

Oxidative Degradation of Plastic Bottle Tops in an Arid, Terrestrial Environment—Identifying Oxidative Degradation by Infrared Spectroscopy

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Abstract

This communication looks at the photo-oxidation of polythene and polypropylene plastic bottle tops that are placed on soil in a hot arid environment. The degree of oxidation of the plastic is monitored by FT-IR spectroscopy. It is noted that while different bottle top types photo-oxidize at different rates, all show an appreciable level of oxidation after half a year of exposure to the environment. The oxidation leads to brittleness of the plastic, which leads to fissure formation in bottle tops of little thickness. This leads to fragmentation of the material upon impact, making plastic bottle tops an appreciable source of microplastics.

Keywords

Plastics, Polythene, Polypropylene, Plastic Bottle Tops, Fragmentation, Microplastics, Infrared Spectroscopy, Oxidation Index

1. Introduction

As of 2024, more than 359 million metric tons of plastic are produced annually [1]. Of this, 70% remains uncollected plastic waste (PW). PW waste that is released into the environment distributes itself between terrestrial and aquatic environmental compartments [2], where the oceans and especially the ocean floor are seen as sinks for PWs [3]. The sources of PWs are manifold, but have been reported from different regions to stem mainly from bottles/caps (14.9%), PET bottles (12.5%), supermarket bags (9.3%), food bags (6.5%), and food containers (2.1%), where the percentages give averaged approximate values [4]-[6]. In both

the terrestrial and the aquatic environment, WPs are exposed to chemical and physical degradation [7]. Chemical degradation includes photo-oxidation [8] and hydrolytic reactions [9]. Photo-oxidation of plastics such as polythene makes them more brittle, leading to an easier fragmentation upon any physical contact. Also, physical degradation of plastics in general can happen by abrasion through sand/soil or wave movement [10] [11] or by impact, either through the contact with a man-made object [12], an organism [13] or weather-related precipitation [14]. In addition to this, slow enzymatic degradation of plastics can occur through microbial action [15]. All of these degradation processes can lead to the fragmentation of plastics to form meso-, micro and nanoplastics [7] [16]. Microplastics (MPs) are defined as plastic particles less than 5 mm in size, with a lower cut-off at 100 nm, nanoplastics (NPs) as particles that are between 1 - 100 nm in size [17] [18]. While MPs and NPs can be found purposefully made in their small size and then find their way into the environment such as constituents in cosmetic formulations [19] or can be side products of processing or maintenance activities such as of plastic bottle manufacture [20] or the washing of textiles [21], many MPs and NPs are produced by the degradation of macro- and mesoplastic that are already existing in the environment. These particles are then called secondary MPs and NPs [22].

Significant efforts have been devoted to establishing baseline studies of MP presence in different environmental compartments in different regions of the world. Apart from the size distribution of the particles, the nature of the polymer involved in the MP or NP is of interest. The polymer type is often determined through micro-IR and/or micro-Raman spectroscopy, where standard plastics are used for comparison. IR data that is taken from the respective samples is also often compared with spectra databases. Nevertheless, with rare exceptions [23] are spectra shown in publications that show degradation. Computer-aided matching would be facilitated with inclusion of the IR spectra of weathered plastics.

IR-spectra can also be used to measure the extent of oxidation in polythene (PE) and in polypropylene (PP) [24]-[26], and to a certain extent in acrylonitrile butadiene styrene (ABS) [27] and polystyrene (PS). This helps understand the degree of degradation of plastics found in the environment and helps gauge the oxidation rate of plastics in the environment, dependent on the environmental conditions the plastics reside in. Furthermore, infrared assists in analyzing the integrity of plastics as they are still in use. Thus, photo-oxidative degradation of plastics can cause product failure. One such example of product failure was found with a particular brand of automobile seat belts due to the degradation of the seat belts' polymeric release buttons, which was reported in 1999, at that time leading to the recall of 8.8 million cars in the US with a with a potential, calculated total cost of \$ 1 billion [28].

In our research on the fate of plastics in arid environments [24] [29] [30] it could be seen that high UV radiation and high temperatures in the summer contributed to a significant oxidation of especially polythene and polypropylene.

Thus, much of the plastic in soils along roadsides in the Middle East is found to be appreciably oxidized. With plastic screw-tops of plastic drinking bottles [24], which are commonly made out of polythene (PE) or polypropylene (PP), it can be imagined that the time dependence of oxidation could be measured, and an approximate determination of residence time of the respective plastic could be made through the oxidation index as determined by IR spectroscopic analysis of the plastic. It would be expected that there would be a seasonal variation of the oxidation rate of polythene plastics exposed to the environment.

Additionally, it can be anticipated that apart from additives to the plastic, also the color of the plastic would have an effect on the oxidative degradation of the material. Many pigments and dyes absorb UV radiation and in so doing protect the polymer. However, absorption can cause the dyes to enter an excited state where they may react with the polymer or transfer energy to O₂ to form damaging singlet oxygen. The blue pigment Cu-phthalocyanine, as an example, strongly absorbs UV light, and the excited Cu-phthalocyanine may act as a photo-initiator by abstracting hydrogen atoms from the polymer [31]. Its interactions may become even more complicated when other additives are present [32]. Fillers such as carbon black can screen out UV light, playing the role of an effective stabilizer of the polymer, whereas flame retardants tend to cause increased levels of photo-oxidation [33].

The current contribution is a continuation of our work on the entry and fate of plastic and microplastic in the UAE terrestrial environment and discusses the oxidative degradation of plastic bottle tops in the arid environment of the Al Ain area, Eastern Region of Abu Dhabi, United Arab Emirates (UAE). Specifically, it was investigated how quickly oxidation of the plastic on the surface of the tops takes place, whether different rates of oxidation could be discerned for different bottle top types and how quickly oxidation of the bottle tops leads to brittleness sufficient for the bottle tops to fragment upon external impact. For this, pristine plastic bottle caps were placed outdoors on available soil and were exposed to the natural sun light throughout the day. The caps themselves stemmed from popular brands of bottled water and soda from the United Arab Emirates, Saudi Arabia and Germany, including international brands such as Pepsi Cola and Canada Dry, and national brands such as Al Ain Farms (UAE) and Mai Dubai (UAE). Assorted bottle tops were collected on specific dates and were subjected to FT-IR measurements to evaluate the oxidation of the top plastic layer of the tops through the oxidation index (see below).

