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Can aged microplastics be transport vectors for organic micropollutants? – Sorption and phytotoxicity tests

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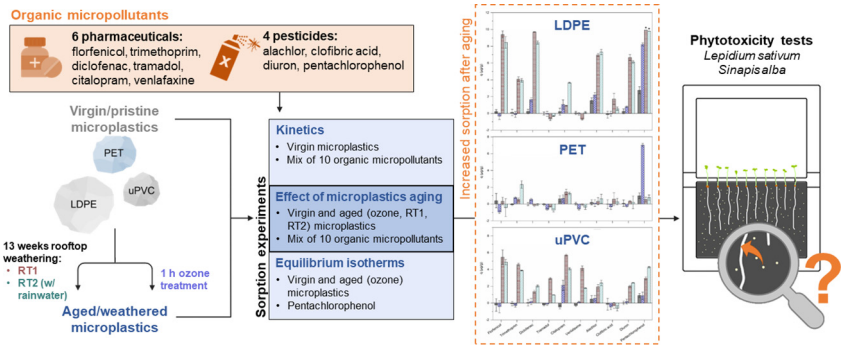
HIGHLIGHTS

- Sorption assessment of 10 organic micropollutants on virgin or aged microplastics
- Ozone exposure or urban weathering increased the sorption capacity of microplastics.
- Most substances studied showed a higher affinity for LDPE and uPVC than for PET.
- Pentachlorophenol equilibrium sorption isotherms on LDPE or PET were studied.
- Null or low phytotoxicity for organic micropollutants-sorbed microplastics

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics have been investigated over the last decade as potential transport vectors for other pollutants. However, the specific role of plastic aging, in which plastics change their characteristics over time when exposed to environmental agents, has been overlooked. Therefore, sorption experiments were herein conducted using virgin and aged (by ozone treatment or rooftop weathering) microplastic particles of LDPE – low-density polyethylene, PET – poly(ethylene terephthalate), or uPVC – unplasticized poly(vinyl chloride). The organic micropollutants (OMPs) selected as sorbates comprise a diversified group of priority substances and contaminants of emerging concern, including pharmaceutical substances (florfenicol, trimethoprim, diclofenac, tramadol, citalopram, venlafaxine) and pesticides (alachlor, clofibric acid, diuron, pentachlorophenol), analyzed at trace concentrations (each ≤ 100 μg L^{-1}). Sorption kinetics and equilibrium isotherms were obtained, as well as the confirmation that the aging degree of microplastics plays a major role in their sorption capacities. The results show an increased sorption of several OMPs on aged microplastics when compared to pristine samples, i.e. the sorption capacity increasing from one or two sorbed substances (maximum 3 μg g^{-1} per sorbate) up to nine after aging (maximum 10 μg g^{-1} per sorbate). The extent of sorption depends on the OMP, polymer and the effectiveness of the aging treatment. The modifications (e.g. in the chemical structure) between virgin and aged microplastics were linked to the increased sorption capacity of certain OMPs, allowing to better understand the different affinities observed. Additionally, phytotoxicity tests were performed to evaluate the mobility of the OMPs sorbed on the microplastics and the potential effects (on germination and early growth) of the combo on two species of plants (*Lepidium sativum* and *Sinapis alba*). These tests suggest low or no phytotoxicity effect under the conditions tested but indicate a need for further research on the behavior of microplastics on soil-plant systems.

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1. Introduction

Contaminants of emerging concern (CECs) – also known as emerging pollutants – encompass a diversified group of substances that, as defined by Directive 2013/39/EU (The European Parliament and the Council of the European Union, 2013), are "currently not included in routine monitoring programs at Union level but which could pose a significant risk requiring regulation, depending upon their potential ecotoxicological and toxicological effects and on their levels in the aquatic environment". Several compounds have been classified as such over the years, like certain pesticides, pharmaceuticals, nanomaterials, and personal care products, among others (Brack et al., 2017). More recently, this definition (expanded to include other environments) was also applied to microplastics (Lambert and Wagner, 2018; Souza Machado et al., 2018; Sridharan et al., 2021; The European Parliament and the Council of the European Union, 2020).

Microplastics (plastic particles or fibers whose longest length is below 5 mm) arised as pollutants of emerging concern due to the increasing knowledge on their abundance, dispersion, persistence, and impacts in the environment over the last decade (European Commission, 2018a; Miranda et al., 2020). Since then, the sorption capacity of microplastics and their potential to carry co-occurring pollutants have been under the scrutiny of the scientific community. Consequently, the hypothesis that microplastics may act as vectors for transporting substances and microorganisms has been raised and is under debate (Dong et al., 2021; Thompson et al., 2004; Verla et al., 2019; Wang et al., 2021; Yu et al., 2021). Furthermore, it has been identified the possibility of a microplastics trojan horse effect, in which the sorbed pollutants (and additive chemicals) are released from the microplastics and transferred into the biota tissues after exposure to this combination through e.g. ingestion (González-Soto et al., 2019; UNEP, 2016).

The interest on the interactions between plastic and organic or inorganic substances is older than the upsurge of microplastics research. Examples include the assessment of different plastics as adequate materials to use for field and laboratory equipment, considering their potential to influence certain analyte concentrations (Hebig et al., 2014; Papiernik et al., 1996), and the use of plastics for medical applications, such as wound dressings host materials (Devetak et al., 2014). However, this research line was focused on their sorption capabilities during their designed life-time. Such studies did not consider their end-of-life as plastic litter, particularly microplastics with physical and chemical properties that differ from the original plastic due to their modifications through time related to their aging in the environment (Deng et al., 2022; Fotopoulou and Karapanagioti, 2017; Menzel et al., 2022; Miranda et al., 2021).

The number of publications on microplastics sorption of chemical pollutants had an exponential growth, particularly since 2015, as detailed in Table S1 of the Supplementary Material (SM) that lists the raw results of specific search terms related to this work in the Scopus database (20th January 2022). Multiple combinations of different polymers and sorbates have been studied so far, with the conventional plastics being the most studied (particularly polyethylene, polypropylene, and polystyrene) and organic sorbates being more explored, although there are several reports on heavy metals (Agboola and Benson, 2021; Alimi et al., 2022; Liu et al., 2022). Most studies have been conducted with virgin or pristine microplastics, whereas studies performing aging treatments (including weathering), using biofilm-developed microplastics, or using environmental samples, for sorption and/or effect studies, are still insufficient (Alimi et al., 2022; Ding et al., 2022; Guo and Wang, 2019; Hanun et al., 2021; Liu et al., 2020; Wang et al., 2021).

