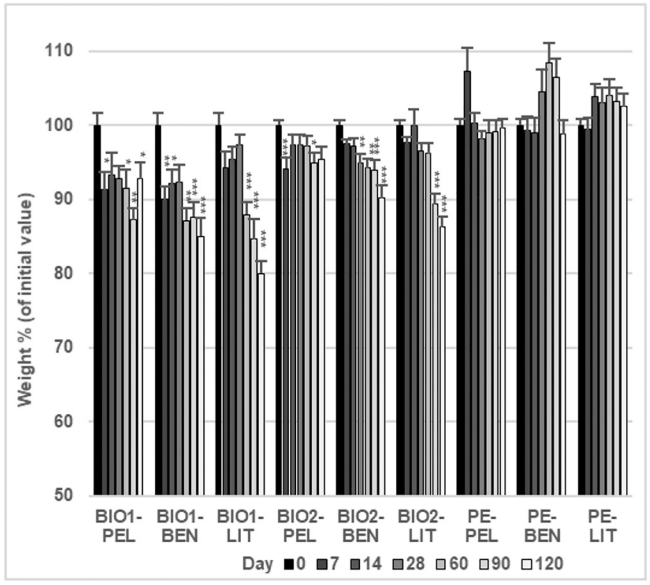

Fig. 4. The graph shows the weight loss over time. Significantly reduced weights compared to day 0 are marked with Asterisks ($p < 0.05$*, $p < 0.01$**, $p < 0.001$***). The error bars indicate the standard error.

highest weight loss after 120 days was measured for BIO1, the home compostable bag, in LIT (20%) followed by BIO1 in BEN (15%). In PEL conditions a weight loss of 7% after 120 days was observed. Weight loss was also observed in the industrial compostable bag, BIO2, which lost 4.4% in pelagic conditions, 10% in benthic conditions and 13.8% in littoral conditions after 120 days (Fig. 4).

CRT's revealed a clear separation of PE from BIO1 and BIO2 as the most important grouping factor, followed by the influence of time, which was confirmed by a three factor ANOVA (S10 & S11). Bonferroni post hoc test identified a significant difference between all types of plastic (S11). Further analyses of PE did neither reveal significant differences between environments nor time related influence on the negative control (S12). Following CRT analysis featuring only BIO1 and BIO2, a growing influence of the marine habitat on the degradation in later stages of the experiment was revealed, which was confirmed with a three factor ANOVA (S13 & S14). Finally, correlation analysis showed that the weight of BIO1 and BIO2 specimens significantly decreased with time in all scenarios, with the highest negative correlations visible for LIT (BIO1-PEL: $r = -0.251$, $p = 0.002$; BIO1-BEN: $r = -0.428$, $p < 0.0001$; BIO1-LIT: $r = -0.768$, $p < 0.0001$; BIO2-PEL: $r = -0.199$, $p = 0.015$; BIO2-BEN: $r = -0.521$; $p < 0.0001$; BIO2-LIT: $r = -0.636$, $p < 0.0001$).

3.5. Toxicity

According to SET results (Fig. 5), BIO1 (TU = 2.65) and BIO2 (TU = 2.37) showed relevant initial toxicity, while PE did not show adverse effects (TU < 1). For both biodegradable bags toxicity was lost within 7 days. In PEL and BEN no further changes of toxicity were observed within the 120 days exposure time (S4). In contrast, in LIT increasing toxicity was observed from day 60 (BIO1 TU = 1.13; BIO2 TU = 1.12) towards day 120 (BIO1 TU = 3.96; BIO2 TU = 1.43). For both plastics strong negative correlations between day 7 and day 120 according to Pearson in LIT conditions (using the control corrected size ΔLc) were found (BIO1: −0.943, $p < 0.0001$, $r^2 = 0.889$; BIO2: −0.943, $p < 0.0001$, $r^2 = 0.898$).

4. Discussion

4.1. Test system

Previous efforts to assess plastic degradation in marine conditions frequently used exposure periods of approximately 1 year (Bagheri et al., 2017; Briassoulis et al., 2019; Campani et al., 2020; Deroiné et al., 2014a, 2014b; Lott et al., 2020; Weinstein et al., 2020). The mesocosm test system here designed to simulate different marine habitats was stable throughout the 120 days of exposure, and this period proved to be sufficient to discriminate the environmental performance among the materials tested. Conditions in the tanks were similar to natural conditions recorded in the sea except for a wider fluctuation in water temperature between night and day in the PEL and BEN tanks, due to the relatively low flow applied to the system. Furthermore, steady concentration of nutrients and organic content were seen in the inoculated artificial sediment within the first 8 days of exposure, indicating a natural behaviour of the sediment. Thus, inoculating artificial sediments with natural solid sediment and sediment pore water seems to have provided a successful method of establishing environmental microorganism populations (Thellen et al., 2008). High environmental realism offers a great supplement to more regulated laboratory studies with the same materials. A combination of laboratory studies with semi-field conditions could give meaningful insight in the degradation/biodegradation ratio experienced.

