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Adsorption of pesticides and personal care products on pristine and weathered microplastics in the marine environment. Comparison between bio-based and conventional plastics

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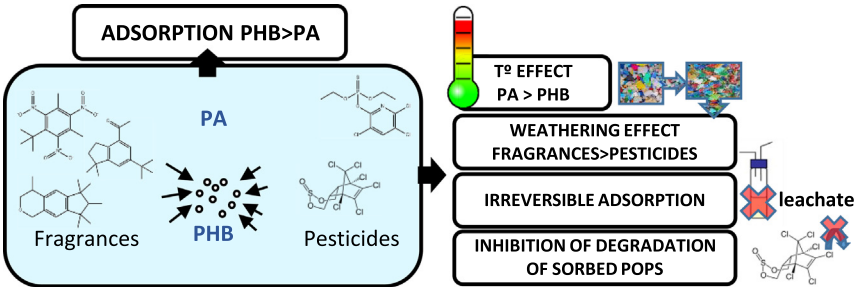
HIGHLIGHTS

- Lower sorption of environmental pollutants to PA than to PHB.
- POPs sorption capacity of PA more affected by water temperature than PHB
- Adsorption irreversible: capacity of PA and PHB to accumulate these contaminants.
- Microplastics can inhibit the degradation of sorbed POPs increasing their lifetime.
- Quality controls and verification of analytical processes provide reliable results.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrophobicity of persistent organic pollutants (POPs) makes them adsorb on microplastics in the marine environment, affecting their distribution, persistence, or their transfer to the trophic chain. Fragrances and non-polar pesticides can be adsorbed by microplastics in the marine environment because of their physico-chemical characteristics.

In this work, the adsorption of two pesticides (α-endosulfan and chlorpyrifos) and 6 musk fragrances (musk xylene, musk ketone, musk moskene, galaxolide, tonalide, and celestolide) on polyamide (PA6) (a petroleum based polymer) and on polyhydroxybutyrate (PHB) (biopolymer) in seawater was studied, considering also the effect of water temperature and plastic weathering.

Results show higher adsorption of the selected pollutants for PHB than PA, being PA more affected by the water temperature and the plastic weathering. The highest percentage of adsorption was achieved in most cases at 24 h. In addition, this process was irreversible, as it showed the leaching assays. Besides, this work revealed that plastics mitigate the degradation of α-endosulfan in aquatic media (hydrolysis), showing that plastics can act as inhibitors of degradation of POPs, increasing its persistence in the environment.

1. Introduction

In the last decade, the presence of plastics and microplastics (MPs) in the marine environment gained interest, due to their ubiquitous presence and persistence in aquatic environments. According to ISO definition, MPs are any solid plastic particle insoluble in water with any dimension between 1 μm and 1000 μm (ISO, 2020) and come from a variety of sources, including fisheries, products and textiles (use and breakdown), agriculture, industry, waste, litter and others (SAPEA, 2019). Plastics and microplastics can cause adverse effects on marine organisms (Chae and An, 2017) due to the liberation of hazardous additives or components of the polymers (Avio et al., 2015; Bejgarn et al., 2015; Hermabessiere et al., 2017), or by leaching

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of hydrophobic contaminants adsorbed and concentrated onto the plastic surface (Bakir et al., 2012; Devriese et al., 2017; Leon et al., 2018). The nature of microplastics, especially their hydrophobicity, and large surface area provide these materials a high adsorption potential and the ability to affect the fate of other contaminants in the environment (Puckowski et al., 2021). This is particularly relevant in aquatic environments, where the amounts of environmental organic contaminants accumulated on the plastic surface can be several orders of magnitude higher than that in the surrounding waters (Atugoda et al., 2021).

Microplastics are well known as vectors for hydrophobic organic contaminants (Bakir et al., 2014; Chen et al., 2018; González-Pleiter et al., 2020; Leon et al., 2018), and there are growing concerns regarding their potential adverse effects on ecosystems and human health (Atugoda et al., 2021).

The adsorption of organic compounds on microplastics depends on the physico-chemical characteristics of the polymer, the characteristics of the organic compounds and also environmental factors (Mei et al., 2020).

Regarding the microplastic characteristics, the degree of crystallinity has a major influence on the hardness, density, transparency, and diffusion properties of plastics (Mei et al., 2020). Sorption generally occurs in the amorphous (not crystalline) plastics or amorphous regions of plastics. The amorphous areas can be "glassy" or "rubbery" depending on the temperature, above or below glass transition temperature (Tg) of the polymer, respectively. A glassy polymer has a smaller diffusivity of organic compounds than a rubbery polymer (Teuten et al., 2009). In addition, hydrophobicity and functional groups of MPs can affect the sorption behavior of chemicals (Tourinho et al., 2019).

The characteristics of the organic compounds, like hydrophobicity and ionic properties, affect their sorption behavior on MPs. Substances with a high hydrophobicity (log K_{ow} > 4) tend to adsorb on organic matter and also to plastics, showing a positive correlation between sorption capacity and log K_{ow} (Li et al., 2018).

The sorption of the most common hydrophobic organic contaminants to plastics has already been studied: PAHs (Bakir et al., 2012; Liu et al., 2016; Zhao et al., 2020), PCBs (Velzeboer et al., 2014; Zhan et al., 2016), PBDEs (Chua et al., 2014) and pesticides (Bakir et al., 2012; Seidensticker et al., 2018). The most tested plastic was polyethylene which together with polypropylene is the most abundant plastic in the world (Beckman, 2018). Some studies tested also PVC, PS and PP (Rodrigues et al., 2019).