2. Materials and Methods

On July 31st, 2024, 300 bottles tops from pristine plastic beverage bottles were weighed and placed on soil within the confines of the campus of the United Arab Emirates University, Shiebat Al Oud, Asharij, Al Ain (GPS coordinates: 24.194529, 55.678917). These were studied until Dec. 19th, 2024. The bottle tops were of different color (85 blue, 30 purple, 11 turquoise, 81 green, 40 brown, 17 yellow, 11

pink, 13 red, 1 red orange, 3 white, and 9 golden). Except for 18 bottle caps, which originated from products bought in Saudi Arabia, and 6 bottles caps originating from Germany, all bottles caps were from products sold in the United Arab Emirates. 9 bottle tops were made from polypropylene, the rest from polythene. In addition, a separate but comparable study was carried out from Jan. 1st to June 30th, 2024 with 50 polythene plastic bottle caps of the same type, but of 5 different colors.

In each case, a small number of bottle tops, one from each type and color, both made of polythene as well as of polypropylene was submitted to FT-IR spectroscopy on day 0, and it was noted that on day 0 none of the bottle tops analyzed showed any oxidation. The temperatures of the soil as well as of the bottle tops were measured using a Trister® infrared thermometer, where prior calibration with a normal immersion glass thermometer was carried out. The measurements were carried out at random timings during day-light hours. For this, 11 bottle tops from different makers or of different color but from the same maker were measured daily. For IR spectroscopical analyses, bottle tops were collected on Sept. 15th, 2024 and on Dec. 19th, 2024, washed with de-ionized water to rid them of soil, and dried for 12h at 37°C (Ecocell MMM, Medcenter Einrichtungen GmbH). The surface at the end of the thread of the plastic bottle caps was abraded with a 200 mm flat rasp (Magnusson®). The resulting plastic powders were measured as KBr (Sigma Aldrich) pellets on a Perkin Elmer Spectrum Two and a Thermo Nicolet Nexus 670 FT-IR spectrophotometer, where the transmittance of the KBr sample pellet was recorded in the range 4000 - 500 cm⁻¹ and processed after 32 scans. To quantify the oxidation of the plastic material, the area A under the absorption centered at around 1715 cm⁻¹ (**Figure 1**, area highlighted in yellow) was compared to the combined areas B under the absorptions caused by the vibration due to the C-H rocking deformation centered around 718 and 730 cm⁻¹ (**Figure 1**, highlighted in red). Some samples exhibited traces of water. In those samples, the ν_2 vibration mode which corresponds to H-O-H bending motion is centered around 1595 cm⁻¹ giving an area that overlaps with the absorption band associated with the C=O stretching vibration at 1715 cm⁻¹. The two bands can be de-convoluted with Origin® software. The areas attributed to both absorptions (**Figure 1**, highlighted in green) were attributed 50% to the C=O stretching vibration, when using the weighing method for the quantification of the areas under the absorption bands, as discussed below. The oxidation index (OxI) was defined as $OxI = A/B$. Areas underneath the absorption bands can be obtained using Origin® software. The authors have compared the data from these calculations with weighing on a micro-balance the cut-out areas from paper-printed spectra and found both methods comparable. The oxidation index calculations presented in this paper stem from the second method. Here, for the weighing a Kern balance ABT 220-5DM (readability limit: 0.1 mg/0.01 mg) was used. All measurements were carried out with a triplicate of bottle tops of the same type for each sampling period. The oxidation indices in the current contribution are given as average values with a

simple standard deviation. For the evaluation of the oxidation index of bottle caps made of polypropylene the ratio was taken of the area under the absorption band centered around 1720 cm^{-1} and the combined areas of the absorption bands centered at 1456 and 1376 cm^{-1} .

The elemental composition of the soil sample was analyzed using a wavelength dispersive X-ray fluorescence (WD-XRF) instrument (Rigaku ZSX Primus IV, Japan) equipped with a Rh X-ray tube and controlled by ZSX guidance software. The sample was placed on a specified sample holder cup and analyzed directly.

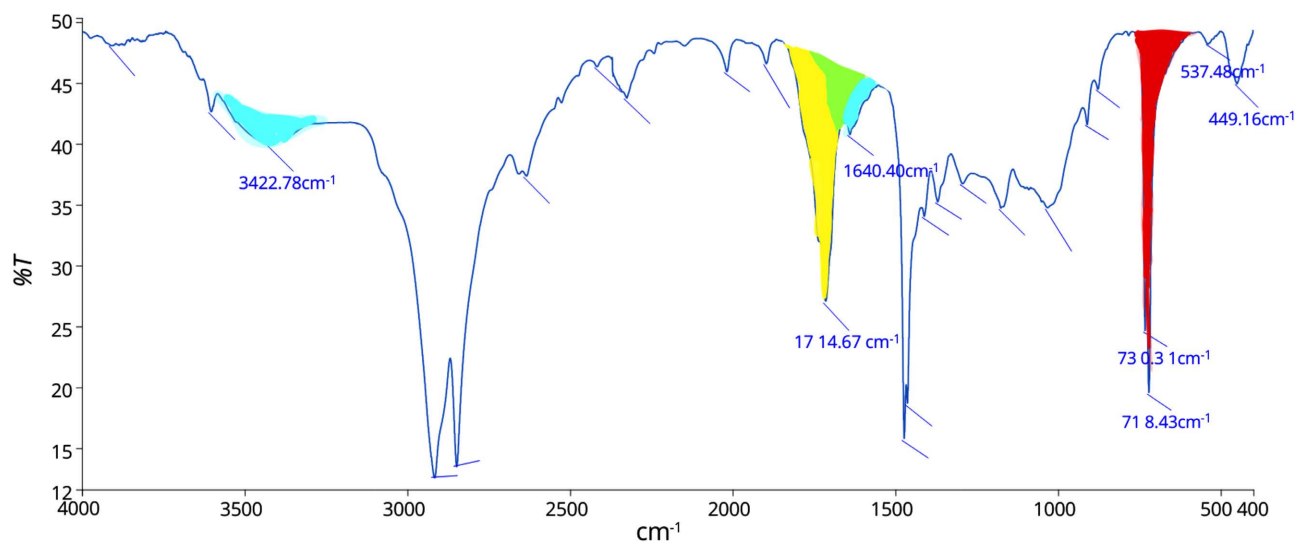


Figure 1. Typical FT-IR spectrum of an oxidized polythene material. In yellow, the band A associated with the oxidation of the polythene in form of C=O stretching vibrations, in red the band C associated with C-H rocking deformation vibration of polythene used as reference, in blue the band B due to H-O-H bending vibration of residual moisture in the material, in green the overlap of absorption bands A and B.

