Evaluation of microplastics release from solar water disinfection poly (ethylene terephthalate) and polypropylene containers

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HIGHLIGHTS

- MPs were detected in the water from the three SODIS devices studied.
- Weathering effects on particle surface can cause misidentification of PP MPs.
- Addition of a clarifier in PP formulation did not have an effect on MP release.
- PP TJCs experienced higher MP release than PET bottles due to low photostability.
- MP particle size has been correlated to potential health hazards in human beings.

GRAPHICAL ABSTRACT
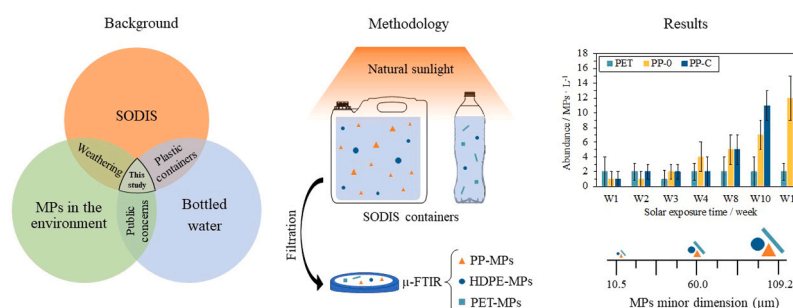
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ABSTRACT

Public health concern associated with the ingestion of microplastics (MPs) released from water packaging materials is increasing. The use of plastic materials for solar disinfection (SODIS) containers has also raised concerns in the SODIS community due to the lack of studies evaluating the presence of MPs in the treated water. In this work, the migration of MPs from poly(ethylene terephthalate, PET) bottles and polypropylene (PP) translucent and transparent jerrycan containers (TJC) into water under natural weathering was investigated using micro-reflectance Fourier Transform Infrared Spectroscopy (μ-FTIR). Containers exposed to sunlight for three months became photodegraded, releasing micro-sized fragments identified as PET, PP and high-density polyethylene (HDPE, from the screw-caps), although with varying degrees of weathering. It is noteworthy that the presence of a clarifying additive in PP formulation did not seem to impact the release of MPs from the containers. The study showed that PP TJC containers released more MPs than PET bottles. Finally, the size of MPs was measured to determine their fate upon ingestion and highlights the need for further studies to understand the safety of these plastic containers for SODIS.

1. Introduction

The earliest evidences of small plastic pieces (1 μm to 5 mm size, now called microplastics, MPs) in seawater were observed by Carpenter and Smith in 1970s [1,2]. Since then, interest in MPs has been ever-growing within the scientific community and society. Over the years, the optimisation of sample preparation procedures, along with the improvement of microscale-focused analytical techniques, has allowed the detection of MPs in many environmental settings: sediments [3], atmosphere [4], freshwater [5], etc. In particular, infrared microspectrometry (micro IR or μ-FTIR) has become the most common technique to identify and characterize putative MPs [6-8].

Recently, the detection of plastic particles in human blood and stool [9,10] has attracted widespread media attention, increasing public concerns. Direct ingestion is one way that MPs can enter the human body [11]. Several studies have detected MPs in mineral water, soft drinks and beverages (beer, milk, etc.) and concluded that their packaging containers were the primary candidate source of MPs [12-14]. Despite a growing body of research providing evidence regarding the presence of MPs, mixed results coupled with a lack of knowledge of the risks associated with the exposure of humans to MPs have raised questions regarding the safety of the use of plastic containers for the storage of potable liquids [15].

In most high-income countries there is a rising demand for bottled water mainly due to intensive commercial marketing and the consumer's perception of its "higher quality" and better "taste" compared to tap water [16,17]. Meanwhile, in low-to-medium-income countries, the lack of guaranteed water treatment facilities cause real concerns about the safety of tap water. Consequently, citizens are often forced towards the use of additional safety precautions before using tap water and/or the purchase of bottled water [18]. Among the poorest and most vulnerable populations in these countries, solar water disinfection (SODIS) is a popular technique to obtain safe drinking water at household level. SODIS involves the solar exposure of microbiologically contaminated water in transparent containers. This technique is simple, inexpensive and sustainable [19].

Usually, 2 L poly(ethylene terephthalate, PET) bottles are used for SODIS treatment as they are low-cost, easily available, portable and robust. In practice, while bacteria can experience direct cell damage through the action of solar UV–A radiation (320–400 nm), the photo-inactivation of viruses and protozoa is negligible without a synergistic temperature contribution since PET does not transmit UV–B radiation (290–320 nm) [20]. As a result, alternative polymeric materials such as polypropylene (PP), poly(methyl methacrylate, PMMA), etc. have been considered suitable for SODIS applications [21]. However, it is well-known that prolonged solar exposure alters the material properties of plastics due to weathering and therefore, potentially affect the final outcome of SODIS.

Weathering refers to all the physical and chemical processes that a polymer undergoes as a result of the combined effect of UV-Vis radiation, temperature, the presence of radical species of oxygen, humidity and other environmental factors. For instance, an investigation conducted by García-Gil et al. [22] found a reduction in radiation transmittance, along with an increase in brittleness of both PET and PP under accelerated weathering conditions. Given that SODIS relies on the amount and type of radiation received by the water [20], researchers have explored the use of additives in the formulation of containers to enhance the optical and mechanical properties, to improve the inactivation efficacy and lifetime, respectively [23,24]. Particularly, clarified PP containers, with enhanced transparency and rigidity [25,26], have also been contemplated for SODIS applications.

The use of additives in plastic formulation has given rise to understandable concerns from users and consequently, have lead to extensive chemical and toxicological studies of water treated by SODIS to demonstrate it is safe for ingestion. Neither mutagenicity nor estrogenicity was detected in water from PET and PP containers exposed to sunlight for six months [27,28]. Nevertheless, they noted that cytotoxicity and endocrine disruptive activities should be considered. O'Dowd et al. [29] conducted toxicity analysis using the MTT assay of water samples stored in PP transparent jerrycans (TJC) over 9 months and they found that all samples had a cell viability of above 80%. According to ISO 10993–5, this indicates the samples are non-toxic to the cell line and are biocompatible. It is worth noting that some preliminary results have shown that MPs induce adverse effects in human cells regarding cytotoxicity and immune responses [30]. However, to the best of the author's knowledge, there is no conclusive information regarding the release of MPs from weathered SODIS containers into disinfected water.

It has been proven that degradation of the polymer surface entails the formation of cracks and holes, ultimately which form the sites for the generation of MPs that can migrate into water [31-34]. This study aims to detect and characterise MPs (if any) in water treated in SODIS containers under natural solar radiation. The paper compares different SODIS containers to understand the effect on the release of MPs of polymer type, the presence of optical clarifier additives in the formulation and weathering of the materials. It also reviews the changes observed in infrared microreflectance spectra due to photodegradation and discusses the importance of a sound spectral interpretation in the correct identification of weathered MPs and their subsequent quantification. Finally, it classifies the measured MP sizes to encourage further studies in the field.