Organic micropollutants (OMPs) are a group of organic pollutants found at trace concentrations (Stamm et al., 2016). They may occur in the same environmental compartments as the microplastics and, therefore, have the potential to be sorbed to them (Aryal et al., 2020; Yu et al., 2021). The OMPs raised concern due to their pseudo-persistence since the conventional treatment technologies were not designed to eliminate them before they enter the environment, as happens for most CECs (Morin-Crini et al., 2022). Specifically, the European Union (EU) has been developing regulations to cope with the presence of OMPs in the environment. Some OMPs are already classified as priority substances in the field of water policy by Directive 2008/105/EC, amended by Directive 2013/39/EU (The European Parliament and the Council of the European Union, 2008, 2013), and have environmental quality standards (EQS). However, many are classified as CECs. Considering the lack of monitoring data for many CECs and the need for a prioritization process to respond more efficiently to this issue, the EU created a dynamic watch list for a limited number of substances to be temporarily included in, until enough quality information is collected for a further risk assessment and a possible update in the list of priority substances. The three previous editions of the EU Watch List (EU Decision 2015/495, EU Decision 2018/840 and EU Decision 2020/1161) and the current one (EU Decision 2022/1307) include synthetic and natural hormones, non-steroidal anti-inflammatory drugs, antidepressant and antihyperglycemic drugs and their metabolites, antibiotics, antioxidants, insecticides, fungicides, herbicides, and sunscreen agents (European Commission, 2015, 2018b, 2020, 2022).

Therefore, in the face of the growing relevance of these two large groups of CECs – microplastic particles (MPPs) and OMPs –, the main goal of the present study is to test the hypothesis that MPPs can be transport vectors of OMPs, with the aging degree playing a relevant role on the sorption capacities of MPPs. The selected polymers are three of the most used plastics that are consistently found as pollutants in the environment (Geyer et al., 2017; Jones et al., 2020; Zhang et al., 2022): LDPE – low-density polyethylene, PET – poly(ethylene terephthalate), and uPVC – unplasticized poly(vinyl chloride). These polymers were aged by an ozone treatment or by actual weathering conditions, aiming to represent more realistic MPPs, particularly from an urban environment, and characterized before and after aging in our previous work (Miranda et al., 2021). The three polymers showed different degrees of resistance to the aging processes applied, making them a good choice to this study considering the diversity of microplastics that can be found in the environment and that will not have equal sorption capacities. In the present work, 6 pharmaceutical substances (florfenicol, trimethoprim, diclofenac, tramadol, citalopram, and venlafaxine) and 4 pesticides (alachlor, clofibric acid, diuron, and pentachlorophenol) were used to study the sorption properties of the virgin and aged MPPs. These OMPs were selected based on: (i) their inclusion in the list of priority substances in the field of water policy (alachlor, diuron and pentachlorophenol) (The European Parliament and the Council of the European Union, 2013); or (ii) their potential as candidates to join that list due to their targeting as relevant CECs by the EU Watch List or by the scientific community (Choi et al., 2020; Gorito et al., 2022; Kye et al., 2020; Yang et al., 2022). Some studies have reported the detection of these OMPs and MPPs in the same environmental samples and ecosystems (Mora et al., 2021; Picó et al., 2020). However, while several publications demonstrate the sorption of pharmaceutical substances and/or pesticides on microplastics, few reports focus on the sorbates selected for the present study (listed in Table S1 of the SM), particularly regarding the influence of the MPP aging in the sorption process. Therefore, sorption experiments were conducted to explore the sorption kinetics of 10 OMPs on each virgin polymer, as well as the effect of aging on sorption. The equilibrium sorption isotherms for the most sorbed pollutant (pentachlorophenol) on MPPs of LDPE or PET were also studied. Furthermore, phytotoxicity tests were used to identify potential effects of the OMP-sorbed MPPs on seed germination and early growth of two species of plants (*Lepidium sativum* and *Sinapis alba*), simulating a possible transport and transfer of OMPs by MPPs from source to fate systems and the OMP mobility between different environmental compartments.

2. Material and methods

2.1. Microplastic particles (MPPs)

MPPs made from LDPE (average particle diameter of 509 ± 221 μm), PET (161 ± 79 μm) and uPVC (159 ± 43 μm) were purchased in powder form from Goodfellow (UK). The main characteristics of the virgin MPPs are listed in Table S2 of the SM, and the characterization results are

included in our previous publication (Miranda et al., 2021). Aliquots of these virgin MPPs were (i) artificially exposed for 1 h to ozone gas or (ii) exposed to natural weathering conditions for 3 months on a building rooftop, to study the MPP modifications by aging in an urban environment, as described in our previous work (Miranda et al., 2021).

In the case of the ozone gas MPP aging, the virgin MPPs of each polymer were supported by lab-grade glass wool fibers inside a glass column that received a flow rate of 150 $Ncm^3\ min^{-1}$ of 50 $gO_3\ Nm^{-3}$ for 1 h. For the weathering experiment, the goal was to expose the virgin MPPs of each polymer to real conditions of weathering (under a temperate climate, during the period of the year with the maximum hours of sunlight per day and higher UV index, in the city of Porto, Portugal) regarding air humidity and temperature, sunlight, and precipitation. For that, an experimental setup, composed of two trays with Petri dishes (soda-lime bottom and quartz top) and a filtration and collection system for rain, was created and installed on the rooftop of the Chemical Engineering Department of the Faculty of Engineering of the University of Porto. In the first tray (RT1), the MPPs underwent aging inside the Petri dishes due to natural solar exposure and temperature variations for 3 months (13 weeks). In the second tray (RT2), the filtered rainwater collected was additionally added inside the Petri dishes, following the precipitation pattern. These three types of aged MPPs were used in the present study. A summary of relevant characteristics of the aged MPPs can be found in Table S3 of the SM, while more details of the specific methodology for the MPP aging are fully described in the above mentioned study (Miranda et al., 2021).

2.2. Organic micropollutants (OMPs)

HPLC (LC-MS) grade methanol (HiPerSolv Chromanorm, VWR) was used to prepare a stock solution (ca. 1000 mg L^{-1}, stored at −18 °C) of each OMP selected: alachlor, citalopram, clofibric acid, diclofenac, diuron, florfenicol, pentachlorophenol (PCP), tramadol, trimethoprim, and venlafaxine. The OMPs were purchased from Sigma-Aldrich (Germany) or Supelco (Germany) in powder form. Tables S4 and S5 of the SM respectively comprise a detailed list of the reagents and a list of the classification, chemical structure, CAS number, molecular weight, log K_{ow}, pK_a and water solubility of the 10 OMPs. Two working solutions were prepared by dilution in methanol (to ensure the OMPs complete dissolution and their stability when stored) of the individual stock solutions: (i) MIX10 – a solution prepared with 5 mg L^{-1} of each of the 10 OMPs, and (ii) PCP solution – a 5 mg L^{-1} solution of pentachlorophenol. The working solutions were stored at −18 °C.