3. Results and Discussion

Discarded plastic bottle tops are an appreciable source of polythene and polypropylene presence in the UAE environment, especially in urban areas. Although many UAE municipalities employ both road sweeping services as well as road cleaners, plastics that reach soils along road-sides or sidewalks can have a prolonged residence time. In addition, daily Aeolian movement and road traffic help spread plastic contamination over wider areas so that the bottle top plastic found is a mix of relatively newly discarded and older plastic, some of which has been moved from location to location after release into the environment. Exposure of the polythene and polypropylene plastics to UV radiation leads to photo-oxidation that bring brittleness to the plastic. Daytime-nighttime expansion-contraction of the plastic with soil temperature differences of more than 35°C in the summer leads to material stress and to the appearance of cracks in the oxidized plastic bottle tops which mark the beginning of a slow fragmentation of the plastic tops without the need of an impact from a second object. Thus, of 18 bottle tops (origin: Saudi Arabia, color: purple, weight: $1.008 \pm 0.011\text{ g}$, diameter: 3 cm, **Figure 2**)

placed, 9 (50%) exhibited a crack through the center of the cap after 142 days (July 31st - Dec. 19th). The formation of cracks does not happen with pristine plastic material. Additionally, it must be noted that the linear coefficient of thermal expansion of low density polyethylene is approximately $2 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ at 20°C , but increases with temperature to $3.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ at 80°C , a temperature that is nearly reached by the immediate soil surface in the UAE in the summer. The expansion coefficient of polypropylene is given as $1.23 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ at temperatures of -10 to 50°C , increasing to $1.63 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ at temperatures of 50°C - 100°C [34]. Therefore, to understand the risk of fragmentation of environmental plastic contamination to smaller particles ultimately leading to microplastics it is important to gauge the degree of oxidation of the material in question.

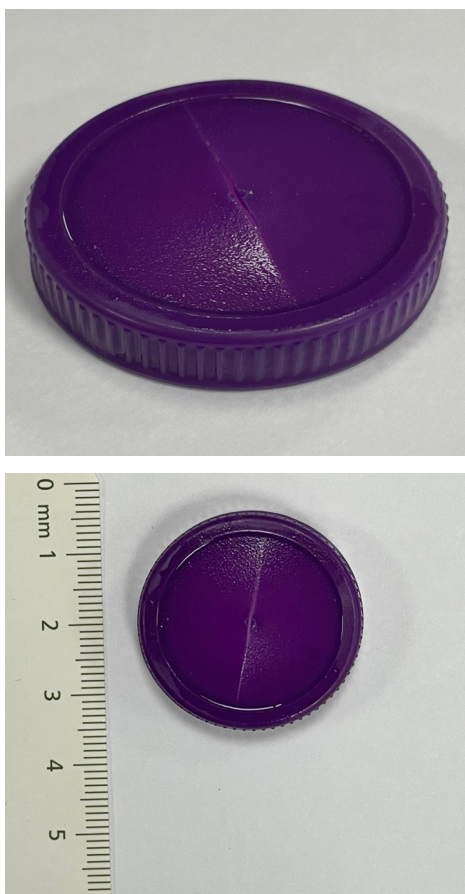


Figure 2. Purple bottle cap with acquired crack through the expansion-contraction process in the day-night cycle showing the brittleness of oxidized plastic.

Infrared is one straightforward technique to probe the integrity of polymeric material and to evaluate the oxidation of at least the upper strata of the plastic. Pure polythene itself exhibits a characteristic infrared spectrum, where the main IR bands have been studied thoroughly [35] and have been assigned to vibration modes as shown in **Table 1**. Similarly, the assignment of the IR vibrations of polypropylene is shown in **Table 2** [36].

Table 1. Assignment of major IR bands of polythene to vibrational modes, adopted from [35].

Wavenumber (cm ⁻¹)	Vibration type	Band intensity
2919	CH ₂ asymmetric stretching	Strong
2851	CH ₂ symmetric stretching	Strong
1473 and 1463	bending deformation	Strong
1377	CH ₃ symmetric deformation	Weak
1366 and 1351	wagging deformation	Medium
1306	twisting deformation	Weak
1176	wagging deformation	Very weak
731 - 720	rocking deformation	Medium

Table 2. Assignment of major IR bands of polypropylene to vibrational modes, adopted from [36].

Wavenumber (cm ⁻¹)	Vibration type	Band intensity
2950	CH ₃ asymmetric stretching	Strong
2920	CH ₂ symmetric stretching	Strong
2870	CH ₃ stretching	Strong
1456	CH ₃ symmetric bending	Strong
1376	CH ₃ symmetric deformation	Strong
1166	C-H wagging, CH ₃ rocking	Medium
996	CH ₃ rocking, C-C stretching	Medium
973	CH ₃ rocking, C-C stretching	Medium
840	C-H rocking	Medium
808	C-C stretching	Weak

According to the literature, degradation of polythene can proceed by photo-oxidative chain cleavage and can lead to the creation of carbonyl functions within the polythene material. In the IR spectrum of polythenes exposed to the environment a band centered at around $\tilde{\nu} = 1715 \text{ cm}^{-1}$ appears. This corresponds to the wavenumbers long chain ketones (alkanones) absorb at, such as 3-decanone ($\tilde{\nu} = 1716 \text{ cm}^{-1}$) or 4-decanone ($\tilde{\nu} = 1715 \text{ cm}^{-1}$) [37]. It must be noted, however, that the absorption band encompasses multiple absorptions of carbonyl functions

at slightly different frequencies due to the diverse chemical environments of the keto carbonyl functions in the polymer chain. Especially, in the early phases of the photo-oxidative process additional bands at higher wavenumbers can be noted which do not develop further with time but rather are enveloped by the absorption centered at $\tilde{\nu} = 1715 \text{ cm}^{-1}$ as time progresses. In the case of polypropylene, the emerging C=O absorption band connected to the oxidation of the material is much broader than for polythene, indicating that more diverse C=O functional groups are present in the polymer. This may include carbaldehyde functions, indicated by a number of emerging C-H vibrations between $\tilde{\nu} = 2550$ and 2750 cm^{-1} . It could be expected that the carbaldehyde functions oxidize to carboxyl groups under environmental conditions, but this has not yet been verified.