The polymers studied in this work were polyamide 6 (PA6) and polyhydroxybutirate (PHB) due to the lack of knowledge on the interaction of environmental contaminants with them. PA, a petroleum based polymer, has been scarcely studied up to now in the marine environment (Hüffer and Hofman, 2016), despite being used in fishery material and released by textiles, and so, reaching easily the marine environment. Thus, PA6 was selected because of its widespread presence in the marine environment (GESAMP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, 2016; Hu et al., 2022; Mistri et al., 2020; Taha et al., 2021; Thompson et al., 2004) representing about 44.7 % of polymers in the marine environment (Mistri et al., 2020), and also because its physico-chemical characteristics and its physico-chemical characteristics. PHB is a poly(hydroxyalkanoate) (PHA), a biodegradable biopolymer produced by microorganisms, first discovered by Lemoigne in 1925 (Tang et al., 2014). It is currently proposed as an alternative to petrochemically derived plastic, in the context of the European Plastic Strategy on Circular Economy (European-Commission, 2018). The importance of considering biodegradable PHB in this study is that the leaching of plastic additives or adsorbed environmental contaminants could be increased by its faster degradation in the environment.

The persistent organic pollutants (POPs) selected to perform the sorption studies were: α-endosulfan, chlorpyrifos, musk xylene, musk ketone, musk moskene, galaxolide, tonalide, and celestolide. α-endosulfan is an organochlorine pesticide (OCP), considered as an endocrine disruptor and very toxic for aquatic life according to the European Chemicals Agency (ECHA) and its use was banned since 2013. α-endosulfan is a ubiquitous contaminant, and has been detected in a variety of environmental media worldwide (Luek et al., 2017; Zhang et al., 2003), even in snow and at surface marine waters of the Arctic Oceans (Weber et al., 2010). Chlorpyrifos is a widely used organophosphorus pesticide (OPP) very toxic for aquatic life according ECHA. Chlorpyrifos has been detected in seawater samples from Bohai and Yellow seas (Zhong et al., 2013), in seawater from California area (Bondarenko et al., 2004) and at Mar Menor (Moreno-González et al., 2013), among other locations.

Regarding fragrances, 3 nitromusks (musk xylene, musk ketone and musk moskene) and 3 polycyclic musks (galaxolide, tonalide, and celestolide) were selected, taking into account their persistence and toxicity for aquatic life (according ECHA), being musk xylene banned in the European Union since 2011 (European_Commission, 2011). Musk fragrances have been detected in all kinds of water samples and, in particular, in the marine environment (Ehiguese et al., 2020; Lee et al., 2010; Nakata et al., 2007; Sumner et al., 2010). In particular, musk galaxolide is considered as a ubiquitous contaminant, and has been detected in many water samples (Celeiro et al., 2019; Montes-Grajales et al., 2017).

Among the environmental factors that may influence the sorption of contaminants to MPs in this work we focused on the effect of seawater temperature and plastic weathering. A modification in the water temperature not only affects the amorphous areas of the plastics (as it was mentioned before) but it also changes the surface tension and solubility, among others. For these reasons, temperature is an important factor to take into account in plastic sorption studies. Weathering of plastics causes physical and chemical changes and therefore may have an effect on sorption. Some changes undergone by plastics during weathering are crystallinity changes, chemical bond breakages in the polymer matrix, increasing surface area and pore size, that are determinant in the pollutant sorption capacity (Jiménez-Skrzypek et al., 2021), whereas oxidation can decrease their affinity for hydrophobic organic contaminants (Hartman et al., 2017) due to the increase on polar functional groups (Fernández-González et al., 2021).

This work studies the adsorption of 2 pesticides (α-endosulfan and chlorpyrifos) and 6 musk fragrances (personal care products, PCPs) on microplastics (PA6 and PHB) in seawater. As far as we know, this is the first study testing the sorption of organic hydrophobic compounds to PHB bio-derived and biodegradable plastic in the marine environment.

2. Experimental

2.1. Plastic materials and target contaminants

Plastics selected to perform the study were PA6 and PHB. PA is typically used in the fabrication of fishing nets and very abundant in the marine environment. PHB is bio-derived biodegradable plastic (Fig. S1). PA is a polar polymer, whereas PHB is partially polar (Atugoda et al., 2021).

Pristine microplastics were manufactured and supplied by AIMPLAS (Plastics Technology Centre, Valencia Spain), and were prepared avoiding the use of additives as far as possible, in order to minimize the influence of the plastic additives on the sorption studies. These microplastics were analyzed prior to the adsorption assays to verify the absence of the target fragrances and pesticides.

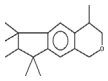
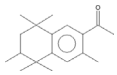
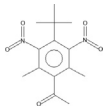
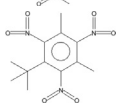
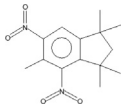
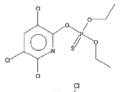
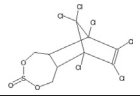
The MPs size range was characterized by a laser granulometer. It showed maximum incremental volume percentages around 250 μm for PA6, whereas for PHB all particles were between 1 and 100 μm. The PHB sample was sieved through 63 μm, to reduce its size range, and make sample handling easier, ensuring the recovery of all the particles during the analytical process.

The selection of the target compounds was achieved by taking into account their solubility in water, their octanol-water partition coefficient (Kow) (provides an estimation about the ratio of concentrations of a chemical between the plastic and the water), and their environmental concern. Some properties of the target compounds are shown in Table 1.

2.2. Materials, reagents and equipment

Individual standards of α-endosulfan (100 μg ml^{-1} in hexane), and neat chlorpyrifos, both PESTANAL®, were supplied by Merck (Darmstadt,

Table 1
Physico-chemical properties of the selected contaminants.

Compound	Structure	Abbrev.	Solubility (W)* mg l^{-1}	Log Kow*	Family	Toxicity (ECHA)
Galaxolide		HHCB	1.75	5.90	Fragrance Polycyclic musk	Very toxic for aquatic life
Tonalide		AHTN	1.25	5.70	Fragrance Polycyclic musk	Very toxic for aquatic life
Celestolide		ADBI	1.15	5.93	Fragrance Polycyclic musk	Very toxic for aquatic life
Musk ketone		MK	0.39	4.30	Fragrance Nitro musk	Very toxic for aquatic life. Suspected carcinogenic.
Musk xylene		MX	0.47	4.40	Fragrance Nitro musk	Very toxic for aquatic life. Suspected carcinogenic. Banned since 2011 in EU.
Musk moskene		MM	0.05	5.30	Fragrance Nitro musk	
Chlorpyrifos		Cp	1.40	4.96	Insecticide OPP	Very toxic for aquaculture and bees.
α-Endosulfan		αES	0.53	3.83	Pesticide OCP	Banned since 2013, but still detected in samples.