2.3. Sorption batch experiments

Three types of sorption batch experiments were conducted to assess the MPP sorption capacities and affinity to OMPs: (i) sorption kinetics of the 10 OMPs on virgin MPPs (LDPE, PET, or uPVC) in order to identify the necessary time to reach the equilibrium; (ii) sorption experiments of the 10 OMPs (at the same concentration as that used in sorption kinetics) under a fixed time to assess the effect of MPP aging on sorption (virgin, ozone gas, RT1 or RT2 MPPs of LDPE, PET, or uPVC); and (iii) equilibrium isotherms to understand the individual sorption of PCP on virgin or ozone gas aged MPPs of LDPE or PET.

2.3.1. Sorption kinetics

For the kinetics experiments, 250 mg of virgin MPPs (LDPE, PET, or uPVC) were weighted and added to each 50 mL ISO blue cap bottle (without the blue outlet ring), except for the control bottles. The load of MPPs (10 g L^{-1}) was selected for this study based on the work of Elizalde-Velázquez et al. (2020) and after preliminary experiments conducted with virgin MPPs, which results showed that lower loads of MPPs did not originate detectable changes in the OMP concentrations in solution. Aluminum foil was used to cover the bottles, avoiding the influence of light in the process. It was also placed between the glass bottle and the blue cap, thus avoiding that unwanted MPPs released from the polypropylene cap could contaminate the solution.

Regarding the OMPs, a solution was prepared (with 100 μg L^{-1} of each OMP) by dilution in Milli-Q ultrapure water (pH = 6.7–6.8) of the MIX10 working solution. An aliquot of the initial solution (t = 0 h) was stored in triplicate in HPLC vials at −18 °C. Then, 25 mL of this dilute solution (with 2 % V/V methanol, pH ca. 5.8) was added to each bottle, including the control bottles (without MPPs). The bottles were placed in a VWR 18 L shaking water bath set to 25 °C and 150 strokes per minute for the following time intervals: 2, 4, 8, 16, 24 and 30 h. Samples were run in triplicate, for each time interval.

All samples, including the controls, were vacuum filtered through 47 mm glass microfiber filters (pore size of 1.2 μm, purchased from VWR) to remove the MPPs from suspension. For that, Normax (Portugal) glass filtration kits, 100 mL Kitasato glass flasks (Normax, Portugal), and a KNF Neuberger (Freiburg, Germany) N035.1.2AT.18 vacuum pump, were used. The filtered samples were stored in HPLC vials at −18 °C.

2.3.2. Effect of microplastic particles aging on sorption

Another type of experiments was accomplished to analyze the influence of MPP aging on the sorption capacity of OMPs by each type of MPPs. The same procedure described in 2.3.1 was used, but all the samples (virgin and ozone or RT1 or RT2) were shaken for 24 h. The initial concentration of 100 μg L^{-1} of each OMP in the MIX10 solution was obtained by the same procedure described before.

As an additional step, the filtered MPPs obtained after the vacuum filtration step were stored in soda-lime glass Petri dishes, which were dried and kept in a desiccator, in the dark. These MPPs were used for phytotoxicity tests (Section 2.4).

For each polymer (LDPE, PET, or uPVC) and aging treatment (ozone, RT1 or RT2), a set of experiments was performed consisting of triplicate bottles of virgin MPPs + triplicate bottles of aged MPPs + a control bottle without the addition of MPPs, resulting in a total of 9 sets of experiments.

2.3.3. Equilibrium isotherms for pentachlorophenol (PCP)

PCP was selected to determine the equilibrium isotherms for virgin or ozone-aged MPPs of LDPE or PET. No isotherms were obtained for uPVC, since PCP did not show significant sorption to the virgin or ozone-aged MPPs of this specific polymer (as described in 3.1.1). The weathered MPPs (RT1 and RT2) were not used to study the equilibrium isotherms of PCP because the recovered mass of MPPs from weathering was not sufficient.

The procedure was similar to that described in 2.3.1. Each set of experiments (triplicate bottles of virgin MPPs + triplicate bottles of ozone-aged MPPs + control bottle without MPPs) was carried out for 5 solutions with different initial concentrations of PCP (t = 0 h) of 50, 75, 100, 125 and 175 μg L^{-1} (with ≤3.5 % V/V methanol, pH ca. 5.9–6.2). The bottles were kept in the shaking bath for 24 h.

2.4. Phytotoxicity tests

Phytotoxicity tests were carried out to determine the effects of the OMP-sorbed MPPs, obtained as described in 2.3.2, on seed germination and early growth (root and shoots lengths) of two species of plants: *Lepidium sativum* (dicotyl garden cress) and *Sinapis alba* (dicotyl mustard). For that, Phytotoxkits (liquid samples) were purchased from Microbiotests Inc. (Kleimoer, Belgium). The Phytotoxkit (liquid samples) standard operating procedure (Microbiotests Inc., 2016) (in accordance with ISO Standard 18763:2016) was thus slightly modified to simulate the presence of MPPs on the "contaminated soil". The procedure is described summarily in section S4 of the SM.

A preliminary set of experiments was conducted to study the effects of the 100 μg L^{-1} MIX10 solution and the effects of each of the three virgin MPPs on seed germination and early growth, with 5 types of test plates (each n = 10) being used for each plant species: negative control (without MPPs and OMPs); positive control (100 μg L^{-1} of MIX10); and LDPE, PET, or uPVC virgin MPPs. LDPE was then selected among the three studied polymers since, as described in Section 3.1, it has an overall higher sorption capacity for the studied OMPs. For the test conducted to study OMP-sorbed