In the performed experiments, the bottle tops were placed on soil with a composition typical for the Al Ain area, where the composition was determined by XRF spectroscopic analysis (**Figure 3**). The soil is abundant in CaCO_3 and SiO_2 . This is in line with the fact that as one goes further inland in the United Arab Emirates the ratio in the soil of silica to calcium carbonate increases [38] [39], with the exception of the Al Ain area in the immediate vicinity of Jebel Hafeet, which itself is abundant in limestone [40]. As the immediate study area constitutes wasteland surrounded by built-up areas with a significant amount of construction waste, soil samples from the study area also showed appreciable amounts of Fe (13.8 w%), Ni (0.42 w%) and Cr (0.64 w%), with all percentages given as weight percentages of the respective oxides (**Table 3**). The soil reacts basic. Due to Aeolian movement, some soil particles can transport on top of the plastic bottle caps, but these were never covered with soil or actually embedded in soil over the time of the experiment. Soil on top of plastic surfaces can influence the amount of sun irradiation the surface is exposed to, the level of absorption of the surface, the temperature of the surface and its chemical environment.

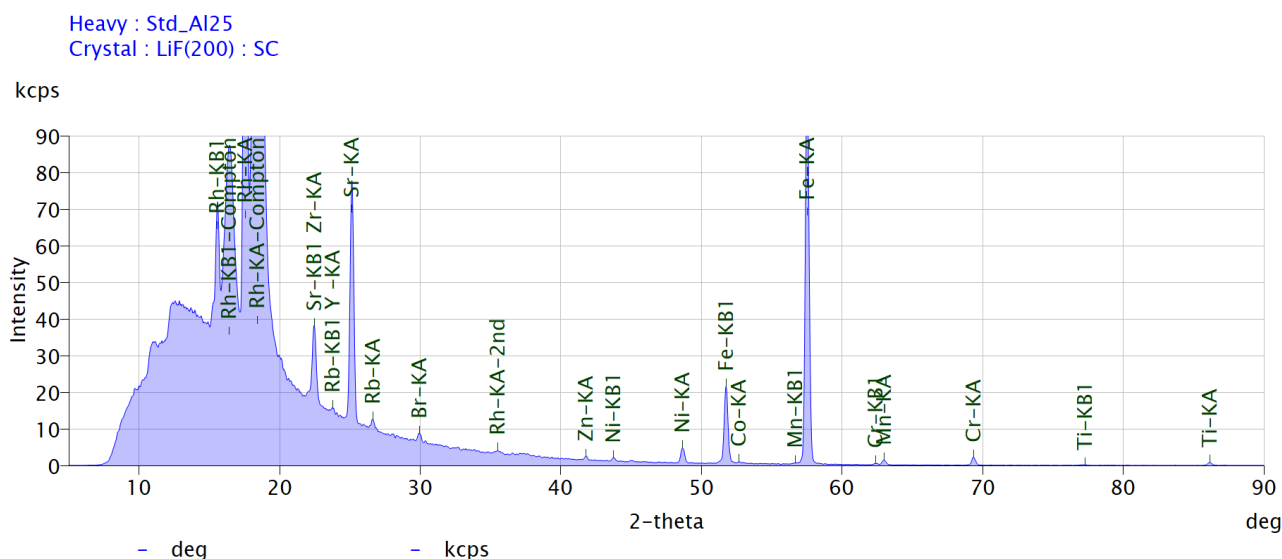


Figure 3. XRF spectrum of a soil sample taken from the surface the bottle tops were placed on in this study.

Table 3. Abundance of different elements in the soil on which the bottle tops were placed.

No.	Element	Result in w% (measured as oxide)	Detection limit	Intensity
1	Na	0.379	0.03730	0.0366
2	Mg	7.32	0.02560	2.2906
3	Al	3.59	0.01176	2.2935
4	Si	28.2	0.02897	18.0162
5	P	0.0873	0.00565	0.0956
6	S	0.352	0.00517	0.3604
7	Cl	0.0783	0.02290	0.0201
8	K	1.61	0.01741	0.7186
9	Ca	43.1	0.03665	18.8399
10	Cr	0.634	0.04392	0.1821
11	Mn	0.238	0.02820	0.1077
12	Fe	13.8	0.02872	9.9798
13	Ni	0.415	0.01187	0.5198
14	Sr	0.272	0.00940	2.4456
15	Zr	0.0278	0.00878	0.8927

Al Ain features a hot desert climate (Koeppen climate classification BWh with an average maximum UV index of 9 from May through August), and this is reflected in the hot temperatures measured for the soil and the bottle tops in August. Specifically, the surface of brown plastic bottle tops reached 60°C a number of times, blue plastic bottle tops of the same type the upper 50's °C, yellow bottles caps the mid 50's °C. The brown bottle tops exhibit a temperature difference of ca. 30°C during daylight hours, between morning and noon, similar to the blue bottle tops of the same type, while the yellow tops show a temperature difference of about 25°C (**Figure 4**).

Peak temperatures then diminish as the year passes. The brown bottle tops peak at 50°C in October and at 45°C in November (**Figure 5** and **Figure 6**) with morning-noon temperature differences of 20°C in October and November. Yellow bottle tops peak at 45°C and 43°C in October and November, respectively, with daytime temperature differences of about 23°C in both months (**Figure 5** and **Figure 6**). The surface temperatures measured for tops of other makers and colors ranged in-between the brown bottle tops and the yellow bottle tops shown in **Figures 4-6**. It must be noted that the brown and yellow bottle tops shown in **Figures 4-6** are from different makers.