* Data obtained from Pubchem. A data from (Ospar, 2004).

Germany). The pesticides working solution (1 μg ml^{-1}) was prepared in methanol (Super Purity Solvent, Romil, Cambridge, GB), and calibration standards were prepared by dilution with hexane (Suprasolv, Merck) (6 calibration points between 2.5 and 80 ng ml^{-1}). A multicompound stock standard solution of musks Celestolide (ADBI), Galaxolide (HHCB), Tonalide (AHTN), Musk xylene (MX), Musk moskene (MM) and Musk ketone (MK) containing 1000 μg ml^{-1}, and also deuterated Tonalide-d_3 (AHTN-d_3, 100 μg ml^{-1}) and Musk xylene-d_{15} (MX-d_{15}, 100 μg ml^{-1}) in acetone were purchased from Techno Spec (Barcelona, Spain). Working solutions of fragrances (1 μg ml^{-1}) and AHTN-d_3 and MX-d_{15} (0.1 μg ml^{-1}) were prepared in methanol. Standard solutions were prepared daily in ethyl acetate (PanReac Darmstadt, Germany). All stock solutions were stored at dark at −4 °C.

The sodium chloride used to enhance the extraction of the fragrances, and the anhydrous sodium sulfate were supplied by Merck.

Synthetic seawater was prepared using ultrapure water (Direct-Q 3UV Millipore system, Millipore, Bedfore, MA, USA) and a sea salts mixture from Sigma-Aldrich (Merck KGaA, Darmstadt, Alemania) (composition in Table S1), salt concentration of 35 %.

Filters used in the filtration experiment were 0.45 μm cellulose filter from Millipore, 0.6 μm glass fibre filter MN-GF-6 (Macherey Nagel, Düren, Germany), 2.2 μm QM-A quartz fibre filter (Whatman International Ltd., England), GNWP nylon filter from Millipore, FM 200 steel filters from Filter Lab (Barcelona, Spain), and Teflon frit in glass reaction tube from Supelco (Bellefonte, USA).

Sep-pack C_{18} cartridges (1 g) from Supelco, and PTFE 0.45 μm syringe filters from Olimpeak™ Teknokroma (Barcelona, Spain) were used for sample treatment.

A Micromeritics Saturn DigiSizer II 5205 V1.04 laser granulometer (Micromeritics Instrument Corporation), was used. A JEOL JSM 6400 scanning electron microscopy (Leol, Tokyo, Japan) and a 400 FT-IR/FT-NIR Perkin Elmer Spectrometer (Perkin Elmer, Norwalk, CT, USA) equipped with a horizontal one-bounce diamond crystal (Miracle ATR, Pike) were used to study the effect of weathering on the polymers. An IKA® KS 260 (IKA, Staufen, Germany) compact flat orbital shaker was used for agitation during the adsorption studies.

For the microplastics extraction, a Vibrax-VXR IKA agitation plate was used.

A Trace GC chromatograph coupled to a triple quadrupole mass spectrometer (TSQ Quantum XLS) and equipped with a Triplus autosampler and PTV injector, all Thermo-Finnigan (Waltham, MA, USA), were used for fragrances determination. An Autosystem XL gas chromatograph with an ECD detector (Perkin Elmer, Norwalk, CT, USA) was used for pesticide determination. ASE® 200 (Dionex Corporation, CA, USA) was used for the leaching study.

2.3. Chemical analysis

Seawater samples were filtered for the separation of microplastics. In the case of fragrances FM 20 steel filters, with 20 μm pore size (Filter lab, Barcelona, Spain) were used to perform the filtration by gravity, whereas a glass syringe with a 20 μm Teflon frit was used (vacuum) in the case of pesticides, in order to reduce losses. The filtration step was studied in this work.

Pesticides were extracted from seawater using vortex assisted liquid-liquid microextraction (VALLME), with 500 μl of hexane and determined by PTV-GC-ECD. Experimental recoveries were 100 % for chlorpyrifos and 105 % for α-endosulfan, with good precision (RSD < 15 %). Extraction of pesticides from microplastics plastics was performed by Ultrasound assisted extraction (UAE) using 2 ∗ 10 ml of hexane, and clean up with Sep-pack C_{18} cartridges (1 g). Anhydrous sodium sulfate was added to the MPs before their extraction in order to remove moisture. The eluate was concentrated in a rotary evaporator, and subsequently dried in a stream of N_2. Finally, the residue was re-dissolved into 0.5 ml with hexane and measured by PTV-GC-ECD. Recoveries obtained when optimizing this method were between 82 and 120 %, except for chlorpyrifos in PHB (63 %).

Fragrances from seawater samples (spiked with 10 μl of the deuterated standards working solution as surrogate standards) were extracted also by

VALLME in an agitation plate with 1.5 ml of ethyl acetate. 0.5 g of sodium chloride were added to improve the extraction efficiency. Recovery percentages of this method are between 76 and 100 %, with good precision (RSD < 10 %). UAE was used for the extraction of fragrances from microplastics, 2 × 10 min with 2 × 5 ml of ethyl acetate, followed by filtration through 0.45 μm PTFE syringe filters. Chromatographic determination was carried out by GC-QqQ-MS/MS. Overall recoveries calculated for this method are between 103 and 130 % (RSD < 10 %).

The leaching study of pesticides and fragrances from microplastics to seawater was performed by pressurized solvent extraction using an ASE® 200 equipment to accelerate the process. Microplastics with the target compounds sorbed on them (96 h contact plastic) were introduced into the stainless steel ASE cell (11 ml). Then, it was extracted at ambient temperature during 10 min of static extraction time, using synthetic seawater as extracting agent. Afterwards, the aqueous extract was analyzed as described above.