4.2. Plastic degradation

Classification and regression trees could show a separation in the degradation behaviour of conventional and bioplastics and for different marine habitats. Significant differences between the two biodegradable bags tested were observed and could be identified predominantly in the later stages of the experiment (S10). Thus, degradation of the plastic bags tested was strongly influenced by the bag composition and to a lesser extent by the simulated habitat (non-significant). Biodegradable bags showed significantly higher degradation than the conventional PE bag, showing 10 to 20% weight loss in 120 days. The home compostable bag, BIO1, showed the highest degradation in all three habitats, followed by the industrial compostable, BIO2. O'Brine and Thompson (2010) reported degradation of compostable bags in the sea after 112 days, whereas conventional or oxo-degradable PE bags did not degrade after the whole (280 days) exposure period. Volova et al. (2011) could show degradation of bioplastics in field exposures within 160 days, but did not detect significant differences between different bioplastics.

Concerning habitats, the aerial exposure, LIT, enhanced degradation rates compared to underwater exposures. Abiotic factors such as UV and mechanical stress greatly affect plastic degradation (Briassoulis, 2005; Gewert et al., 2015; Rånby, 1989; White and Turnbull, 1994). Those factors were predominantly featured in the LIT scenario. Napper and Thompson (2019) also found faster degradation in aerial compared to aquatic exposures, and associated this finding with greater levels of UV radiation and oxygen. Regarding the subaquatic habitats, a trend