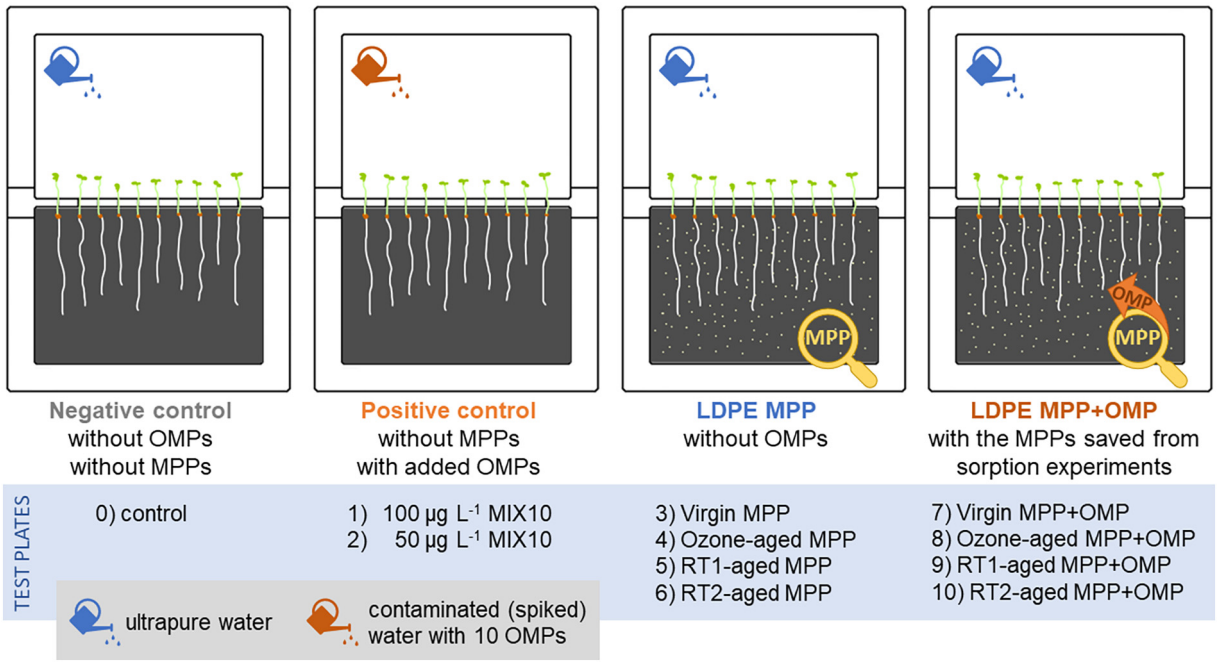

Fig. 1. Schematic of the test plates used for the LDPE phytotoxicity test.

LDPE MPPs, 11 types of test plates (each $n = 10$) were assayed (Fig. 1): 0) negative control (without MPPs and OMPs); 1) positive control 1 (100 µg L^{-1} of MIX10); 2) positive control 2 (50 µg L^{-1} of MIX10); 3) virgin MPPs; 7) virgin MPP + OMP (after sorption experiment); 4–6) ozone, RT1, or RT2 aged MPPs; 8–10) ozone, RT1, or RT2 aged MPP + OMP (after sorption experiment).

In parallel, OMPs desorption was evaluated to account for the LDPE test, particularly for the test plates with OMP-sorbed MPPs. For that, 2 mg of MPP + OMP (virgin, ozone, RT1, or RT2 aged) and 20 mL of Milli-Q ultrapure water were added to 50 mL ISO blue cap bottles that were kept near the test plates for the duration of the experiment (3 days). The bottles were not shaken, and aluminum foil was used to cover the bottles and placed between the glass bottle and the blue cap.

2.5. Organic micropollutants quantification

An ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analytical method was adopted to determine the concentration of the selected OMPs in the samples from the sorption batch experiments. The Shimadzu (Japan) UHPLC-MS/MS system used comprises a Nexera X2 UHPLC unit and a LCMS-8040 triple quadrupole mass spectrometer detector, with an electrospray ionization source operating in both positive and negative ionization modes. A Phenomenex (USA) Kinetex 1.7 µm XB-C18 100 Å (100 × 2.1 mm) column was used, with the respective pre-column, in the system with the oven temperature set at 40 °C. The mobile phase flow rate of 0.2 mL min^{-1} was 50/50 (*V*/*V*) Milli-Q ultrapure water and HPLC gradient grade ethanol (LiChrosolv, Supelco, Germany), under isocratic mode. The injection volume was 20 µL. The quantification was performed using the transition between the precursor ion and the most intense fragment by selected reaction monitoring. Detailed information on the UHPLC-MS/MS settings and analytical method (including the limits of detection and quantification) is described in Table S6 and Table S7 of the SM. Shimadzu LC Solution Version 5.41SP1 software was used to convert raw data to each OMP concentration, based on the triplicate 10 points calibration curve (range 1–200 ppb) on Milli-Q ultrapure water.

2.6. Data analysis and statistics

The amount of OMPs sorbed per unit of mass of MPPs, q (µg g^{-1}) (q_e if sorption equilibrium is reached) was estimated using Eq. (1):

$$q = \frac{(C_{control} - C_{sample})}{m} V \quad (1)$$

where, $C_{control}$ is the concentration of each OMP (µg L^{-1}) in the control bottle liquid phase at a given time interval, C_{sample} is the concentration of each OMP (µg L^{-1}) in a sample bottle liquid phase (same as C_e if sorption equilibrium is attained), V (0.025 L) is the volume of the solution added to each bottle, and m is the mass (g) of MPPs added to the bottle. The concentration of OMPs in the control bottles liquid phase ($C_{control}$) was used instead of the initial concentration (C_0) to exclude any possible degradation or loss of the OMPs during the sorption experiment, e.g. due to the possibility of sorption to the ISO blue cap bottles, filtration system and/or the microfiber filters. Nevertheless, C_0 ($t = 0$ h) was used as a reference to ensure that the experiment was well conducted and to compare with $C_{control}$, as discussed in 3.1. Since samples were run in triplicates, the mean and respective standard deviation (SD) were calculated for all q results.

Two mathematical models were used to analyze the kinetics of the sorption reactions studied: pseudo-first-order model (PFO) and pseudo-second-order model (PSO) (Agbovi and Wilson, 2021; Ho and McKay, 1998; Lagergren, 1898). Three mathematical models were used to analyze the PCP equilibrium sorption isotherms: Langmuir, Freundlich, and linear (Agbovi and Wilson, 2021; Freundlich, 1907; Langmuir, 1916). Additional information on model fitting to experimental data is given by section S5 of the SM. The statistical analysis of the phytotoxicity results (section S7 of the SM) included the calculation of the average root and shoot lengths ($n \leq 10$, depending on the seed germination), and the respective SD. Additionally, the root and shoot lengths were compared for all the test plate results of each test using One-Way ANOVA and the post hoc Tukey test (OriginPro 9 software). The following assumptions were validated for the ANOVA model using the same software: independence, normality (normality tests e.g. Anderson-Darling test) and homogeneity (Levene's test).

The percentage effect of the different combinations tested of OMPs and/or MPPs on root and shoot growth was estimated by Eq. (2):

$$\%effect = \frac{A-B}{A} \times 100 \quad (2)$$

where, A is the average root length or average shoot length in the negative control test plate, whereas B corresponds to the MPPs and/or OMPs test plates (Microbiotests Inc., 2016).

3. Results and discussion

3.1. Evaluation of microplastic particles capacity to sorb organic micropollutants

In order to assess the MPPs capacity to sorb the selected OMPs, the sorption kinetics of the mixture of 10 OMPs were studied for each polymer, as well as the effect of MPP aging on sorption, and the equilibrium isotherms of the most sorbed OMP – PCP – on MPPs of LDPE or PET.