2.4. Artificial weathering

Microplastics were weathered artificially by exposition to constant irradiation using three metal halide lamps (UV–Vis radiation, ca. 12,200 lx illuminance, 24 μW cm^{-2}) (one in zenital and two in ground level position) simulating the natural UV–Vis irradiation conditions, during 5 months (Andrade et al., 2019).

The weathering was monitored monthly by ATR-FTIR measures, looking for changes in the IR spectra, especially in the crystallinity bands. Measures were taken in the attenuated total reflectance mode in the MIR region (4000–650 cm^{-1}) to include the fingerprint region of the polymers (1500–500 cm^{-1}). The measurement parameters, studied in a previous paper (Andrade et al., 2019) were: 4 cm^{-1} nominal resolution, Beer-Norton strong apodization, 50 scans per spectrum, background-, depth-penetration- and baseline-corrected. In addition, scanning electron microscopy (SEM) was used to visualize the superficial weathering and the changes on the particles surface.

2.5. Experimental design

In order to ensure the robustness of the results, the adsorption on microplastics was evaluated in two different ways. Determining the removal efficiency from water, analyzing the seawater sample and using the following equation

$$\textit{estimated removal efficiency}\ (\%) = \frac{C_{ct} - C_t}{C_{ct}} \times 100$$

where C_t is the concentration of analyte measured in seawater at time t (24 h, 48 h, 96 h or 7 days), and C_{ct} is the concentration of analyte in the control sample corresponding to the same contact time. Then, microplastic samples taken at the final time (7 days) were also analyzed to confirm the amount of contaminant adsorbed to the plastic.

To obtain enough amount of MPs with adsorbed contaminants for a reliable analysis, assays were performed using a higher concentration of MPs in seawater (2 g l^{-1}) than the real concentration in the marine environment (Phuong et al., 2016). The MPs concentration was selected as an average of the values used in literature about adsorption of contaminants to plastics: 25 g l^{-1} (Liu et al., 2019a), 0.5 μg l^{-1} (Haddad et al., 2019), 2 g l^{-1} (Zhang et al., 2018b). Synthetic seawater, prepared as explained in Section 2.2, was used to perform the adsorption studies as it was previously reported by other authors (Dong et al., 2019; Guo and Wang, 2019; Liu et al., 2019a).

The concentration of target compounds was selected taking into account their typical levels in seawater and also the quantitation limits of the analytical methods. The concentrations spiked in seawater for pesticides was 300 ng l^{-1}, whereas for musk fragrances was 100 ng l^{-1}. Assays for fragrances and for pesticides, were performed separately, since the filtration, extraction and determination methods were specific for each family.

The adsorption experiments were performed at two different water temperatures: 20 °C (close to 17 °C, the average surface water temperature (Cifuentes-Lemus et al., 1995)) and 4 °C (average oceanic temperature over all depths (Cifuentes-Lemus et al., 1995)). Glass transition temperature (Tg) for PHB is 5 °C (Omnexus, 2018) and therefore at 20 °C PHB is in rubbery state (soft and flexible), whereas at 4 °C PHB should be at a glassy state. Therefore, the adsorption capability could be different at both temperatures. For PA6 Tg was 60 °C (Omnexus, 2018) and, therefore, this polymer remains at a glassy state at both studied temperatures.

Microplastics were introduced in 100 ml glass bottles containing artificial seawater (100 ml) spiked with the contaminants, and then agitated in an orbital shaker at 500 rpm for a total contact time of 7 days, and water samples were analyzed at 24 h, 48 h, 96 h and 7 days (one individual bottle was analyzed per contact time). The sampling time was selected following previously published procedures (Hüffer and Hofman, 2016; Li et al., 2022; Lin et al., 2019; Liu et al., 2019b) to ensure that the equilibria are reached. For each temperature assay, the pristine and weathered PHB and PA6 microplastics were studied. In addition, control bottles, containing the same concentration of analytes in absence of microplastics were analyzed for each time. The controls are used to ensure that the decrease in concentration of analytes in seawater is due to plastic adsorption, and not caused by degradation of the analytes or adsorption at the flask's walls. Duplicates of all samples were analyzed.

3. Results and discussion

3.1. Characterization of weathered polymers

The artificial weathering of the polymers was monitored by ATR-FTIR and by SEM. As it can be seen in Fig. 1 some relevant changes were observed in the IR spectra of both plastics after 5 months weathering. More specific details on PA weathering can be found at our previous published studies (Fernández-González et al., 2021). The SEM images confirmed cracks, cavities, exfoliation and fractures appeared in PA and clear changes in the surface of both polymers. For PHB, fractures were not detected at the maximum magnification (3000×). Due to the isolating character of polymers, it was not possible to use higher magnifications than 3000× with a proper resolution. Small particles of PHB can be observed in the photographs, even though the polymer was sieved by 63 μm, but these particles are agglomerated (as can be seen in the figure) creating bigger particles that were retained by the 63 μm sieve.

3.2. Study of the filtration step

In order to analyze the aqueous and plastic phases separately, a proper separation step of both phases is needed. Although centrifugation was considered initially, it was finally discarded after some tests. The reason was that when PHB was in contact with seawater a slurry was formed, that could not be separated from the seawater. Therefore, the use of filters was studied. It is worth noting that frequently, the influence of the filtration step in the final results is underestimated, and is not often studied, considering that the use of a "common" type of filter is enough to obtain good results.

In this work, a detailed study of the filtration step was made for pesticides and musk fragrances in seawater. The assays were performed using the artificial seawater, to avoid the interference due to the adsorption of the compounds to particulate matter. The filters considered here were cellulose, glass fibre, quartz fibre, nylon, steel filters, and Teflon frit in glass column (Table 2). To perform the experiment, samples were prepared using 100 ml of artificial seawater, spiked with 300 ng l^{-1} of pesticides and 100 ng l^{-1} of fragrances (assays were developed separately for each family). Spiked samples were agitated 1 min using a vortex. Then, samples were filtered through each type of filter (all analyses were duplicated). In addition, two samples were directly extracted without filtration for comparison. The filters and filtration methods assayed are included in Table 2.