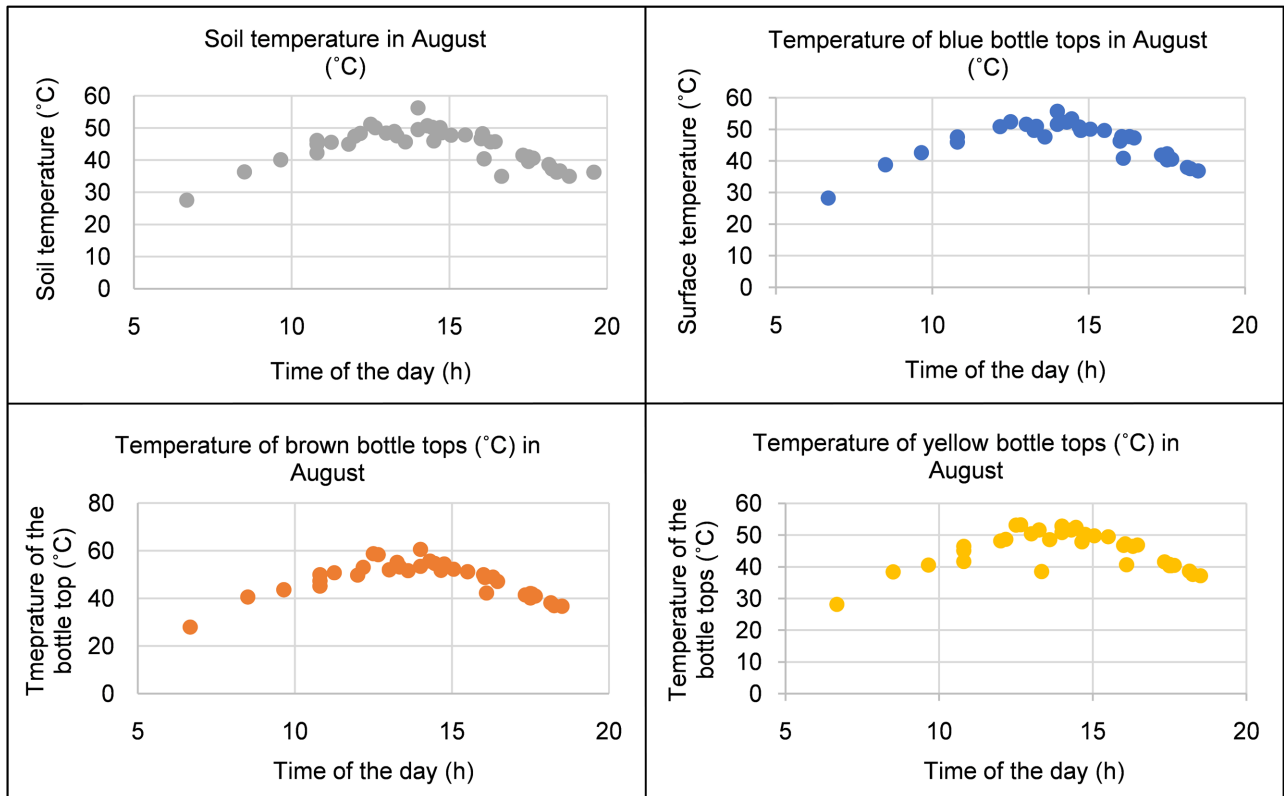


Figure 4. Temperature profile of the soil and bottle tops of different colors (blue-brown-yellow) in August.

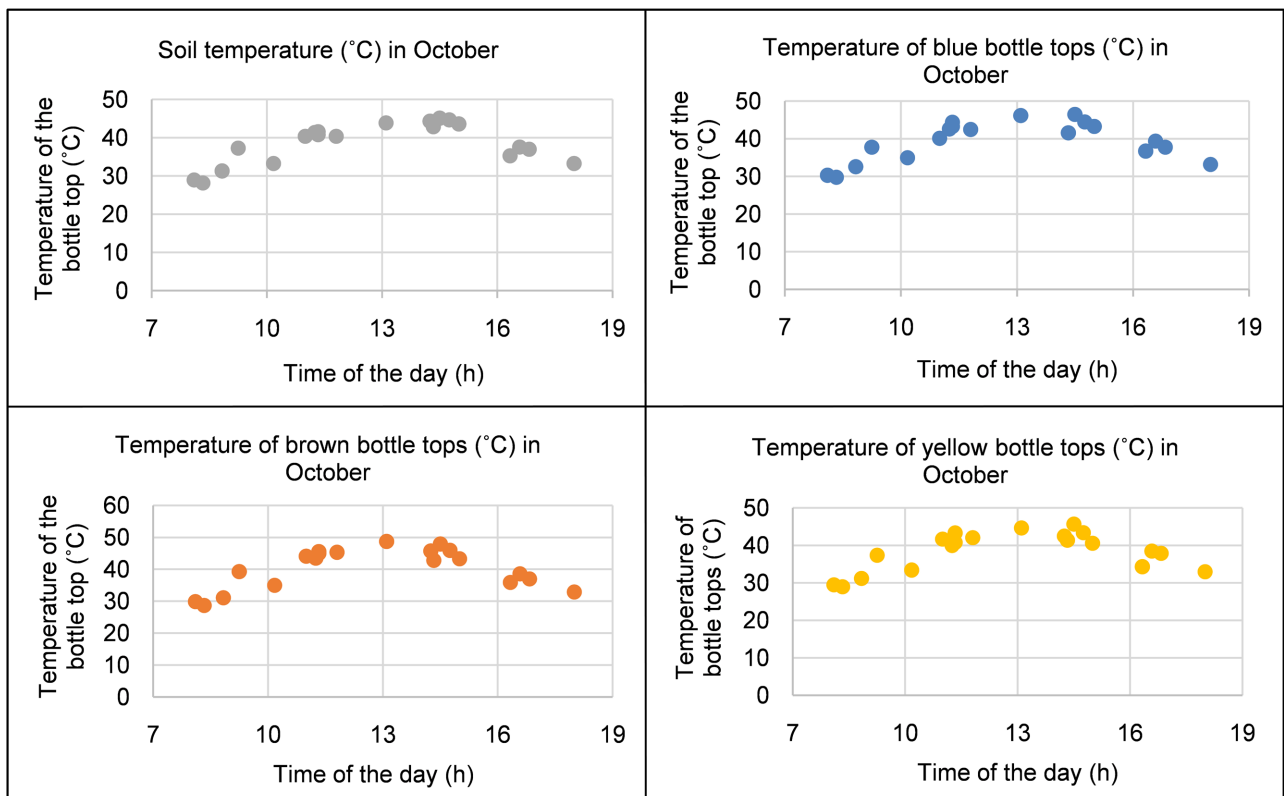


Figure 5. Temperature profile of the soil and bottle tops of different colors (blue-brown-yellow) in October.