2. Materials and methods

2.1. Samples – SODIS containers

SODIS practitioners usually use 2 L PET bottles, which, individually, do not provide the quantity of treated water needed for a typical family. Higher volume SODIS containers can meet these requirements and have been implemented in several studies. These include 19 L polycarbonate containers in India [35], 20 L PP buckets in Malawi [36], and 25 L PET jerrycans in Ethiopia [23]. In the present study, the release of MPs into water from plastic surfaces was analysed for three types of SODIS containers: 2 L PET bottles and two different 10 L PP jerrycans – translucent (without clarifier additives in the formulation) and transparent (with a clarifier additive).

Two litre PET bottles of an international brand of mineral water were purchased at a local supermarket. These were emptied and their labels removed. The 10 L transparent and translucent jerrycans (TJCs) used in this work were supplied by Glow Packaging Pvt. Ltd. (New Delhi, India) and belong to a collection of prototypes developed within the PANI-WATER project (see www.paniwater.eu [37]), for use in resource-poor areas in India. The 10 L TJCs were made of food-grade PP and were manufactured via blow moulding.

Polypropylene was chosen as the most suitable material for the manufacturing of TJCs because it allows a trade-off between lifetime, cost and disinfection efficacy [21,22]. Since pure PP is a translucent material, transparent PP jerrycans were fabricated with 3% w/w of a clarifying additive (CL-PPRO®, Penn Color, Pennsylvania, United States). The 10 L PP TJCs, without and with clarifier, are denoted as "PP-0″" and "PP-C", respectively (see Fig. 1). Both types of SODIS containers had high-density polyethylene (HDPE) screw-caps. Details regarding the optical and mechanical properties of the container materials can be found in [22].

2.2. Experimental procedure

All PET bottles and TJC containers were thoroughly rinsed and filled with 2 and 10 L of ultrapure water (Milli-Q®, Millipore Corp., Germany, 18 MΩ·cm resistivity), respectively. The capped containers were then exposed to natural sunlight on the rooftop of one of the Rey Juan Carlos University facilities (Móstoles, Spain, −40.34° N, 3.88° W, see Fig. 1) between the end of January and April 2021. The containers were placed
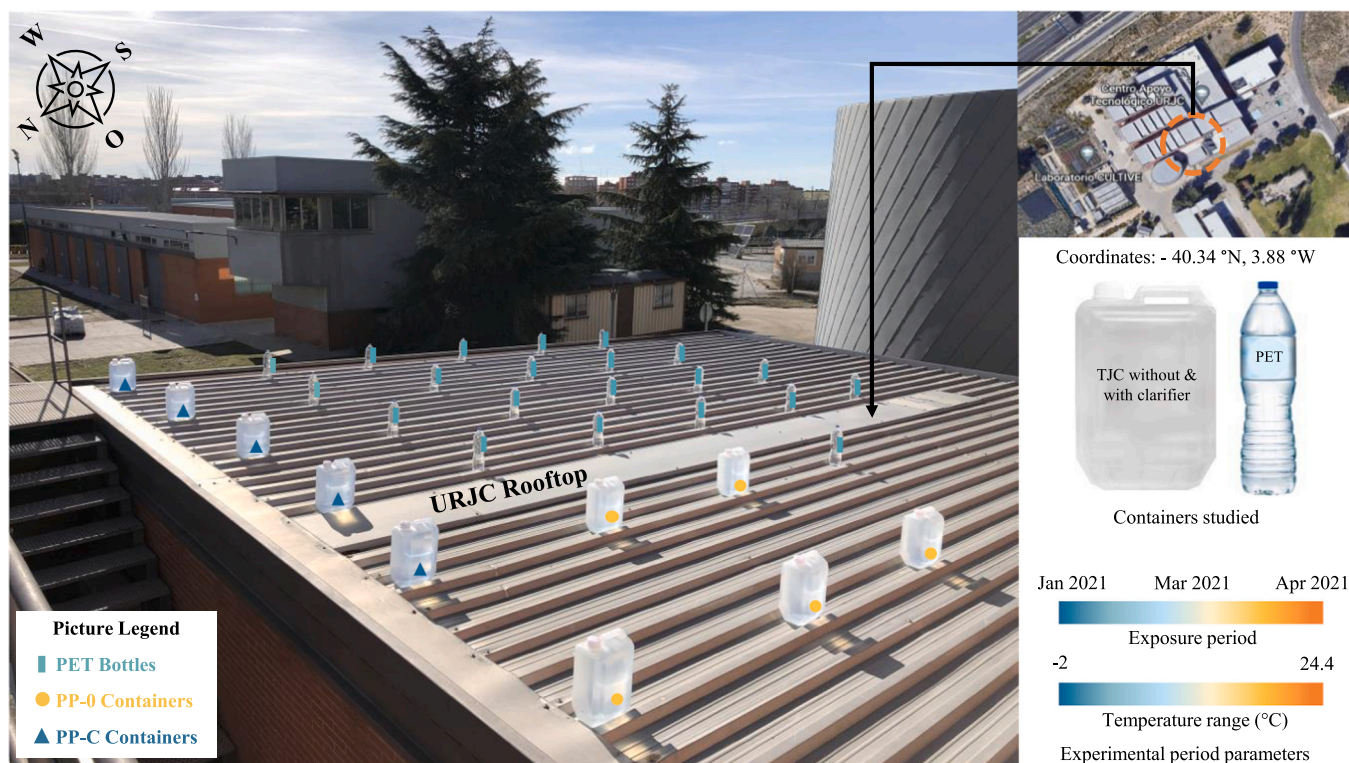
Fig. 1. Arrangement of containers on the rooftop at Rey Juan Carlos University (URJC) facilities under natural solar radiation.

at equal distances from each other to ensure unobstructed exposure. Containers of the same type were deployed in triplicate for each sampling time. The bottles were exposed for a total of 12 weeks and the samples were obtained at weeks 1, 2, 3, 4, 8, 10 and 12. Exposure and sampling dates, along with the average temperature at each exposure time, are listed in Table S1 (Supplementary Material, SM). Note that the samples correspond to a full bottle/container of water, no aliquots were withdrawn.

PET is amenable to hydrolysis [38-41] and, hence, to ascertain this effect three bottles were kept away from light, at room temperature, for 4 and 12 weeks. These dark control samples have not been carried out for the PP TJCs because it was reported that for PP the rate of hydrolysis is several orders of magnitude lower than thermal- and light-induced degradation [42].