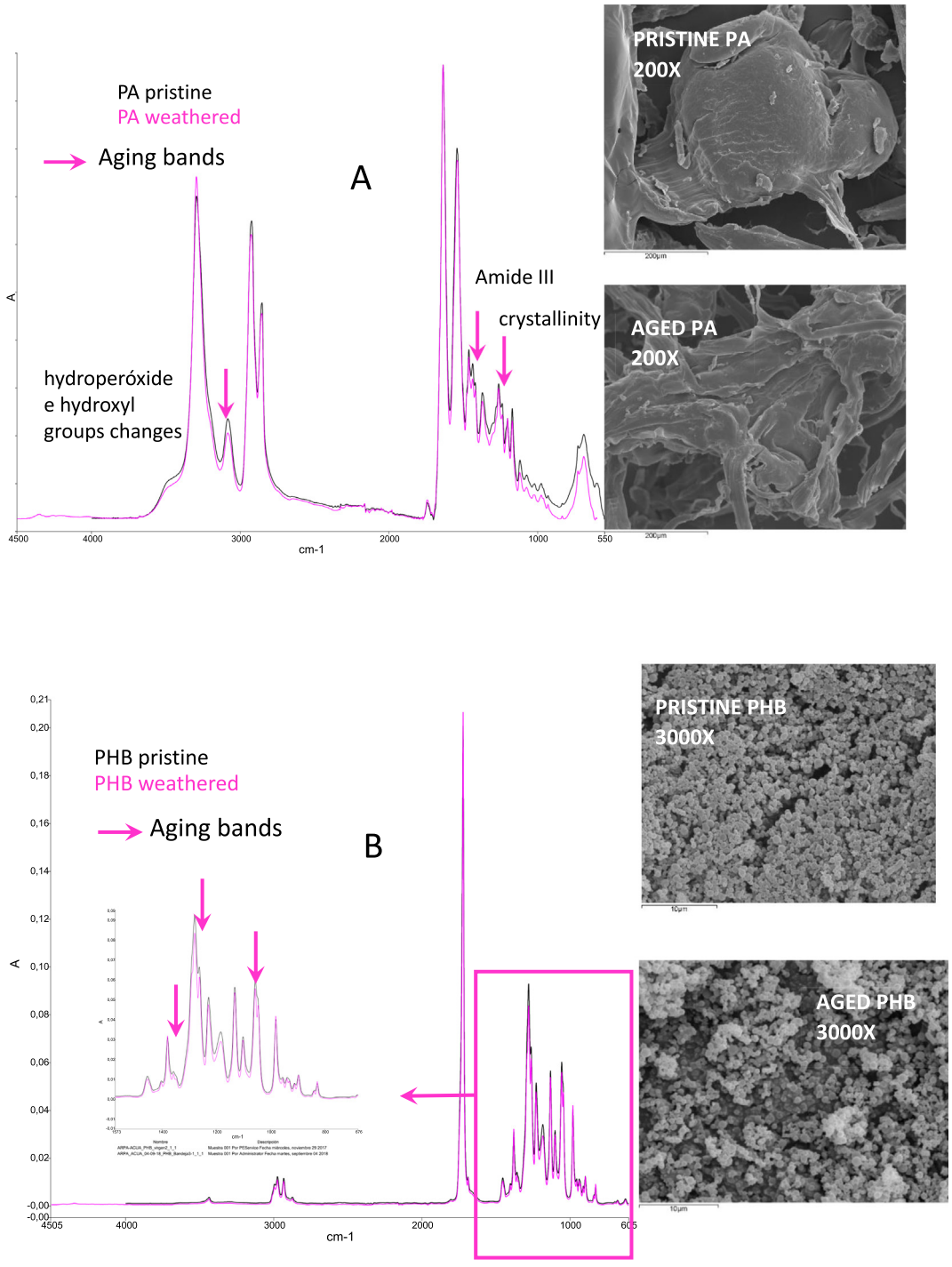


Fig. 1. FTIR spectra of PA (A), and PHB (B) before and after the artificial weathering and scanning electron microscope (SEM) images of the weathered microplastics.

Results are presented as relative recoveries regarding the unfiltered aliquot (A). As it can be seen in Fig. 2, common cellulose filters (B) that are frequently used for water prefiltration, retain completely α-endosulfan and musk fragrances. Other typical filters, like glass fibre (C) or quartz (D) cause retention of about 50 % of the compounds. The best results for fragrances were obtained using steel filters (G), with losses <30 %, and therefore this filter was selected to perform the filtration in the fragrances assays. For pesticides, a glass column with the Teflon frit (H) was selected for filtration as pesticides were almost totally recovered (losses around 3 %).

Table 2
Characteristics of the filters tested in the study of the filtration step.

Filter type	Cellulose	Glass fibre	Quartz fibre	Nylon filter	Steel filter	Teflon frit in glass column
Assay	B	C	D	E	F	G
Pore size	0.45 μm	0.6 μm	2.2 μm	0.2 μm	20 μm	20 μm
Filtration mode	Vacuum	Gravity	Gravity	Gravity	Gravity	Vacuum

3.3. Stability of compounds in seawater

Seawater control samples (without MPs) were analyzed at 24 h, 48 h, 96 h and 7 days, to ensure the stability of the analytes during all the experiment. They showed that all the analytes remained stable during all the