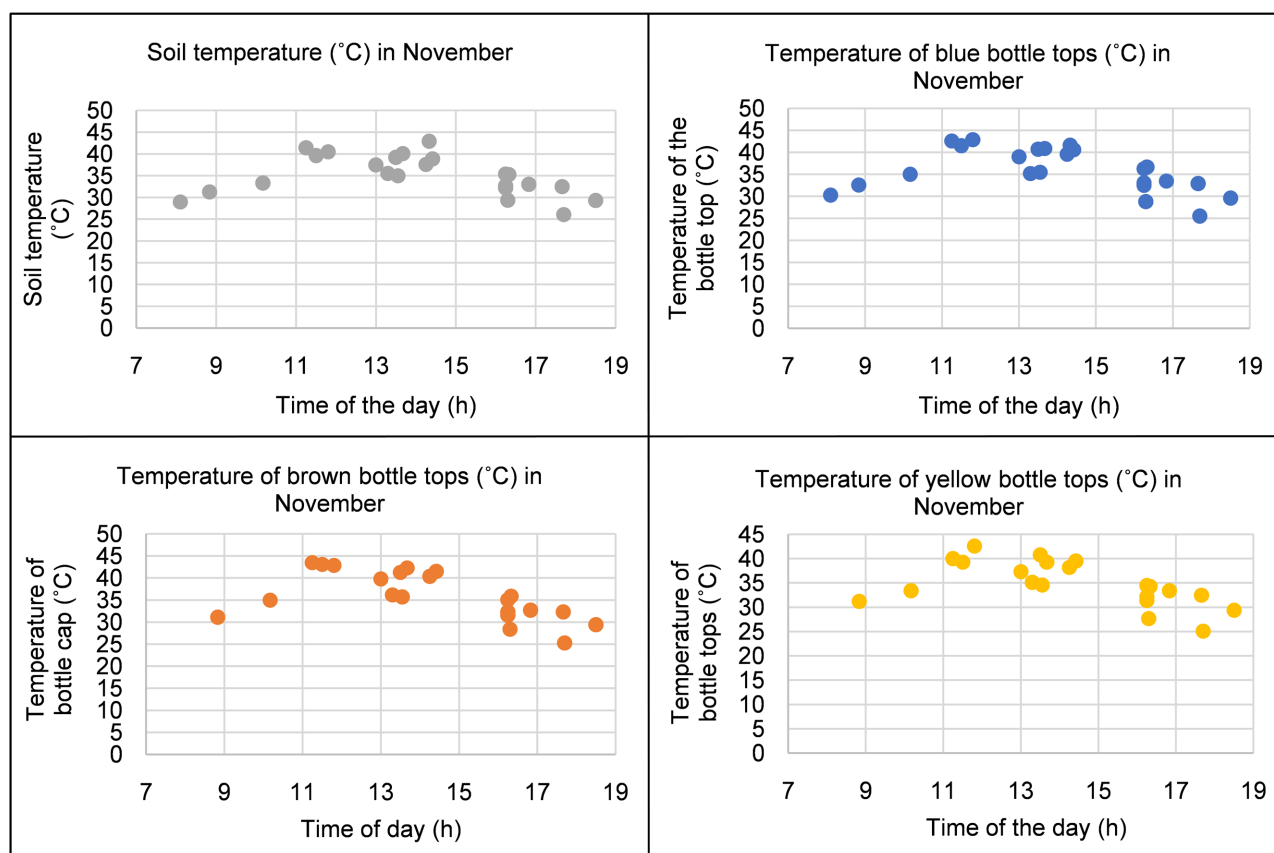


Figure 6. Temperature profile of the soil and bottle tops of different colors (blue-brown-yellow) in November.

Table 4 shows the oxidation of different bottle tops after 46 days (July 31st - Sept. 15th). The blue and brown bottle tops with 0.177 ± 0.054 and 0.180 ± 0.048 showed a slightly higher oxidation index than the yellow bottle tops with 0.154 ± 0.046 , where blue, brown and yellow bottle tops are the same as in **Figures 4-6**. Furthermore, blue bottle tops (PC) from a famous international brand showed an oxidation index of 0.1575 ± 0.015 . At this point, none of the bottle tops are significantly brittle.

After 142 days exposure to the outdoors, there is a much wider range of oxidation indices for the plastic screw caps under investigation ranging from 0.211 ± 0.065 to 0.863 ± 0.010 (**Table 5**).

The thickness of the bottom of typical plastic screw caps can range from 40 - 100 mils (1.01 - 2.54 mm), and interestingly both cap types KSA and UNI belong to the category with the smaller thickness. Oxidation indices of over 0.8 in bottle tops with a small thickness make the bottle tops prone to fragmentation upon the slightest impact. In addition, daytime-nighttime temperature differences can lead to cracks in the bottle cap's bottom as discussed above (**Figure 2**). Interestingly, one type of bottle cap derived from a German product, exposed to the arid hot conditions of the UAE with significant UV irradiation, also showed with 0.604 a high oxidation index. These bottle caps, however, have a much greater thickness than either KSA and UNI and are therefore much less prone to fragment.

Table 4. Oxidation indices of assorted plastic bottle screw caps (polythene, PE) after outdoor exposure for 46 days ($n = 3$).

Short description	Color	Dimensions*	Oxidation index
AF blue	Blue	diameter: 3.95 cm height: 0.95 cm	0.177 ± 0.054
AF green	Green	diameter: 3.95 cm height: 0.95 cm	0.144 ± 0.029
AF brown	brown	diameter: 3.95 cm height: 0.95 cm	0.180 ± 0.048
SC	yellow	diameter: 3.95 cm height: 0.9 cm	0.154 ± 0.046
PC	Blue	diameter: 3.0 cm height: 1.0 cm	0.1575 ± 0.015
KSA	purple	diameter: 3.0 cm height: 0.65 cm	0.166 ± 0.013

*The diameter is the outer diameter of the cap's neck.

Table 5. Oxidation indices of assorted plastic bottle screw caps (polythene, PE) after outdoor exposure for 142 days ($n = 3$).

Short description	Color	Dimensions*	Oxidation index
AF blue	Blue	diameter: 3.95 cm height: 0.95 cm	0.256 ± 0.085
AF green	Green	diameter: 3.95 cm height: 0.95 cm	0.262 ± 0.080
SC	Yellow	diameter: 3.95 cm height: 0.9 cm	0.375 ± 0.096
PC	Blue	diameter: 3.0 cm height: 1.0 cm	0.508 ± 0.131
KSA	Purple	diameter: 3.0 cm height: 0.65 cm	0.863 ± 0.010
UNI	Turquoise	diameter: 3.1 cm height: 0.7 cm	0.807 ± 0.059
MD	Red	diameter: 3.1 cm height: 0.7 cm	0.281 ± 0.085
GER-1	turquoise-green	diameter: 2.95 cm height: 0.95 cm	0.604 ± 0.026
GER-2	Red	diameter: 2.9 cm height: 0.85 cm	0.211 ± 0.065

*The diameter is the outer diameter of the cap's neck.