2.3. Sample collection

At each predefined time (see above), the entire contents of the SODIS containers were stirred manually and filtered through a 47 mm diameter, 0.7 μm glass microfiber filter (GF; Mervilab S.A., Spain) using a vacuum pump (Optic Ivymen System, COMECTA, Spain) and a vacuum glass filtration system (Mervilab S.A.). Filters were then placed in capped 60 mm diameter × 15 mm height polystyrene (PS) Petri dishes (Fisherbrand®, United States) and dried at 37.5 °C for 48 h in a heating chamber (Binder GmbH, Germany). Any possible MP contamination originating from these Petri dishes can be excluded since PS does not constitute a target MP in this work.

2.4. Contamination control

All components of the filtration system were washed with soapy water and rinsed with ultrapure water prior to every filtration process. All glass- and metalware were covered with aluminium foils when not in use. In order to set negative controls, 2 L and 10 L of ultrapure water were filtered through glass microfiber filters the same day the SODIS

containers were filled. Neither PP nor HDPE were detected in any blank sample, hence confirming that the source water tank is not a source for MPs. However, synthetic (polyacrylic and polyester, predominantly) and cellulosic fibers, likely from the laboratory environment were found in samples because clean air conditions could not be ensured during this study. For that reason and to avoid overestimations, an additional atmospheric control sample was made. Fibers observed in the samples of interest were not counted. For further information on the fibers detected, refer to Supplementary data (Figs. S1-S3).

2.5. Analytical characterisation

A visual examination of all suspicious particles retained on an area corresponding to one quarter of the filter was performed using a Spotlight 200i® microscope coupled to a 400-Frontier FTIR spectrometer (PerkinElmer, United States). The microreflectance spectrum of the particles deposited on the filter membrane were recorded using the instrumental parameters listed in Table 1. The settings reported in this study are in line with the minimum requisites stated in Andrade et al.

Table 1
Instrumental settings for the FTIR microreflectance measurements throughout this work.

Instrumental parameter	Setting
Working technique	Reflectance mode
Microscopy scanning aperture	Adjusted according to particle size
Wavenumber range	4000–600 cm^{-1}
Nominal spectral resolution	8 cm^{-1}
Number of scans per spectrum	20
Background	For each particle analysed / gold surface
Apodization mode	Strong
Spectral treatment	Baseline correction, unit normalisation and Kubelka-Munk transformation.

[6], to enable reproducibility when using μ-FTIR for the analytical characterisation of MPs.

To correct for ambient conditions affecting IR spectra, background scans were performed periodically on a gold-coated surface. However, since the microscope aperture has to be adjusted for different sizes of particles, corresponding backgrounds were carried out accordingly. Spectral processing consisted of a baseline correction (data points in the region of 4000–3800 cm^{-1} were set to zero), a unit normalisation to a [0,1] range and a Kubelka-Munk transformation. The Kubelka-Munk algorithm was applied to transform raw reflectance data to absorbance-like spectrum since particles with a rough surface diffusely scattered the IR beam. Thus, all spectra presented in this article are expressed in Kubelka-Munk (K-M) units.

Note that the spectra of the polymers exhibit a rising curvature due to interference from the underlying glass fiber (GF) filter. This curvature was not suppressed for further analysis, as it was seen that characteristic reflectance features of the polymers were clearly distinguishable, as seen in Fig. 2.

For the purpose of this study, an ad-hoc library was created with microreflectance spectra of pristine polymers, recorded using the settings listed in Table 1. For each candidate particle observed, its reflectance spectrum was compared with those included in the ad-hoc spectral library using the Spectrum software (version 10.5, PerkinElmer, Inc., 2015) which calculates a correlation index (CI) between the two spectra. Only matches with CI > 0.7 were considered and, additionally, the spectra of the unknowns and the proposed assignations were assessed visually to avoid false identifications. The ad-hoc library was continuously updated with reliable weathered spectra obtained in this study for each sampling time. A schematic representation of the steps involved in the identification and analysis of MPs can be seen in Fig. S4.

The surface morphology of the MPs was observed using a JSM-7600 F Field Emission Scanning Electron Microscope (SEM, JEOL, Japan) at an accelerating voltage of 5 keV. The glass fiber filters were cut, deposited on a carbon foil tape and mounted on aluminium stubs. To minimise charging, samples were sputtered with a thin layer of gold using a Q150RS rotary pumped coater (Quorum Technologies, United Kingdom).

For comparisons between containers, it is worth noting that the results presented in the following sections of this article are based on the number of particles detected in one litre of filtered water. This was carried out in two steps. First, by extrapolating the total number of particles in one quarter to the whole filter area to calculate the total number of particles on the filter. Next, this value was divided by the total volume of filtered water to estimate the number of particles per litre of water.
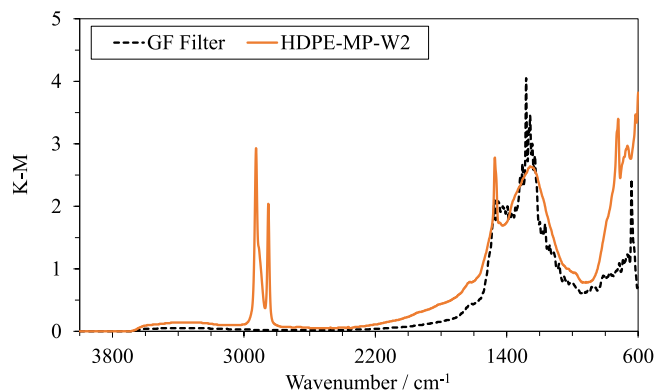

Fig. 2. Effect of the underlying glass fiber (GF) filter on the baseline of an HDPE MP microreflectance spectrum.

2.6. MP size estimation

Particle size is an indicator of the potential effect on health, since it influences their final destination within the human body [43,44]. To measure the size of the MPs, their major and minor axis dimensions were measured using the ImageJ software (v.1.53a) after uploading the photographs obtained from the Spotlight 200i PerkinElmer microscope.

2.7. Statistical analysis

A Student's *t*-test was conducted to determine if the release of MPs from the different SODIS containers (PET bottles vs TJC containers) is similar, at each exposure time. Based on the number of samples in each dataset, a one-sided analysis has been chosen [45] and the compared means were the average of the triplicates detailed above. Error bars represent the 95% confidence level (p = 0.05) using the Student's *t*-test.

3. Results and discussions

The presence of MPs in treated water from SODIS containers was analysed by filtration of the contents after exposure to sunlight over a period of time. From a visual inspection under the microscope, the appearance of certain micro sized particles were observed on most of the filters. For instance, Fig. 3 shows particles found after 2 weeks of solar exposure. Their subsequent characterisation confirmed their polymeric nature (spectra in Fig. 3) and thereby, the release of MPs from SODIS containers under natural solar radiation. Only MPs corresponding to the three target polymers (PET, PP and HDPE) have been considered in this study. Other particles of unknown nature have not been counted and/or reported.

In the following sections of this article, the release of MPs is discussed for each type of SODIS container first (Sections 3.1 and 3.2), after which a comparison between them is drawn (Section 3.3.) and finally, the size distribution of the detected MPs is evaluated (Section 3.4.).