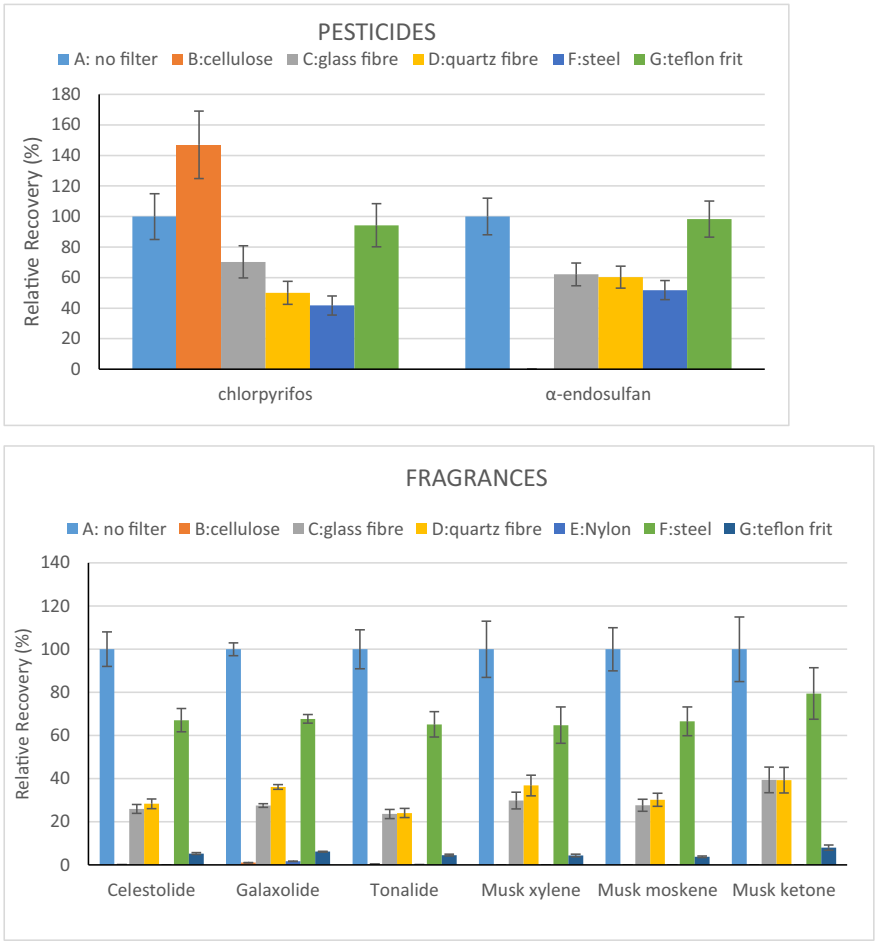


Fig. 2. Losses of the spiked pesticides and fragrances in seawater by sorption in the filtration step ($n = 2$). Unfiltered aliquot (A), cellulose filters (B), glass fibre filter (C), quartz filter (D), nylon filters (F), steel filters (G), Teflon frit (H).

experiments performed at 4 °C and at 20 °C, except for α-endosulfan. A reduction in its concentration was observed (50 % at 48 h and 94 % reduction at 7 days; Fig. 3). α-endosulfan hydrolyzes in aquatic environment, and this hydrolysis depends on the pH (it increases at basic pH) and on the temperature, generally increasing as the temperature increases (Hengpraprom, 1998). This fact could explain the reduction of α-endosulfan concentration in the control at 20 °C. This underlines the importance of considering control samples in adsorption experiments, in particular when quantification is made on the aqueous phase, in order to ensure that the reduction in concentration is only attributable to adsorption on plastics. For this reason, all samples were quantified with reference to the concentration of the analyte on the control samples at the same exposure time.

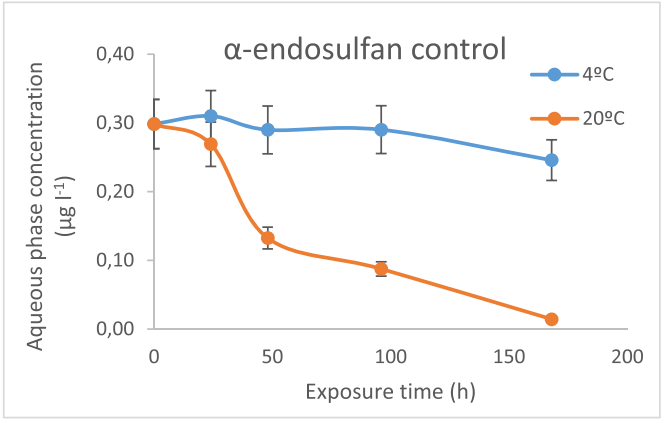


Fig. 3. Concentration of α-endosulfan in the aqueous phase in the control samples (without microplastics).

3.4. PA adsorption study

The adsorption profiles to PA obtained for all the analytes (by analyzing the aqueous phase) were very similar, showing that the maximum adsorption (and therefore, the reduction in the seawater concentrations) is achieved at 24 h, when the equilibrium was reached, as it can be seen for musk ketone at 20 °C as an example in Fig. 4A. In most cases, the percentage of adsorption remains below 80 % (100 % adsorption was not achieved in any case). PA has polar groups that allow it to retain hydrophilic compounds (Jiménez-Skrzypek et al., 2021), but this can reduce its ability to retain hydrophobic substances. The variation of the concentration of musk ketone in the seawater of the control experiment can be observed in Fig. 4a. That can be due to adsorption of the compound to the walls of the flask (95 h) or to a concentration due to water evaporation. The adsorbed percentages were calculated as mentioned above to avoid such effects that can alter the results. For the purpose of simplifying the explanation of the results the values obtained at the end of the study (168 h) are considered from now on, except for α-endosulfan (24 h was selected) due to its low stability at 20 °C. The percentages of compounds adsorbed on PA were quite variable. The highest adsorption (90 % average) was obtained for 4 °C and 5 months aged PA, whereas at 20 °C the sorption was below 50 % on average. In Fig. 4B the effect of the seawater temperature and microplastic weathering on the sorption of chemicals can be noted. All compounds, but chlorpyrifos, were more adsorbed at 4 °C than at