The sorption kinetics for virgin MPPs were evaluated to define an adequate contact time for further sorption experiments. These first experiments revealed that only alachlor on LDPE and PCP on the 3 polymers were discernibly sorbed under the conditions tested, when working with virgin MPPs (Table S8 of the SM). An apparent equilibrium was reached between 16 h and 24 h (Tables S9 and S10, Fig. S1 and S2 of the SM). Despite other studies reporting different timeframes to achieve equilibrium, such as Loncarski et al. (2020) for PCP adsorption on polyethylene and PET, it is known that the sorption rate is affected by multiple factors such as the characteristics of the MPPs. Therefore, 24 h was considered enough to reach equilibrium, under the conditions studied.

Considering the adj. R^2 and RSS values (Table S10), the PFO model (Fig. S1) fitted better for the combination LDPE-alachlor, PET-PCP and uPVC-PCP, with the PSO model (Fig. S2) being more adequate to represent the sorption of PCP on LDPE over time. Taking into account that PCP is a relatively hydrophobic compound, it can explain why the PSO model fitted better for LDPE-PCP, since the interaction of hydrophobic compounds with the surface of hydrophobic microplastics is higher than when the sorbate is a more hydrophilic compound. One possible explanation for the PFO model fitting better for PET and uPVC is that the used MPPs of these two polymers have fewer active adsorption sites than those of LDPE. As alachlor is a hydrophilic to hydrophobic compound, it has a higher difficulty in sorbing on microplastics than PCP and is better represented by the PFO model, which is also associated to the external diffusion or the internal diffusion being the rate controlling steps (Wang and Guo, 2020a).

It should be noted that the concentration of the antidepressant citalopram in control samples (i.e., without MPPs in suspension) reached values of ca. 60 μg L^{-1} (C_0 ca. 100 μg L^{-1}), suggesting that it could be potentially sorbed on other surfaces or degraded. For this reason, and as explained in Section 2.6, the sorption capacity was estimated based on the control sample concentration of each OMP instead of the initial concentration.

3.1.1. Effect of microplastic particles aging on sorption

3.1.1.1. Low-density polyethylene (LDPE). LDPE sorption capacities were most impacted by aging (Fig. 2a) than those of PET (Fig. 2b) or uPVC (Fig. 2c). Additional data on these experiments can be found in Tables S11 and S12 of the SM.

In the particular case of LDPE (Fig. 2a), all the aging treatments studied led to changes in the sorption capacity of this polymer MPPs. Moreover, the rooftop weathering without and with rainwater (RT1 and RT2, respectively) led to a similar increase of the sorption capacity for most OMPs (different only for diclofenac, citalopram and clofibric acid), when compared with virgin LDPE, this increase being higher than that observed with the ozone treatment.

PCP and alachlor are the only two OMPs with significant sorption to the virgin LDPE, whereas the aged LDPE sorbed all other OMPs except tramadol and venlafaxine (ozone: PCP ≫ > alachlor ≥ diclofenac = citalopram = diuron; RT1: PCP ≥ diclofenac = florfenicol > alachlor = diuron > trimethoprim > clofibric acid = citalopram; RT2: PCP > florfenicol = diclofenac > alachlor > diuron > trimethoprim = citalopram). The two OMPs that showed no affinity to virgin or aged LDPE – tramadol and venlafaxine –, have high pK_a and similar log K_{ow}. Although no universal rule (direct or indirect correlation) was found between pK_a or log K_{ow} and the affinity between the polymer and the OMPs, in most of the cases the sorption on LDPE (particularly for RT1 and RT2 samples) was higher when the log K_{ow} is higher. Furthermore, the OMPs with lower water solubility, such as diclofenac and PCP, were observed to have higher affinity to LDPE, especially after weathering.

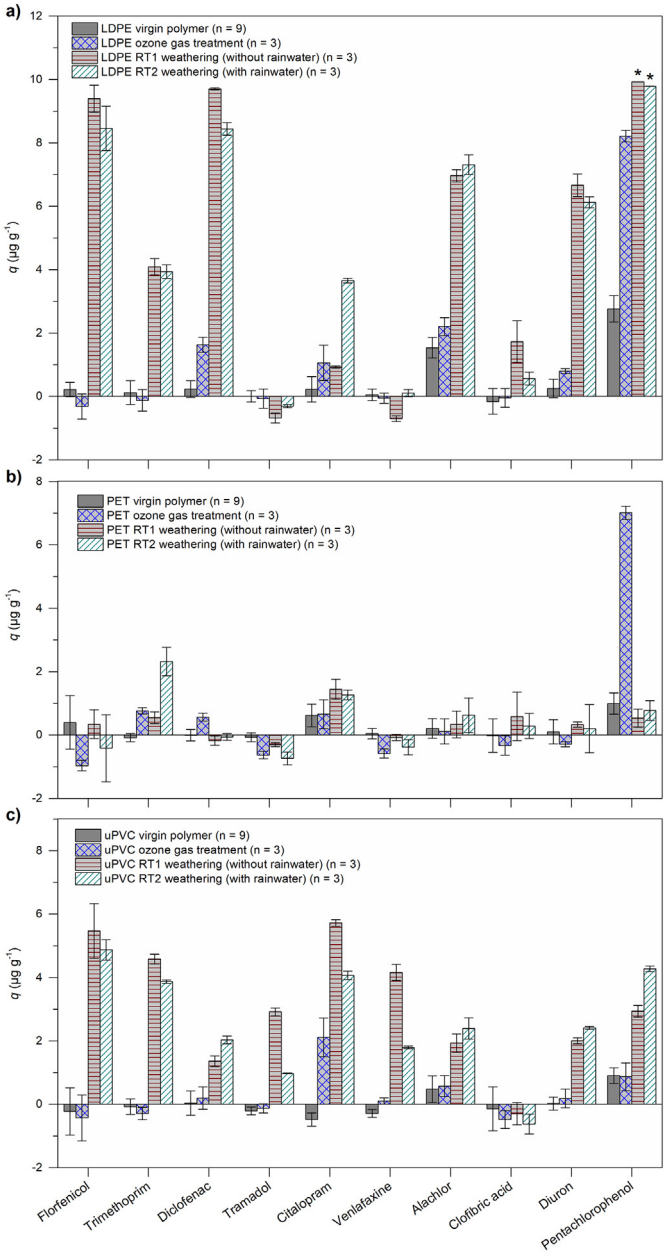

Fig. 2. OMPs sorbed per unit of mass of MPPs (virgin, aged by ozone treatment or rooftop weathering without – RT1 and with – RT2 rainwater), for a) low-density polyethylene (LDPE), b) poly(ethylene terephthalate) (PET) and c) unplasticized poly(vinyl chloride) (uPVC). * Pentachlorophenol concentration in solution after 24 h was below the method detection limit for LDPE RT1 and RT2 triplicated samples. Therefore, q was calculated admitting a null concentration for those samples.