3.1. Microplastics released from PET bottles

Two clearly distinguishable types of polymeric particles were observed on the filters, i. e., PET and HDPE, as the microreflectance spectra were in close agreement with their respective pristine counterparts (like those observed in Fig. 3). The number of PET and HDPE MPs found from PET bottles over the period of solar exposure is plotted in Fig. 4a. It is apparent that for PET bottles, the release of MPs (regardless of polymer type) is practically constant over time.

PET spectra remained essentially unchanged over time with weathering (see Fig. S5). This finding is consistent with Fernández-González et al. [32], who concluded that the stiffness and high thermal stability of commercial PET polymers (which contain UV-protecting additives, termed scavengers) led to negligible changes during the studied weathering time.

Photo-oxidative degradation resulting from the action of UV radiation and oxygen radicals [46] is the primary pathway for the weathering of plastics. However, for PET, hydrolytic degradation can accelerate its weathering. For that reason, dark control samples from Section 2. 2. were filtered and analysed to identify and quantify the number of MPs released by PET bottles as a result of hydrolysis, unrelated to solar exposure. No MPs were observed on the filters, confirming that no PET fragmentation took place in the dark during the studied storage time. This agrees with Gewert et al. [39], who stated that hydrolysis under room temperature conditions is extremely low. Therefore, the potential contribution of hydrolytic degradation to the overall number of MPs released has been neglected in this study.

3.2. Microplastics released from TJC containers

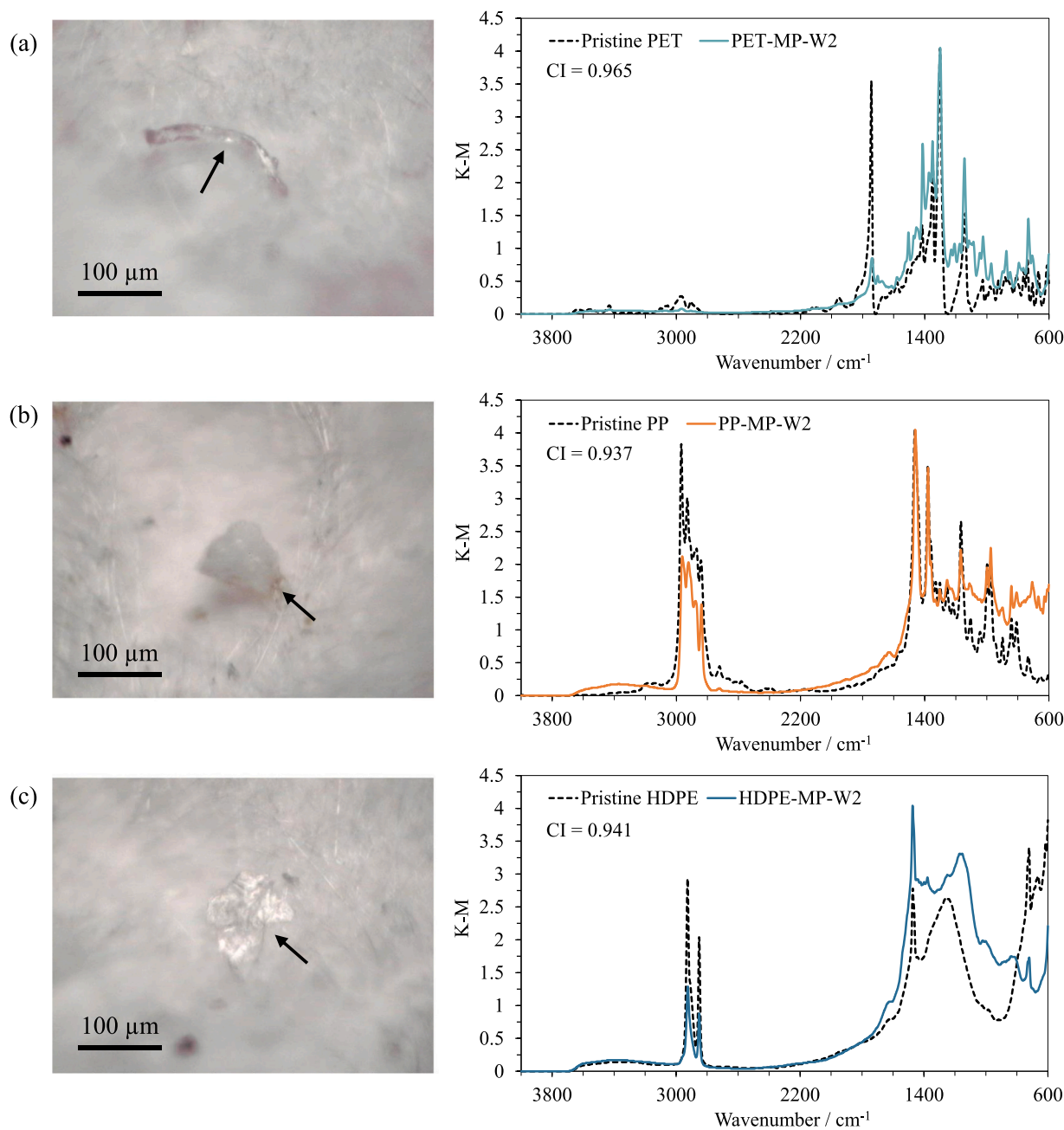In the case of filters taken from TJC containers, MP particles were

Fig. 3. Comparison between the IR spectra of putative MPs in water recovered from SODIS containers after 2 weeks (W2) of solar exposure (alongside their photographs) and pristine polymers (from ad-hoc library) – (a) PET, (b) PP and (c) HDPE.

identified as PP and HDPE when compared to the pristine spectrum. The abundance of MPs is presented in Fig. 4b. Note that to provide an overview of the MPs released from TJC containers, an average of the total number of MPs detected from both types of containers (PP-0 and PP-C) was taken, based upon the observations presented in Section 3.2.2.

In contrast to PET bottles, the release of PP MPs from TJC containers exhibited an exponential increase with solar exposure time (Fig. 4). This might be related to the rise in monthly average temperatures during the study, as temperature affects the degradation of PP [41]. Experiments described here were conducted during winter and spring in central Spain (January – April 2021, see supplementary data for weekly average temperatures). However, this trend is not seen in the case of HDPE MPs, whose abundance was found to be fairly constant across all the exposure times.

3.2.1. Effect of weathering on the spectra of PP MPs

After a certain period of exposure, the spectra of some particles could not be unambiguously related to the pristine PP polymer (contrary to those observed in Fig. 3). Although some apparent similarities in the spectral profile were seen, deviations between the spectra of pristine PP and those corresponding to the recovered particles (see Fig. 5) were investigated further.