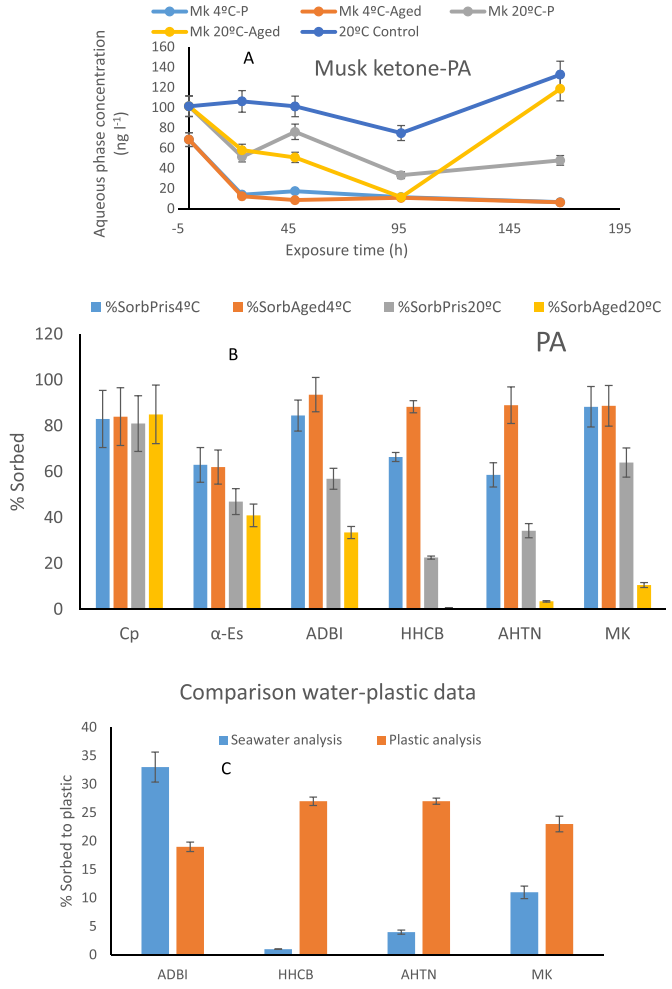


Fig. 4. Adsorption profile for musk ketone on PA (A), effect of weathering and temperature on adsorption of fragrances and pesticides on PA (B), and comparison between evaluation of adsorption by analysis of aqueous phase or plastic phase (aged PA at 20 °C) (C).

20 °C. This result is attributable to a decrease in the water solubility of these compounds as temperature decreases, favoring their adsorption to plastic, as previously reported (Dong et al., 2019; Mei et al., 2020; Zhang et al., 2018a). Regarding the effect of plastic weathering, different behavior was observed at 4 °C than at 20 °C. At 4 °C the polycyclic musks (celestolide, galaxolide and tonalide) were more adsorbed in 5 months aged PA and no differences were observed for the remaining contaminants. Photodegradation of PA causes random chain scission or polymer cross-linking, resulting in a decrease in molecular weight and an increase in amino end-groups.(Sait, 2019) and these amine groups can form hydrogen bonding with the carbonyl groups of fragrances (Li et al., 2018), increasing their adsorption. But at 20 °C, weathering seems to reduce the adsorption capacity of PA. Due to the surprising data obtained for fragrances at 20 °C by analyzing the seawater, these data (for aged PA) were compared with the data obtained by the extraction of the polymer microparticles (aged, 7 days contact) (Fig. 4C). Some relevant differences were observed in this case. The analysis of the aged (5 months) microplastic showed about 30 % adsorption, similar to the sorption obtained for pristine PA at the same temperature (20 °C). This result reveals the importance of the analysis of both matrices (seawater and microplastics) to ensure the reliability of the sorption studies.

Therefore, PA interacts with fragrances or pesticides probably through to its polar carbonyl and amine groups (e.g. by hydrogen bonding) (Hüffer and Hofman, 2016). PA is also more hydrophilic than other polymers, exhibiting a high sorption affinity for hydrophilic organic compounds (Tourinho et al., 2019) but a lower affinity by the hydrophobic contaminants, which could explain the lower sorption capacity of PA in comparison with PHB for the selected pollutants.

Adsorption coefficients were determined as $Kd = C_p/C_w$, where C_p is the equilibrium concentration of the contaminant in the microplastics and C_w the equilibrium concentration of the contaminant in the seawater (Table 3). For α-endosulfan, log K_d is quite similar to log K_{ow} in all the conditions tested, which could indicate that the sorption is mainly defined by the hydrophobicity of α-endosulfan. Regarding chlorpyrifos, log K_d was lower than log K_{ow}, but with slight differences between experiments. Finally, for the musk fragrances, there is a large difference between log K_d and log K_{ow}, being the assay at 20 °C the one that provides lower log K_d values.

3.5. PHB adsorption study

PHB was also subjected to the same study in order to compare its behavior to PA. PHB profiles shows almost a complete adsorption of the target compounds (about 100 %) after 24 h of exposure (Fig. 5A). As it can be seen in Fig. 5B, the adsorption of fragrances and pesticides by PHB was less affected by changes in the temperature or microplastic weathering than by PA. Slight differences were observed between the experiments. As mentioned above, lower temperatures decrease water solubility of the compounds, and therefore, a high adsorption at 4 °C than at 20 °C is expected. But, in this case, both assays show similar adsorption. The reason could be the change in the viscoelastic properties of PHB. Thus, PHB is at a glassy state at 4 °C, but it turns to a rubbery state after 5 °C (Tg = 5 °C), and therefore, should be at a rubbery state at 20 °C. The higher the rubbery component of MPs, the stronger the adsorption capacity for organic compounds (Mei et al., 2020), and therefore, the increasing of temperature increase sorption capacity of PHB.

Musk moskene and musk xylene were not included in the graph because they were not detected in water, which could indicate a very high adsorption to PHB.

When PHB microplastics were analyzed (Fig. 5C) the presence of musk moskene and musk xylene was confirmed, with percentages between 80 and 100 %. For chlorpyrifos, a big difference was observed between seawater and microplastic, maybe due to the low extraction recovery of chlorpyrifos for this polymer.