In our previous study (Miranda et al., 2021), in which the MPPs were aged and characterized, several modifications were observed in the chemical structure of the LDPE MPPs after the aging treatments. That information can help to explain the increased sorption of these aged MPPs, since the aging processes are known to increase the oxygen-containing functional groups on the plastics, affecting their surface hydrophobic properties and allowing additional interactions (Hüffer and Hofmann, 2016; Liu et al., 2019; Yu et al., 2020). The most substantial modification observed (assessed by ATR-FTIR – Attenuated Total Reflection - Fourier transform infrared spectroscopy) was the formation of carbonyl species (C = O), with the carbonyl absorbance peak intensity (and the Carbonyl Index estimated from it) being linked to the exposure time and the effectiveness of each aging treatment on each polymer. While the ozone gas aging treatment (1 h) was sufficient to detect an increase of the Carbonyl Index from 0.004 ± 0.001 (virgin) to 0.100 ± 0.002, the weathering treatments significantly increased this index up to 0.243 ± 0.011 (13 weeks RT1) and 0.246 ± 0.006 (13 weeks RT2). Accordingly (Fig. 2a), RT1 and RT2 aged LDPE samples revealed similar sorption capacities, which are higher than those obtained with ozone-aging. Some other modifications detected after aging the LDPE MPPs (Miranda et al., 2021) were the formation of hydroxyl species (new absorption band at 3673–2960 cm^{-1} associated with O–H bonds) for RT1 and RT2 samples, and the increased intensity (or new absorption peaks) at 1468–717 cm^{-1} after the weathering treatments (to a lesser extent after the ozone gas treatment).

Pronounced modifications of the surface morphology (i.e., more and deeper cracks assessed by SEM – scanning electron microscopy), evidence of colonization by microorganisms (detected by SEM and validated by Raman microspectroscopy) and a higher increase in the degree of crystallinity (determined by XRD – X-ray diffraction) were observed after RT2 weathering, but not (microorganisms) or to a less degree (changes in the surface morphology and crystallinity) for RT1 weathering (Miranda et al., 2021). Since the two weathering treatments originated slightly different profiles only on the sorption capacities for diclofenac, citalopram and clofibric acid, this could suggest that the affinity and consequent sorption of most of the studied OMPs on LDPE MPPs were mainly governed by the surface chemical structure. The antidepressant drug citalopram was the only OMP that sorbed more on RT2 than on RT1 and, therefore, the identified differences observed between RT1 and RT2 samples might benefit the affinity of the LDPE MPPs to some specific compounds.

3.1.1.2. Poly(ethylene terephthalate) (PET). Aged PET (Fig. 2b) showed a very distinct sorption behavior when compared to the other two polymers (Fig. 2a and c). Most of the studied OMPs showed very little to no affinity (particularly tramadol and venlafaxine) to either pristine or aged PET (Fig. 2b), but a clear exception was found for PCP which is markedly sorbed on PET aged by the ozone treatment. This result confirms that ozone can be an effective aging agent in inducing specific changes in the behavior of PET MPPs, as suggested in our previous study (Miranda et al., 2021). In fact, the increased sorption of PCP, from 0.99 ± 0.34 to 7.01 ± 0.21 μg g^{-1} with the ozone-aged samples, may be linked to the widening of the 1714 cm^{-1} peak base, associated with the formation of carbonyl species as detected by ATR-FTIR analysis of PET MPPs aged by ozone (Miranda et al., 2021).

Another noteworthy result is the higher sorption of trimethoprim by the samples obtained in the RT2 weathering experiment (Fig. 2b), which may be related to a new absorption band at 3615–3115 cm^{-1}, associated with O–H bonds as observed in our previous study (Miranda et al., 2021). The formation of hydroxyl species and the increase of the trimethoprim compound sorption were also observed for weathering samples of LDPE (Fig. 2a) and uPVC (Fig. 2c). Thus, hydrogen bonds between the OH groups on these MPPs and the amine groups of trimethoprim may justify these results.

3.1.1.3. Unplasticized poly(vinyl chloride) (uPVC). Both weathered (RT1 and RT2) uPVC samples have evident increased sorption capacities, but RT1-aged MPPs showed an overall higher sorption (Fig. 2c). Although low sorption was verified for both virgin (PCP > alachlor) and ozone-aged (citalopram ≥ PCP = alachlor) uPVC MPPs, the weathering treatments led to the sorption of almost all OMPs (RT1: citalopram = florfenicol = trimethoprim ≥ venlafaxine > PCP = tramadol = diuron = alachlor ≥ diclofenac; RT2: florfenicol = PCP = citalopram = trimethoprim > diuron = alachlor = diclofenac = venlafaxine ≥ tramadol). However, the sorption degree of most of OMPs (florfenicol, diclofenac, alachlor, clofibric acid, diuron, and PCP) was inferior to that observed for LDPE, and clofibric acid was not sorbed to uPVC.

Similarly to LDPE, no universal rule was found between pK_a or log K_{ow} and the affinity between uPVC and the OMPs. Still, there seems to be a different trend by which higher pK_a usually leads to higher sorption capacity on uPVC. This suggests that the OMPs molecular or cationic forms have a higher affinity for uPVC (at pH ca. 5.8, where the surface of uPVC is expected to be negatively charged) (Wu et al., 2019), indicating that electrostatic interactions may also be a relevant mechanism in the sorption process, as has been reported in the literature for PVC (Guo et al., 2019a, 2019b; Puckowski et al., 2021). Nevertheless, further experiments would be necessary to examine the effect of the solution pH and the interaction of each individual OMP studied with uPVC.

The increase of the carbonyl and polyene absorbance peaks intensity in the ATR-FTIR analysis previously reported (Miranda et al., 2021) for the weathered uPVC MPPs may be linked to the increased sorption capacity observed for these samples. Moreover, this assumption is further supported by the higher Carbonyl Index of RT1 samples (virgin: 0.73 ± 0.15; RT1: 4.82 ± 0.27; RT2: 3.37 ± 0.12) and the higher sorption capacity observed for several compounds on RT1-aged uPVC MPPs, with the main exceptions being diclofenac, alachlor, diuron and PCP. The low sorption capacity observed in the present study for ozone-aged MPPs is corroborated by the lack of major changes in uPVC after aging (Miranda et al., 2021). Therefore, similarly to aged LDPE, the Carbonyl Index can be a good indicator to estimate the global sorption capabilities of uPVC MPPs, although it is not valid for every single OMP.