The spectra of such particles retained the two main characteristic peaks of PP, not masked by the GF filter: 1458 cm^{-1} (attributed to the asymmetric and symmetric bendings of the methyl and methylene groups, respectively) and 1376 cm^{-1} (due to the symmetric and asymmetric bendings of the methyl and methylene groups, respectively). However, they presented broad bands in regions where water absorbs IR radiation; i.e., the broad band centred at 3300 cm^{-1} and ca. 1600 cm^{-1}. This corresponds to water molecules entering the polymeric chain
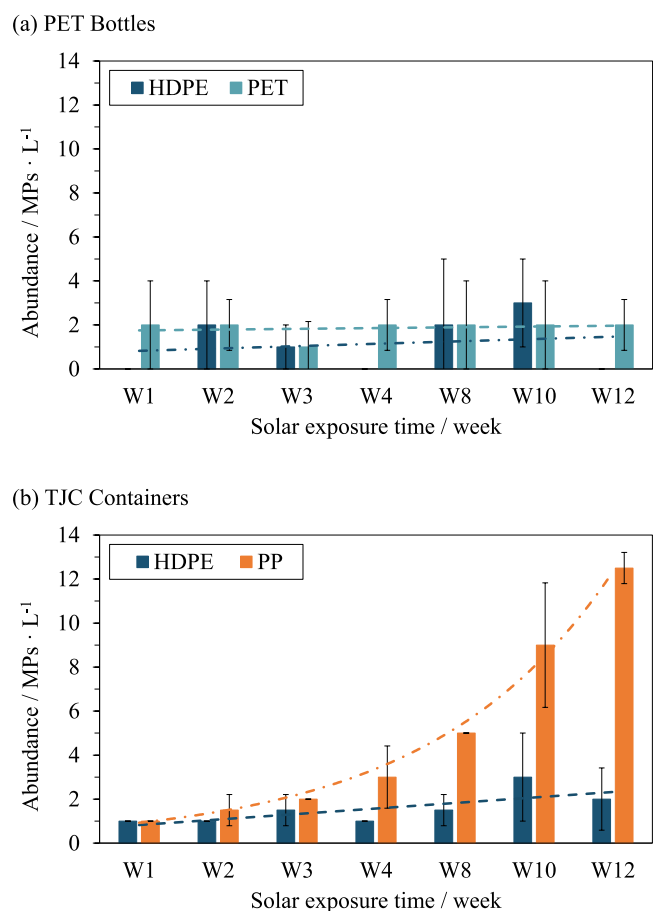
(a) PET Bottles

(b) TJC Containers

Fig. 4. Release of MPs from containers and screw caps (HDPE) for – (a) PET bottles and (b) PP TJC containers. Bars correspond to the average of the total number of MPs detected from PP-0 and PP-C.

through hydration. Additionally, the presence of a clear, strong band ca. 1700 cm^{-1} is associated with the presence of carbonyl groups due to photo-oxidation [32] providing further evidence of weathering in these particles. Given these deviations, it was decided to label them as PP weathered spectra (PP-WS).

Initially, between weeks 1 and 4, the MPs detected are almost pristine whereas from week 4 (for PP-0) and week 8 (for PP-C) onwards, the number of weathered particles (PP-WS) detected, rises sharply until the end of the exposure period (Fig. 6a and b). Obvious differences are visible between orange bars, representing the number of particles clearly identifiable as PP polymer, and dark blue bars that illustrate the sum of all the particles found (PP and PP-WS). This fact highlights the critical need for a re-examination of obtained spectra to ensure that correct identification and estimation of MPs is achieved, instead of relying solely on an automatic identification based on the correlation index. If not, the most weathered particles might be misconstrued and affect the overall count of released MPs.

The photographs obtained indicate that "pristine" particles presented a flat surface and well defined sharp corners, while weathered particles exhibited an irregular shape with undefined edges and a rough surface (Fig. 5). Surface roughness was confirmed with SEM analysis. Similar to the observations made by Mao et al. [47], the surface roughness of the MPs found in this study increased with weathering (Fig. S6). This explains why the number of particles with weathered spectra, increased with exposure time. Additionally, it is well known that reflectance microspectrometry is sensitive to morphological features of particles. Surface irregularities can scatter the IR beam, resulting in distorted spectra [6,8]. This would explain why broad bands

corresponding to the stretching vibrations of the C-H bonds between 3000 and 2600 cm^{-1} appeared slightly distorted in PP-WS, even upon the application of Kubelka-Munk algorithm to the measured spectra.

3.2.2. Effect of a clarifier in the polymer

A clarifying agent is a plastic additive used to improve mechanical performance and alter the optical transmission properties of semi-crystalline polymers (such as PP) by modifying their crystallisation behaviour and morphology during manufacture [48,49]. The addition of a clarifier increases the stiffness of the polymeric materials [25], so it was expected that the release of MPs might be influenced as well, for PP-C (with clarifier) when compared to PP-0 (without clarifier).

Fig. 7 shows the results of the total number of particles detected in both TJC containers (with and without clarifier). In principle, a lower fragmentation of PP-C was expected due to its increased stiffness, thus resulting in a lower release of MPs compared to PP-0. However, clear similarities are evident in the number of MPs detected between both PP containers. This may be due to the fact that the addition of a clarifier improves the transparency in PP-C and increases the number of photons crossing the container wall. As a result, the radiant energy reaching the interface between the material and water is higher compared to PP-0, resulting in a similar photodegradation rate between both PP containers. In any case, it seems that the potentially high photodegradation rate counteracts the higher stiffness of the material.

The addition of a clarifier was recently reported to have no significant impact on the microorganisms' inactivation processes [24]. Similarly the release of MPs is unaffected by the presence of clarifier. Therefore, in the following discussions, these containers will only refer to TJC.

3.3. Comparison between SODIS containers

Container material and exposure time are crucial for SODIS processes to achieve effective disinfection of microbiologically contaminated water and to provide safe drinking water. While this is true, given the rising interest in MPs and their impact on human health, it is important to evaluate the suitability of SODIS containers in terms of MP presence as well. The section compares the two SODIS containers – PET bottles and TJC containers.

Weathering of the containers is expected to increase with cumulative exposure time and, similarly, the amount of MPs [33]. Fig. 8 plots the abundance of MPs in PET bottles and TJC containers. Note that the data presented in Fig. 8 is the total amount of MPs seen from each container.

At first glance, the number of total MPs released by both SODIS containers seems to be low (< 6 MPs·L^{-1} and < 16 MPs·L^{-1} for PET and TJC, respectively). From weeks 1 to 8 of exposure, the release of MPs from both containers is similar and statistically comparable (Student's t-test, p < 0.05). For subsequent exposure times (weeks 10 and 12), a significant difference (t-test, 95% p < 0.05) was observed between the two types of containers. The error bars plotted in Fig. 8 are the 95% confidence intervals. It is clear that in weeks 10 and 12, the number of total MPs released by TJC containers is significantly higher than for PET bottles.