The adsorption coefficients were also determined for PHB in seawater (Table 3). The log K_d were higher than those for PA, confirming the larger adsorption of these compounds to PHB. The log K_d for the studied pesticides were quite similar to log K_{ow} (as for PA), whereas for the fragrances the log K_d were lower than log K_{ow}.

3.6. Leaching of contaminants from plastics

After demonstrating the adsorption of the target compounds to PA and PHB in seawater, we evaluated their possible leaching. This study was performed using ASE200 system to accelerate the leaching, using synthetic seawater as extracting solvent in the conditions described in Section 2.3. For all the compounds leaching was negligible for both types of plastic

Table 3
Sorption coefficients (log K_d) of the studied contaminants onto PA and PHB microplastics (pristine and aged) in the different conditions studied.

	log K_d								log K_{ow}
	PA 4 °C Pris	PA 4 °C Aged	PA 20 °C Pris	PA 20 °C Aged	PHB 4 °C Pris	PHB 4 °C Aged	PHB 20 °C Pris	PHB 20 °C Aged	
Chlorpyrifos	2,75	2,66	2,48	2,58	3,22	3,40	3,86	4,32	4,96
α-Endosulfan	3,13	2,98	3,15	3,05	3,73	3,83	4,23	5,72	3,83
Celestolide	2,17	2,58	1,98	1,03	3,03	2,61	2,66	2,57	5,93
Galaxolide	2,30	2,23	1,73	1,01	2,58	2,37	2,38	2,27	5,90
Tonalide	1,90	2,41	1,81	0,99	2,36	2,21	2,14	2,07	5,70
Musk ketone	2,08	1,92	2,10	0,98	2,92	2,87	2,83	2,81	4,30

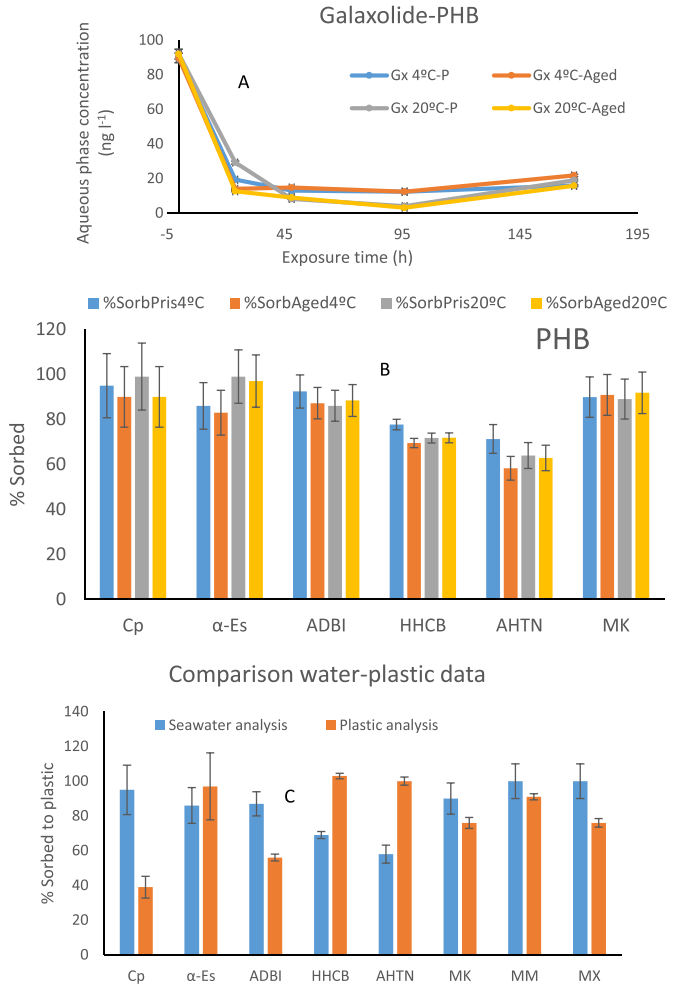


Fig. 5. Adsorption profile for galaxolide (A), effect of weathering and temperature on adsorption of fragrances and pesticides on PHB (B) and comparison between evaluation of adsorption by analysis of aqueous phase or plastic phase (pristine PHB at 4 °C) (C).

(<1 %), without differences between pristine and aged microplastics. This result showed that adsorption was irreversible under these conditions, and therefore these pollutants can be accumulated in the microplastics.

4. Conclusions

The adsorption to PA and PHB microplastics of the 2 pesticides and 6 musk fragrances studied here was achieved at 24 h in almost all conditions, remaining constant during all the experiment (7 days). The sorption capacity of the plastics was lower for PA than for PHB. The former was affected more by changes in temperature, being the compounds more adsorbed at 4 °C than at 20 °C. No differences for the adsorption of pesticides between the weathered and pristine PHB or PA. However, for PA an increase on the retention capability of the fragrances on the weathered polymer was observed in the sorption at 4 °C, although at 20 °C the effect was the opposite.

Once the studied compounds were adsorbed they stayed at the microplastics (migration was <1 %), which indicates the capacity of PA and PHB microplastics to accumulate and transport these pollutants in the marine environment.

In addition, it is worth noting that at 20 °C α-endosulfan hydrolyzes in the control samples, reducing its concentration, but when microplastics are present, the adsorption remained high, between 40 and 91 %. This fact indicates that the presence of plastic can inhibit the degradation of this compound in the environment, likely increasing its lifetime.

Furthermore, the inclusion of controls in the sorption experiments and of using proper filters proved very relevant for the quality of the analytical method to ensure the reliability of the results of adsorption studies.

CRediT authorship contribution statement

Estefanía Concha-Graña: Conceptualization, Methodology, Investigation, Writing-Original Draft.

Carmen Mª Moscoso-Pérez: Methodology, Investigation, Validation, Writing – Review & Editing.

Purificación López-Mahía: Methodology, Supervision, Project administration.

Soledad Muniategui-Lorenzo: Conceptualization, Supervision, Funding acquisition, Project administration.

Data availability

Data will be made available on request.

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.scitotenv.2022.157703.

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