3.1.1.4. Comparison to other reports in the literature. The sorption capacities obtained in the present study are overall much lower than those reported in the literature for the same polymers and OMPs already investigated, namely for: diclofenac with virgin and Fenton oxidized PET and high-density polyethylene (HDPE) (Munoz et al., 2021); PCP with virgin and extracted from personal care products LDPE and PET (Loncarski et al., 2020; Tubić et al., 2019); and trimethoprim (in freshwater or seawater matrices) with virgin polyethylene and PVC (Li et al., 2018). Nevertheless, other studies showed more similar results, as that published by Elizalde-Velázquez et al. (2020), studying diclofenac sorption (diclofenac: q_e < 0.08 μg g^{-1} for C_0 ca. 2.5 mg L^{-1}) on virgin ultra-high molecular weight polyethylene (UHMWPE) and average molecular weight polyethylene (AMWPE) (among other OMPs and polymers), using the same load of MPPs (10 g L^{-1}) of the present study. The study of diuron sorption on LDPE, PET and PVC obtained from plastic waste was demonstrated by Godoy et al. (2020) to be negligible, which agrees with that observed for virgin MPPs and all PET samples in our study, but not for the samples of weathered MPPs of LDPE and uPVC. The ambiguity between the sorption capacities reported in the literature can result from different methodologies followed and also depends on the MPPs used (e.g., particle size distribution).

3.1.2. Pentachlorophenol sorption on microplastic particles

The sorption behavior of PCP on both virgin and ozone-aged MPPs of LDPE (Fig. 2a) and PET (Fig. 2b) justified the selection of this OMP for further experiments aiming to study its sorption equilibrium isotherms on these types of MPP samples. The results show that for each polymer, the ozone-based aging greatly increased the sorption capacity (Table S13 of the SM; Fig. 3).

From the three investigated mathematical models (Langmuir, Freundlich and linear), Langmuir fitted better for ozone-aged PET, while Freundlich was the best fitting for the other 3 datasets (Table S14 of the SM). Thus, equilibrium PCP sorption on ozone-aged PET seems to be better represented by a monolayer homogeneous adsorption model than the virgin PET and virgin and ozone-aged LDPE. As reported previously, even

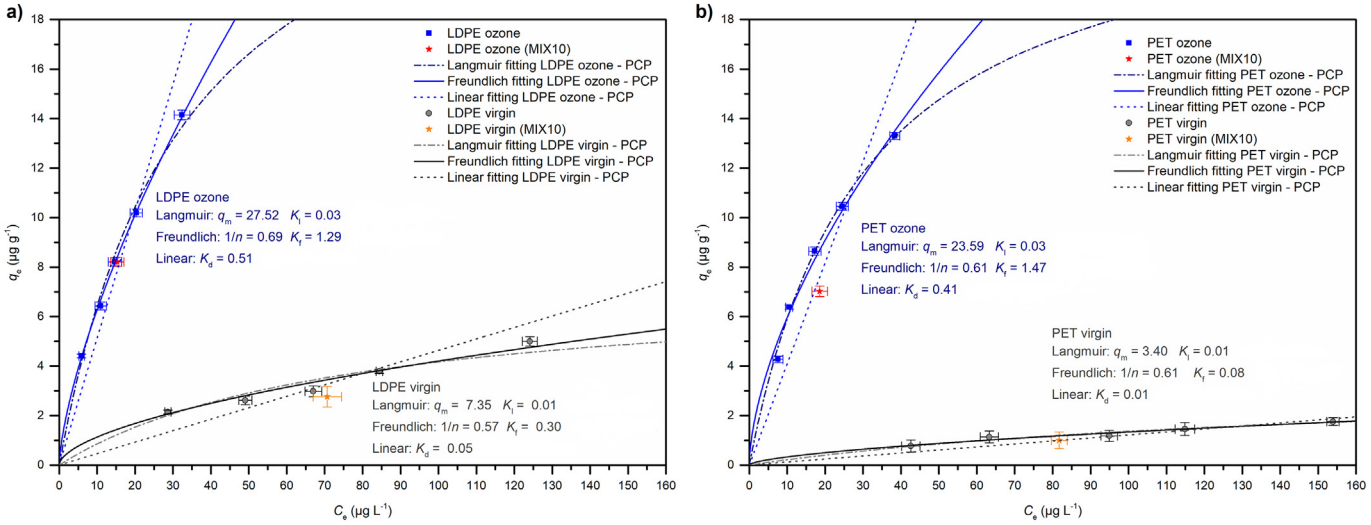

Fig. 3. Sorption equilibrium isotherms: pentachlorophenol (PCP) sorbed per unit of mass of MPP (virgin and aged by ozone treatment), for a) low-density polyethylene (LDPE), and b) poly(ethylene terephthalate) (PET). ★ represent the experimental data of PCP in Fig. 2a and b, i.e. the PCP sorption on (virgin or ozone aged) LDPE or PET when in solution with a total of 10 OMPs.

though microplastics can have irregular shapes and non-uniform surfaces when analyzed under the microscope, the sorption can be represented by the Langmuir isotherm, by which there is macroscopic homogeneous adsorption (Wang and Guo, 2020b).

PCP had a higher affinity for LDPE than for PET under all the conditions tested but more discernibly for virgin MPPs, as respectively inferred in Fig. 2a and b, and supported by Fig. 3. The opposite behavior was described by Loncarski et al. (2020), i.e. PCP sorption isotherms for virgin MPPs of polyethylene and PET showed higher affinity of PCP to PET, and also higher sorption capacities of both polymers when compared with our results.

Although it cannot be excluded the competition and synergistic effects among the 10 OMPs studied, the results of PCP sorption either when spiked individually or spiked simultaneously with other 9 OMPs are similar (Fig. 3), making these effects mostly negligible under the conditions tested. The use of sorbates at trace concentrations helps reducing these effects, while also allowing to perform the study in more environmentally relevant concentrations and with multiple analytes in solution.

More studies need to be developed in this field since this OMP is already targeted as a priority pollutant and considering that the realistic conditions in our environment favor the occurrence of aged MPPs.

3.2. Phytotoxicity of microplastic particles carrying organic micropollutants

MPPs have been identified as emerging pollutants in soil-plant systems, although there are still research gaps regarding the behavior and the extent of the effects of MPPs on these systems (Zhang et al., 2022). One of the identified sources of both soil MPPs and OMPs is the use of treated wastewater and biosolids in agriculture, since many OMPs are not efficiently removed during wastewater treatment (Chavoshani et al., 2020; Ng et al., 2018; Pérez-Reverón et al., 2022). Considering the observed sorption of some of the studied OMPs on MPPs in the previous section (3.1), it is worthy to investigate the MPPs being transported into soil-plant systems while carrying OMPs. Therefore, phytotoxicity tests were carried out with two species of plants: *Lepidium sativum* and *Sinapis alba*. The seed germination and the roots and shoots length mean and SD for each type of test plate and experiment are listed in Table S15 of the SM. The results were compared and analyzed using the one-way ANOVA and post hoc Tukey test, and the percentage effect of the different combinations tested of OMP and/or MPP on root and shoot growth was estimated (Table S16 of the SM).