After removing the possibility of external contamination, photo-degradation of the inner plastic surface and screw-caps have been identified as the sources of MPs. It is well known that plastic photo-stability depends on the inherent molecular structure of the polymeric material [39] and thus can be assumed to directly affect the rate of MPs released. PET consists of aromatic rings combined with aliphatic chains making the molecule stiffer than linear polyolefins, such as PP or HDPE, which results in a lack of mobility of the structure, which translates into higher thermal stability and greater resistance to abiotic attack [38]. Moreover, PET has been reported to have moderate photostability [21] thanks to self-stabilising effects. This polymer absorbs light in the near UV region causing degradation and rearrangement at the surface, thus protecting the bulk of the polyester [50]. Polypropylene is formed by
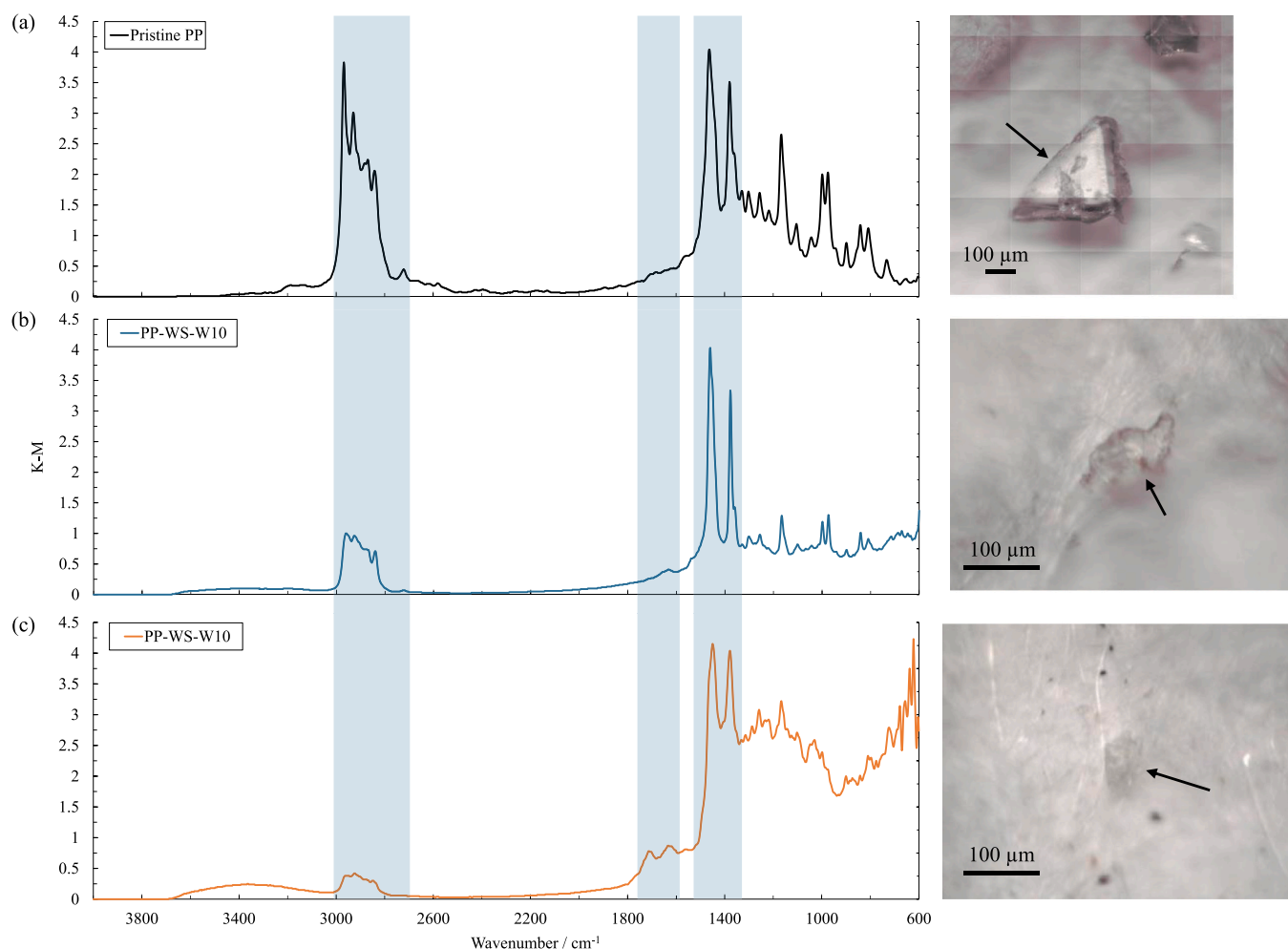
Fig. 5. Comparison between the IR reflectance spectra of (a) a pristine PP particle (from ad-hoc library) and putative particles (b) slightly weathered PP and (c) strongly weathered PP, each recovered after 10 weeks (W10) of exposure time (alongside their photographs).

aliphatic chains where the substituent is a methyl group (-CH$_3$). When exposed to high temperatures and UV solar radiation, the tertiary hydrogen atoms within PP chains are susceptible to attack by oxygen radicals, thus initiating the degradation process [38]. These facts explain what can be seen in Fig. 8. Therefore, the number of PP MPs detected in the PP TJC containers is considerably higher than the number of PET MPs obtained from PET bottles. The PP polymer spectra appeared more weathered and difficult to identify than PET MP spectra.

However, for both types of containers, the number of HDPE MPs does not vary with exposure time and is relatively constant. A note of caution has to be stated here since the screw-caps were not opened/closed during the experimental time period. It is interesting to note that the screw-caps became increasingly brittle with time (due to the low photostability of HDPE polymer) and were prone to breakage with little force applied when the containers were emptied. This has also been reported by Winkler et al. [51], who detected a small number of single flakes of HDPE polymer (comparable to those found in this study, Fig. 3c) from PET bottles with HDPE caps as a result of the application of externally simulated mechanical forces.

Due to photodegradation and absorption of water, potential manufacturing defects on the inner surface of the containers can break off the walls to form cracks and, subsequently, holes. Each crack is a potential source for the release of MPs into the bulk water. Within these cracks, the degree of weathering increases with time until the MPs are released into the bulk. After a certain point of solar exposure time, the MPs are released into the bulk of the container resulting in the obtained

weathered particles. Released MPs submerged in water receive a lower intensity of solar radiation and hence are subjected to a lower photo-oxidation rate [52]. This implies that MPs can remain in water without experiencing additional weathering. This process is schematically presented in Fig. 9.

Once the MP has been released into the bulk, an enlarged surface area of the exposed surface of the inner wall will be subjected to weathering. In this case, the new pristine region is now not only in contact with the water but also closer to the outside layer of the container exposed to sunlight. This layer is much more prone to further degradation than the previous layer and hence is more easily released into the water, especially considering that structural defects are already formed [32].