After 142 days (July 31st - Dec. 19th), polypropylene bottle tops (CD, diameter 3.0 cm, height 1.4 cm) exhibited an oxidation index (as defined above) of 1.113 ± 0.174 . Here, also the rim of the neck of these caps where the abrasion of the plastic for the investigation of oxidation index took place was brittle enough to fragment upon the slightest impact.

Finally, bottle tops of the same maker but of different color (AA, diameter 3.1 cm, height 0.85 cm) were exposed to the environment for 182 days (Jan. 2024 - June 2024), while being placed on the same soil as for the experiments discussed above (Table 3). Here, a color dependence of the oxidation index was noted (Figure 7), with orange bottle caps exhibiting an oxidation index of > 1.1 . The further gradation of the oxidation index of yellow bottle tops $>$ green bottle tops $>$ blue bottle tops is in juxtaposition to results of the experiment described earlier where after 46 days the gradation was found to be blue bottle tops $>$ yellow bottle tops $>$ green bottle tops but does coincide with the results found after 142 days of exposure in the first described experiment. It must be noted, however, that while the blue and green bottle tops of the first experiment were of the same maker, the yellow bottle tops were from another manufacturer. The manufacturers of the bottle tops used in the first experiment and the manufacturer of the bottle tops for the second experiment are different.

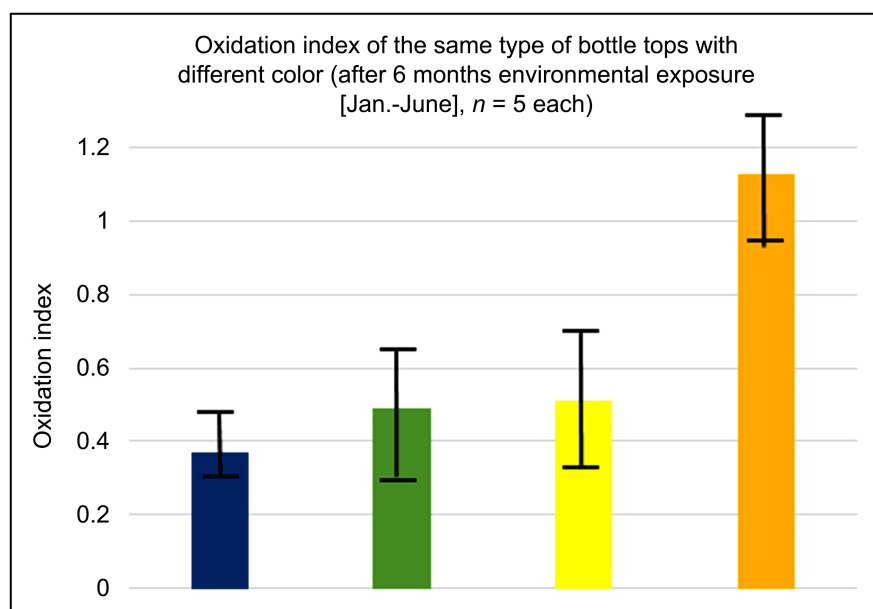
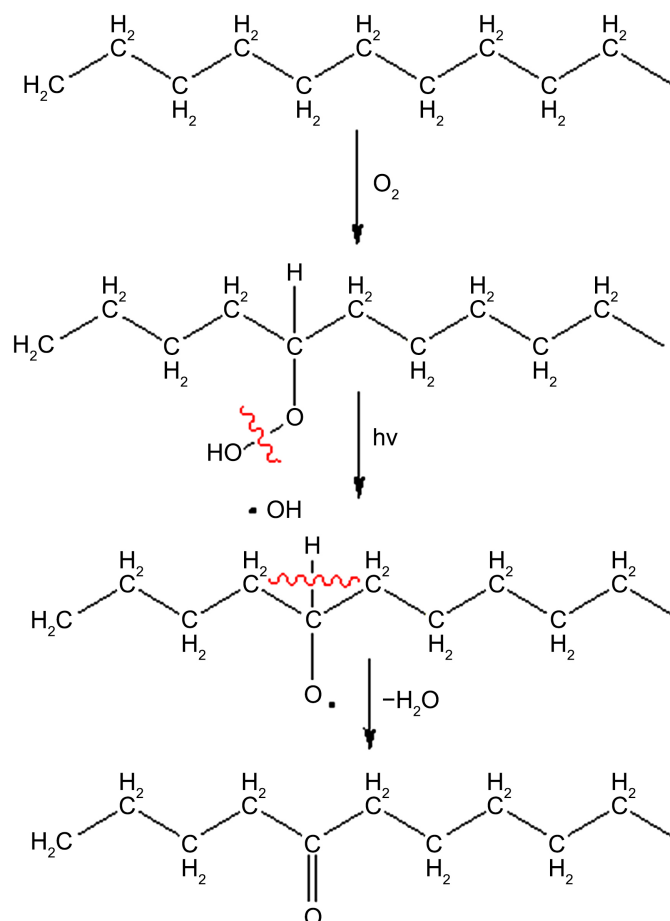


Figure 7. Degree of oxidation of bottle tops of the same make (AA), but of different color after being exposed to the outside environment for 182 days (Jan. 1 - June 30, 2024).

Mechanisms for the oxidation of polythene and polypropylene have been studied extensively [32] [41]-[44]. One such mechanism involves the photo-oxidation of the polymer. Here a hydroperoxide intermediate can be formulated (Scheme 1) that is photolytically cleaved homolytically. It is imagined that the formation of the hydroperoxide itself also proceeds through a radical site in the polymer that

may form with the help of metal catalyst residues left over from the production process of the polymer itself [45] [46]. Although it is known that singlet oxygen leads to hydroperoxidation of also slightly activated Csp³-H bonds [47], a possible role of singlet oxygen in a further transformation of the hydroperoxide formed has not yet been investigated. Once carbonyl groups are in place, Norrish type 1 and 2 reactions can proceed, (Scheme 2) leading to C-C bond breakage and to cleavage of the polymer strands.