For both species of plants, the seed germination does not show signs of being affected by any of the conditions tested, with only one seed of *Lepidium sativum* developing a root with <1 mm in length (ozone-aged LDPE). The species *Lepidium sativum* early growth was impacted when a solution containing at least 50 µg L^{-1} of each of the 10 OMPs was used (roots = 40 % effect; shoots = 32 % effect), but no significant changes were observed when the seeds were exposed to virgin MPPs (LDPE, PET or uPVC) or virgin/aged LDPE with or without sorbed OMPs (roots ≤0 % effect; shoots ≤9 % effect). A study of MPPs acute toxicity (6 days) by Pignattelli et al. (2020) has shown that virgin polyethylene and PVC can negatively affect the germination rate and plant growth of *Lepidium sativum*, but this effect was not observed in our study.

On the other hand, *Sinapis alba* early root growth decreased when at least 50 µg L^{-1} of each of the 10 OMPs was used (roots = 57 % effect), but that concentration was not sufficient to originate significant changes in the shoots early growth (shoots = 9 % effect). For that species, a higher concentration of the 10 selected OMPs is needed (such as 100 µg L^{-1}: roots = 70–79 % effect; shoots = 35–39 % effect) to lead to the decrease of the shoots early growth. Consequently, as expected, no significant changes were observed for the *Sinapis alba* shoots early growth when virgin MPPs or virgin/aged LDPE with or without sorbed OMPs were used (shoots ≤9 % effect). Overall, for both species, the roots early growth is more negatively affected by the presence of other substances than the shoots.

Contrary to what was observed with *Lepidium sativum*, *Sinapis alba* roots length results suggest that the presence of MPPs with OMPs may negatively affect the early growth of the species, specifically for the MPPs of LDPE that were aged by 13 weeks of weathering (roots = 16 % effect). Nevertheless, these results show a very low decrease of the early growth of this species and, although significantly different (at a 0.05 level) from the negative control, are not significantly different from the other test plates with LDPE MPPs.

The desorption test (Table S17 of the SM) carried out in parallel to the LDPE phytotoxicity test confirmed that the MPPs obtained from the sorption experiments are able to release some of the sorbed OMPs, although the concentration is overall below the method quantification limit when they are detected in solution. Additionally, this desorption test also allowed to confirm, once again, that the weathered LDPE samples (RT1 and RT2) have higher sorption capacities than virgin or ozone-aged LDPE, consequently leading to the higher desorption of OMPs (measured as larger peak areas in the chromatograms). However, the potential release of substances from the MPPs that result from the aging processes was not studied, and that could also contribute to the toxicity of the MPPs since the results are not significantly different between any virgin or aged LDPE MPPs and the correspondent OMP-sorbed MPPs.

These results are compatible with the theory that MPPs can be transport vectors of other pollutants, such as the OMPs studied, with potential adverse effects to biota. However, considering the undetected (*Lepidium sativum*) or very low decrease (*Sinapis alba*) in the species early growth for the controlled conditions tested, the amount of OMPs necessary to negatively impact the early growth of these plants, and the amount of MPPs used and their low release of OMPs, it is unlikely that the combinations of MPPs and OMPs studied may cause major changes to the dynamics of the early growth of *Lepidium sativum* or *Sinapis alba*. Nevertheless, since MPPs can transport OMPs, it cannot be yet excluded their potential adverse effects under specific scenarios, such as with more aged-advanced MPPs, under long-term chronic exposure, or in combination with other sources of OMPs (e.g., other particulate matter with sorbed pollutants). Additionally, other combinations with different OMPs and polymers, outside of those studied, may have more severe impacts.

Therefore, this shows that there is a need to study in more depth the impacts of MPPs on soil-plant systems, particularly after undergoing aging and interacting with co-occurring pollutants. These results should be beheld as a starting point to further understand this capability of MPPs and still leave the toxicity of the combinations studied on soil-plant systems as a possibility.

4. Conclusions

This study allowed to examine the potential of MPPs to be transport vectors for OMPs, demonstrating the major role of the aging degree of MPPs in the sorption process:

- Of the 3 polymers selected, LDPE sorption capacities were the most greatly increased by both ozone exposure and weathering. Likewise, uPVC sorption capacities increased, although mainly after weathering. For these two polymers (LDPE and uPVC), the Carbonyl Index can be a valuable indicator in a preliminary estimation of the global sorption capabilities of the aged MPPs in comparison to virgin ones. PET MPPs were the least affected by aging and, consequently, conserved their very low sorption capacities for almost all OMPs, with the interesting exceptions of PCP on ozone-aged MPPs and trimethoprim on RT2 weathered MPPs.
- Most of the OMPs selected had very low to no affinity to virgin MPPs. While PET kept very little affinity for almost all OMPs even after undergoing aging, few substances had no appreciable sorption on LDPE or uPVC after the aging treatments: LDPE – tramadol and venlafaxine, and uPVC – clofibric acid. PCP was the most sorbed OMP on LDPE and PET, for both virgin and aged MPPs, and thus further experiments were performed to study PCP sorption on LDPE or PET. This provided us with a more clear picture of the sorption of this pesticide on virgin or ozone-aged MPPs.

However, additional research is still needed to understand the sorption process of OMPs to aged MPPs in more complex matrices and to analyze the effect of ionic strength, pH, temperature, and organic matter in solution, as well as other particulate matter that can compete with MPPs (e.g., carbon-based nanomaterials).The undetected or very low decrease in the early growth of the plant species *Lepidium sativum* and *Sinapis alba*, under the conditions tested with LDPE MPPs, suggests that the studied combinations of OMPs and MPPs are unlikely to deeply affect the early growth dynamics of these plants. Still, since MPPs can sorb and, consequently, transport OMPs, and aging can increase their sorption capacities, there is a need for further research on the toxicity of MPPs with sorbed pollutants on soil-plant systems.

Considering the importance of the MPPs aging degree in their sorption capacities, it is imperative that future studies on microplastics behavior and effects use aged samples, obtained from aging virgin samples in controlled conditions, to work with more environmentally relevant MPPs and to avoid underestimating the sorption capacities of the polymer under study. Nevertheless, virgin samples should also be included in each study, as that will help to compare results between different research projects and studies, since there is still no standard methodology for aging microplastics for this type of research. It should be considered that by working with aged MPPs obtained by controlled aging treatments, there will be a limitation on the number of experiments that can be performed based on the amount of MPPs recovered from those aging treatments. Thus, it is fundamental to develop protocols for aging microplastics specifically for sorption experiments and/or for assessing the effects on biota, allowing more collaborative efforts and faster and more efficient progress in this field of research.

CRediT authorship contribution statement

Mariana N. Miranda: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **Ana R. Lado Ribeiro:** Methodology, Writing – review & editing. **Adrián M.T. Silva:** Supervision, Methodology, Writing – review & editing. **M. Fernando R. Pereira:** Supervision, Conceptualization, Funding acquisition, Writing – review & editing.

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.2022.158073.

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