To summarize, the above discussions confirm and help justify the suitability of PET for SODIS applications. It should be noted that the water analysed within this study does not perfectly represent that used in regular SODIS applications, since containers would be refilled every day and the water not stored for several weeks. Nevertheless, although the safety of the treated water is not compromised over a short period of time, PP TJC containers are not suitable for long-term (more than 4 weeks) SODIS treatment for providing safe drinking water.

3.4. MPs size distribution

Existing studies on animals detected that large quantities of MPs can cause reproductive health decline, inhibit growth rates and organ
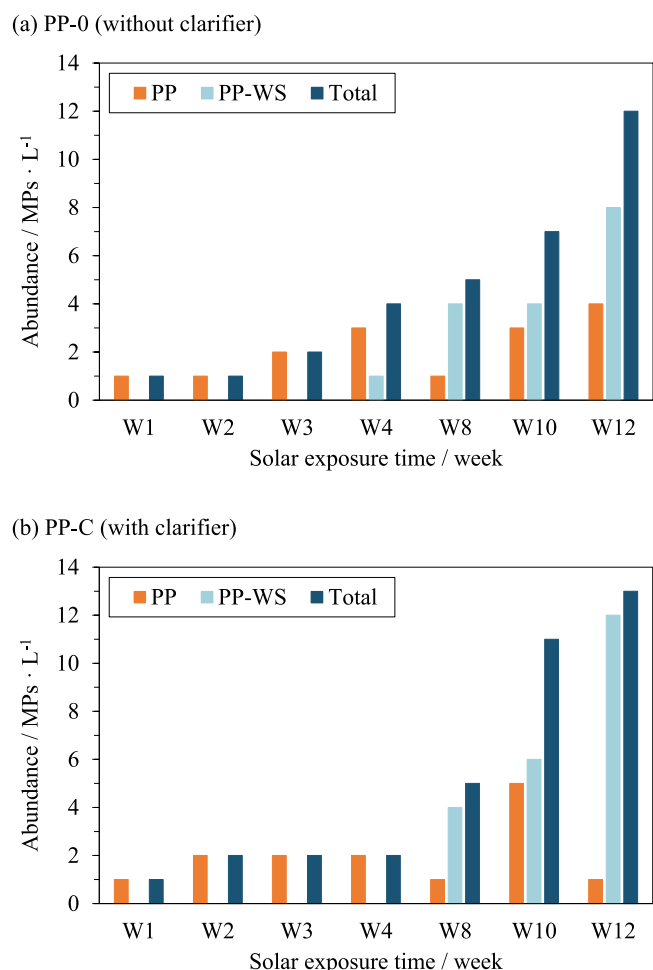
(a) PP-0 (without clarifier)

(b) PP-C (with clarifier)

Fig. 6. Comparison of the number of MPs identified with the spectrum of the pristine PP and those with weathered spectra (PP-WS) for (a) PP-0 container and (b) PP-C container.
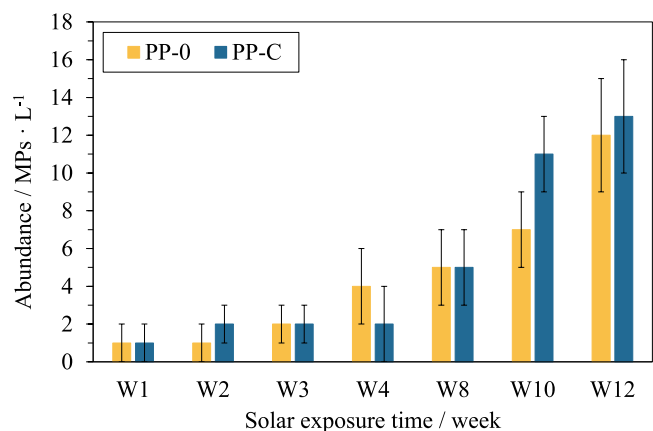

Fig. 7. Release of MPs from containers without (PP-0) and with (PP-C) a clarifier additive (error bars denote standard deviation).

toxicity [53-56]. However, the risks posed by MPs consumed through drinking water on human health are not yet quantified, as there appears to be a lack of extensive and high-quality data. Based on current knowledge, MPs < 20 μm can potentially enter the bloodstream through the intestinal wall and lead to organ damage, while larger particles (50–500 μm) will be excreted via the gastrointestinal system [43,57,53, 44]. Since MP size has an influence on their retention and elimination,
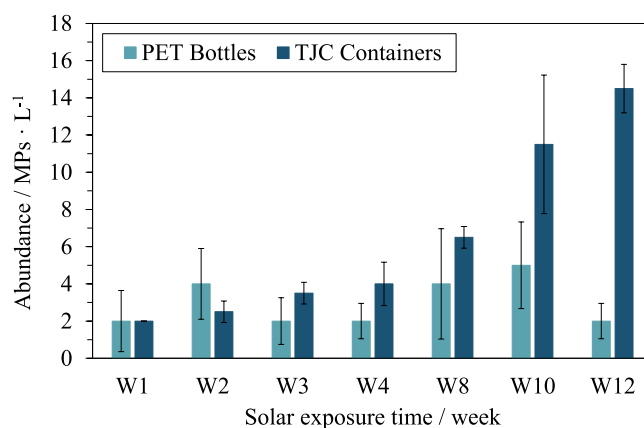

Fig. 8. Comparison of the abundance of total MPs released by SODIS containers (error bars denote confidence interval).

size distribution of MPs detected were analysed to elucidate potential health hazards for SODIS users. Although it is necessary to define three dimensions to describe an irregularly shaped MP, so far IR microscopes cannot measure the third dimension and, thus, only major and minor dimensions were measured for discussions. Results for each target polymer are presented in Fig. 10, irrespective of exposure time.

As can be seen in Fig. 10a, the MPs were in the range of 20–310 μm (major dimension) and 10–110 μm (minor dimension) with the majority of the particles being in 20–80 μm and 10–40 μm ranges, respectively. While PP and HDPE presented more similar values for both dimensions, PET MPs were rather longer in one dimension relative to the other (for example - one particle was 256.3 μm x 15 μm).

Relative particle abundance was classified into 5 size ranges based on the minor dimension: < 20 μm, 20–40 μm, 40–60 μm, 60–80 μm and > 100 μm (Fig. 10b). The occurrence of MPs in the < 20 μm range was not too high (except for PET). While the 20–40 μm size range was identified as the most dominant one, it is worth noting that the instrumental working limit is at 10–20 μm. Some particles with both dimensions < 20 μm were observed on the filters, however, they could not be characterised because small scanning apertures lead to low IR energy reaching the FTIR detector and, subsequently, to a low signal-to-noise ratio, making the spectrum noisy and undefinable [6]. This is a general problem associated to the instrumental limit of detection of any system and should not be overlooked. Unfortunately, little is known about the effect of this size of MPs on human health. Finally, it should be noted that as the particle size increases, their relative abundance decreases.