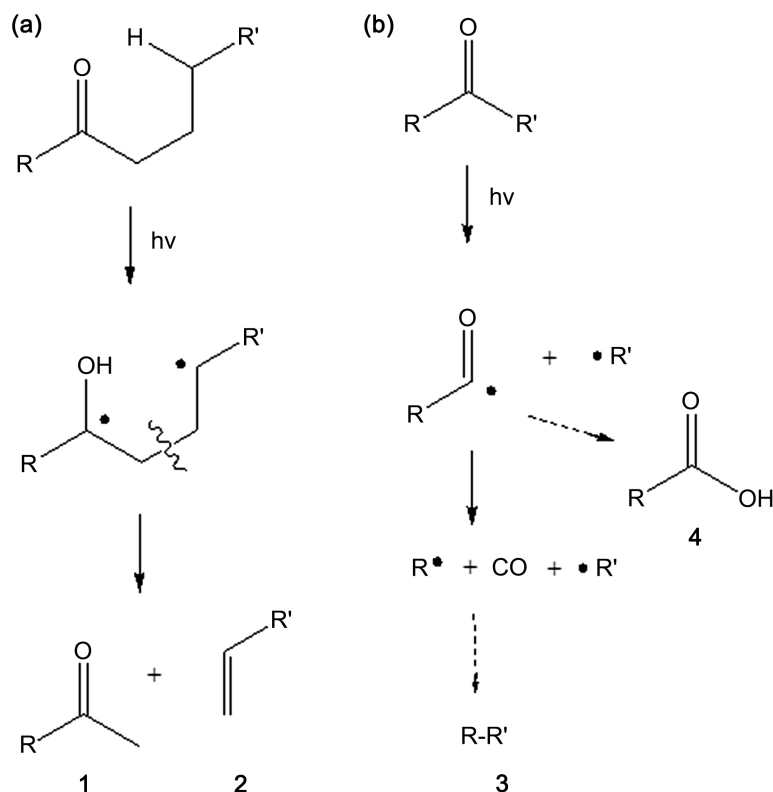


Scheme 1. Likely mechanistic pathway in the oxidation of polythene.

It must be noted that the C=O IR band seen in weathered polythene and propylene materials is in fact a composite of overlying carbonyl bands [48]. Also, contribution of carboxyl groups to the broad absorption band centered at around $\tilde{\nu} = 1715 \text{ cm}^{-1}$ has been postulated [48].

The oxidation of the polymer would lead to a greater mass of the polymer, however, over the time period of half a year and also over time periods spanning more than 2 years for other, non-published experiments, no significant weight loss or weight gain of the bottle tops was noted. Only after the beginning of actual physical fracturing of the bottle top material, often commencing with fissures in the material discussed above (Figure 2), does sporadic weight loss start, associated

with the loss and dispersal of plastic fragments from the bottle top. The maintaining of the mass over long periods of exposure time, measured in months, if not years, could potentially be explained by either of the scenarios: 1) the oxidation of the polymer is limited to the upper layers of the polymeric material and introduced carbonyl groups are few. 2) oxidation of the polymer resulting in weight gain and cleavage of small fragments from the polymer, resulting in weight loss hold a balance. To have a better insight, CH elemental analysis and ablation—mass spectrometric analyses of the materials would be helpful.



Scheme 2. Photochemical Norrish Type 1 (b) and Norrish Type 2 (a) reactions that lead to bond cleavage α - and β - to the carbonyl group of ketones. In our experiments it was shown that the signal for carbonyl group in the plastic was building over time. This would speak for unreacted A/B as well as for Norrish type 1 (b) reaction.

All in all, it must be noted that plastic bottle tops in the environment are a source of microplastics upon oxidative degradation over longer periods of time. A way to alleviate this problem is a significant reduction of plastic bottle waste that are discarded and thus enter the environment. While in many countries a surcharge is levied on plastic bottles that will be paid back upon handing back the plastic bottle to be recycled, this concept is still in its infancy in the United Arab Emirates. Traditionally, in countries such as Japan and Germany, it is the main body of the bottle that is rewarded with a refund, and it does not play a role, if the bottle carries its cap. This has led to some accumulation of plastic bottle caps even in countries in which the plastic bottles are meticulously collected. To find a

solution to this problem, the European Union within its Single-Use Plastics Directive requires as of 2024 that plastic bottle caps remain attached to their bottles [49]. The directive was set into place with the prognosis that such action would reduce the plastic contamination on European beaches by 10% [50].

4. Conclusions

Plastic bottle tops made of polythene or polypropylene oxidize over time when exposed to environmental conditions. Oxidation leads to brittleness of the material, which then fragments upon impact into smaller particles, ultimately leading to microplastics. Infrared spectroscopy is a direct method to quantify the oxidation status of the polymeric material through the ratio of the areas underneath the C=O stretching band around 1715 cm^{-1} and the C-H rocking deformation centered around 718 and 730 cm^{-1} for polythene and the ratio of the C=O stretching band around 1720 cm^{-1} and the combined areas of the absorption bands centered at 1456 and 1376 cm^{-1} for polypropylene. These ratios were called oxidation indices in this communication.

In the hot arid environment of inland United Arab Emirates, the studied plastic bottle tops made of polythene show oxidation indices of between 0.211 ± 0.065 and 0.863 ± 0.010 after 142 days of exposure. Thus, an appreciable oxidation of the plastic bottle tops does take place, but the rate of oxidation is very much dependent on the exact type of polythene material and additives. In a series of bottle tops of the same type a color dependence of the oxidation was noted. Day and night heating-cooling cycles for differently colored plastic bottle tops can differ by as much as 5°C . The fragility of bottle top material exhibiting a high oxidation index depends on the thickness of the plastic. Thin bottle tops with high oxidation indices tend to show fissures due to expansion-contraction cycles of the material due to night vs. day temperature differences.

Oxidation indices of polythene and polypropylene materials can give an indication of their residence time in the open environment. However, the exact type of polymer (HDPE vs. LDPE vs. LLDPE, etc.) as well as polymer additives including pigments have a significant effect on the rate of oxidation of the surface as well as the rate of follow-up reactions such as C-C cleavage. This would mean that environmentally conditioned reference materials used to gauge the residence time in the environment of different plastics under study should be used only with great care. Rather the use of separate reference materials for each plastic type, which includes the specific additives employed, would be preferable.

Finally, as plastic bottle tops are a source of plastic pollution in the environment and also constitute a source of microplastics, ways need to be sought to reduce the entry of plastic bottle wastes including plastic bottle tops into the environment. This may include regulatory measures that incentivize the collection and recycling of plastic bottles and may also include regulations similar to the European Union Single-Use Plastics Directive that mandates that bottle tops are physically connected to the respective bottles.

In future work, the individual effects of the environmental factors UV radiation, temperature, humidity, and soil composition on the oxidation of plastics need to be studied further in controlled experiments. Long chain model alkanes are to be exposed to environmental conditions, where the oxidation products are monitored mass spectroscopically to better elucidate reaction mechanisms leading to the weathering of polythene and polypropylene.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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