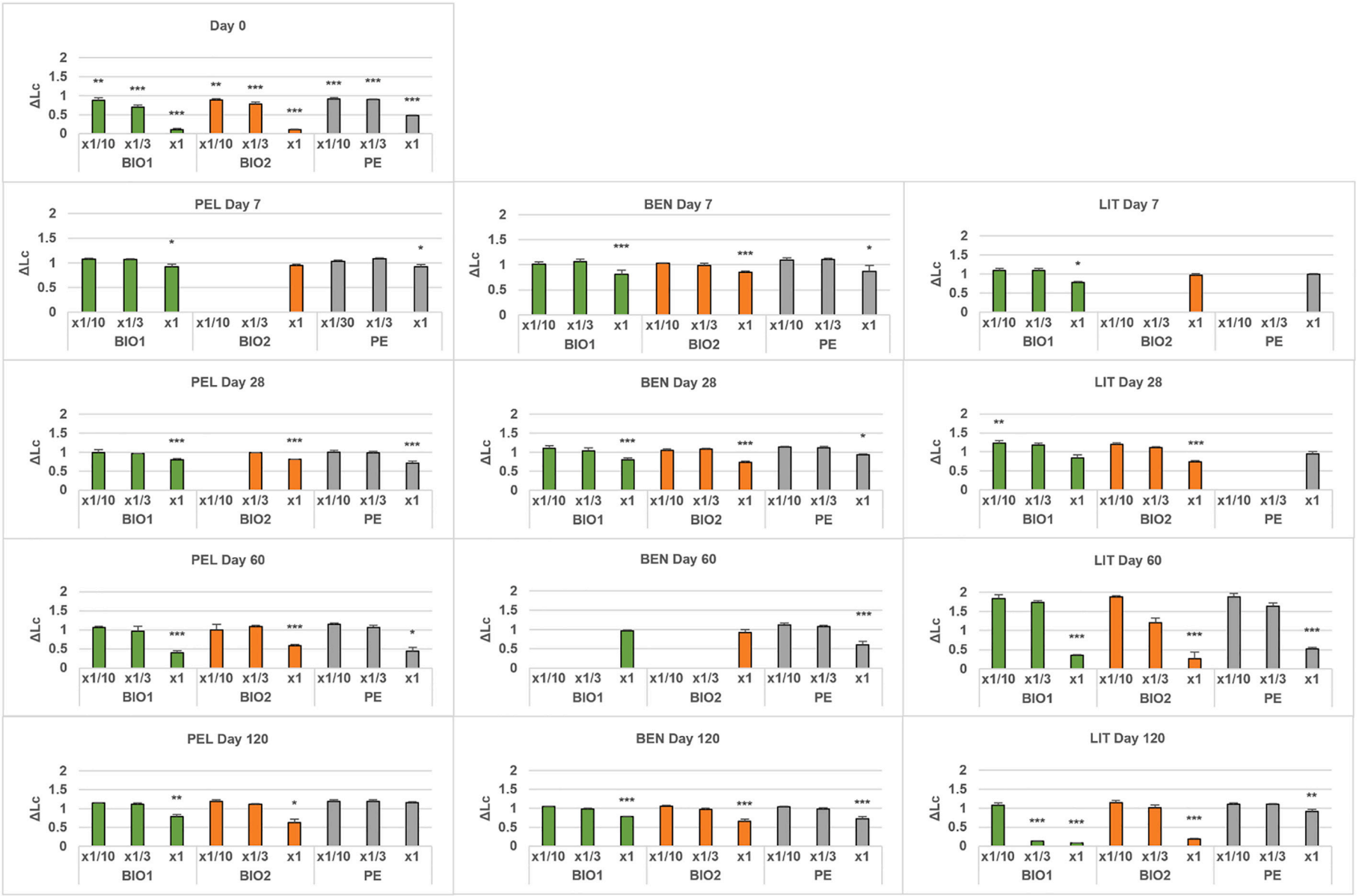

Fig. 5. P. lividus control corrected larval size increase (ΔLc) in serial dilutions (x1/10, x1/3, x1/1) of 1 g/l lixiviates of undegraded (day 0) and degraded (day 7, 28, 60 and 120) polymers (BIO1, BIO2, PE) in different exposures (PEL, BEN, LIT). Asterisks refer to significant differences from the control. *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$. Bars indicate the standard deviation ($n = 4$).
BEN- benthic; PEL- pelagic; LIT- littoral, BIO1- green; BIO2- orange; PE- grey.

towards higher degradation in the BEN compared to the PEL scenario was observed, although differences did not reach statistical significance. Potential differences between the PEL and BEN scenarios are most likely induced by microorganism composition (Oberbeckmann et al., 2014), as the abiotic factors above mentioned are expected to be very similar. Higher degradation of plastics in contact with sediments compared to water-column exposures are in line with previous studies (Beltrán-Sanahuja et al., 2020; Lott et al., 2020, 2021; Tosin et al., 2012). Further research describing the different consortia of microorganisms grown on the plastic may contribute to better explain the differences found between sediment contact and water column. Even though no polymer reached full disintegration within 120 days, the ranking of degradation roughly follows the biodegradability labelling of the bags. The home compostable bag experienced the greatest material loss, followed by the industrial compostable bag, whereas the non-degradable PE bag showed the lowest decay.

4.3. Exposure to UV light induces toxicity in the biopolymers

In contrast to PE, BIO1 and BIO2 pre-exposed materials showed relevant toxicity to sea-urchin embryos, most likely due to the presence of chemical additives in the polymers (Beiras et al., 2018, 2019, 2021; Cormier et al., 2021; Oliviero et al., 2019). Supporting this, toxicity was lost in all simulations within 7 days of exposition, in line with rapid leaching of additives, not covalently bond to polymeric chains, in aquatic environments (Barrick et al., 2021; Hansen et al., 2014). Simultaneously increasing levels of nitrogen were measured in the tanks featuring biopolymers, which could result from degradation of additives with amine groups, such as oleamide (Eyerer et al., 2005; Farrell and Merkler, 2008; McDonald et al., 2008; Pajares and Ramos, 2019). Interestingly, after 90 days in the LIT simulation the toxicity of the bioplastics rose again. Main driver of the toxicity development could be either transformation products and the formation of small sized particles (NPs) (Gewert et al., 2018), or a higher degree of degradation leading to the availability of previously non-available particles (Town and van Leeuwen, 2020). We conclude the key factor for the increased toxicity to be UV light, as the formation of toxic metabolites upon UV was described before (Bejgarn et al., 2015; Gewert et al., 2021; Jahnke et al., 2017; Ouyang et al., 2021; Rummel et al., 2022). In addition, degradation of polymers might produce nano sized particles, which may play an important role in the toxicity found in the biodegradable bags at advanced stages of weathering (González-Pleiter et al., 2019).

5. Conclusions

Biodegradability tests in environmentally relevant conditions are highly needed to gain a better understanding of the polymer degradation in the open nature. This study presents the first open, flow-through mesocosm study investigating the degradation of two biodegradable plastic bags in comparison to a conventional PE bag in three different marine zones simultaneously. Disregarding habitat, the bag labelled as home compostable showed enhanced degradation compared to the bag labelled as industrial compostable. Thereby, the test system proved good performance and was capable to clearly discriminate the environmental performance of the three tested materials in 120 days, a period markedly shorter than previous efforts. The use of a standard artificial sediment with natural inoculum provided semi-controlled benthic conditions and enables the system to be implemented in climatically different regions for comparative studies. In addition, this study confirmed different degradation speeds in different marine zones. LIT exposed samples showed the highest degradation, most likely to be caused by photodegradation and erosion, followed by the BEN and PEL simulation. Ecotoxicological analyses of plastic in different stages of degradation were successfully integrated in the trial and a time related toxicity increase was demonstrated, indicating a correlation between degradation progress and toxicity. These findings strongly call for integrated toxicity assessments in degradability trials of plastics, especially bioplastics.

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CRediT authorship contribution statement

Jakob Quade: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing, Visualization. **Sara López-Ibáñez:** Conceptualization, Investigation. **Ricardo Beiras:** Conceptualization, Funding acquisition, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.113673.

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