Considering the results obtained in this study, gastrointestinal uptake of the majority of MPs found seems unlikely. However, they could become reservoirs for pathogenic bacteria such as *E. coli,* in untreated water, as the MPs serve as sites for biofilm formation. The biofilm matrix may provide protection to the bacteria, thereby reducing the disinfection efficiency of SODIS technique and increasing the risk of infections upon ingestion [58,59].

4. Conclusions

This study demonstrated that SODIS containers release MPs into water when exposed to natural solar radiation. Microparticles of PET, PP and HDPE were identified using microreflectance FTIR spectrometry. Spectra of PP particles from TJC containers showed clear evidence of weathering. The use of a clarifier additive did not significantly impact the release of MPs. The origin of the MPs in this study can be two-fold: screw caps and the inner surfaces. It was found that MPs released by the screw caps were quantitatively lower than from the inner surfaces and remains constant with exposure time because the bottles remained unopened until their measurement. Polypropylene TJC containers showed
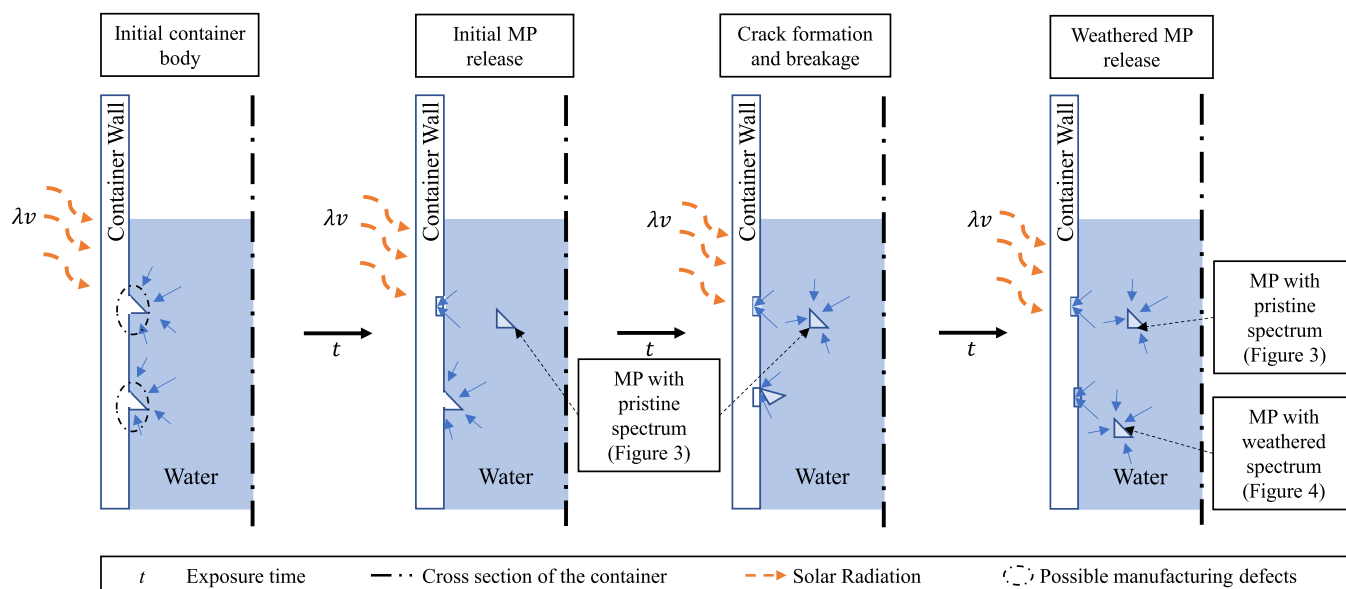
Fig. 9. Schematic representation of the MP release process (not to scale).
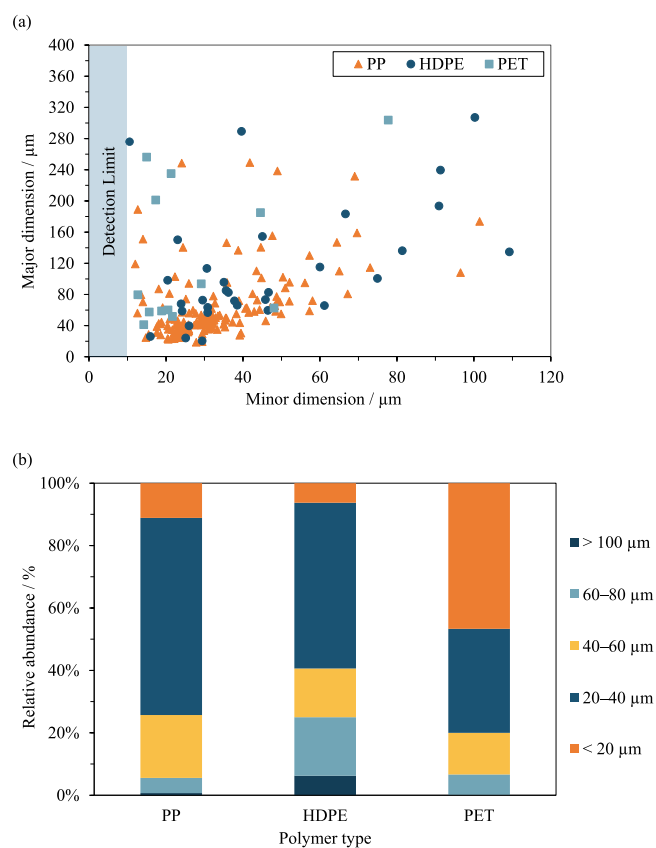

Fig. 10. Size distribution of MPs as a function of polymer type, presented as (a) ratios of major and minor dimensions and (b) abundance based on the minor particle dimension.

an exponential increase in the release of MPs that compromises their long-term suitability for providing safe drinking water via the SODIS process. In contrast, PET bottles showed an almost constant and relatively negligible release of MPs into the water, even within the same water exposed for 12 weeks, confirming its suitability for the production of safe drinking water by solar disinfection of contaminated water

sources. Finally, this study found that PP and HDPE MPs accumulated in the region of 20–40 μm whereas PET MPs portrayed a wider size distribution.

Environmental implication

Solar water disinfection technique (SODIS) employs plastic materials cleared for safety in beverage containers. However, innocuous materials can become hazardous when used for applications other than their intended uses. During SODIS process, the photodegradation of plastic containers can potentially lead to the release of microplastics (MPs) into the treated water, posing a risk on human health. Therefore, the suitability of widely used plastics in the market needs to be evaluated to ensure its safety. At the same time, issues regarding misidentification of MPs have been addressed, serving as a basis for studies on MPs found in the environment.

Declaration of Competing Interest

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

Data Availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.133179.

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