Plastic to microplastic in the United Arab Emirates – plastic bottle caps in a hot, arid environment

Selem, B.,[1] Alkarbi, A.,[1] Alhosani, A.,[2] Ahmad, F.,[2] Elemam, M.,[2] Iftikhar, S.H.,[3] Mourad, A.H.,[3] Thiemann, T.[1]

[1]Department of Chemistry, College of Science, United Arab Emirates University, PO Box 15551, Al Ain, United Arab Emirates
2Department of Biology, College of Science, United Arab Emirates University, PO Box, 15551, Al Ain, United Arab Emirates
[3]Department of Department of Mechanical and Aerospace Engineering, College of Engineering, United Arab Emirates University, PO Box 15551, Al Ain, United Arab Emirates

*corresponding author: Thies Thiemann
e-mail: thies@uaeu.ac.ae

Abstract The degradation of plastic bottle tops as a common contributor to plastic waste in the environment was assessed under the hot, arid conditions of the hinterland of the United Arab Emirates. 500 bottles tops were collected from 5 different locations in the Al Ain area and their surface oxidation index was determined through FT-IR measurements. The hardness of pristine bottle tops and bottle tops aged in the environment was compared.

Keywords: secondary microplastics, plastic bottle tops, surface oxidation index, degradation, plastic hardness

1. Introduction

Microplastics are plastic particles less than 5 mm in size. Microplastics can be primary or secondary microplastics. Primary microplastics are plastics that are manufactured in their small size for a purpose (eg., abrasive materials), secondary microplastics stem from the degradation of larger plastic items (eg., from macro- and mesoplastics). Primary microplastics reach our environment either through spillage or through incorrect disposal at the end of life. A typical example published from the Al Ain area are plastic pellets for toy guns [Habib 2022a]. Secondary plastics reach our environment through the degradation of macroplastics that already are part of the plastic pollution in our environment or by degradation of plastic containing material that is still in use [Chamas 2020; Huang 2021] (eg., abraded material from car tires [Habib 2022b]).

The current research is concerned with the route to microplastics by the degradation of macroplastics that are already a part of the plastic pollution in our environment. For this, the macroplastic pollution in two areas within the Al Ain area was assessed (**Figure 1**). It was noted that plastic wastes from the food industry were dominating. This included plastic food containers (PS = polystyrene or PE = polythene), plastic wrappers, PET (polyethylene terephthalate) bottles, and their hard plastic tops (PE = polythene or PP = polypropylene). In addition, single use plastic bags and plastic sheets were found to be relatively common.

It was decided to concentrate on the fate of hard-plastic bottle tops that had been discarded in the environment.

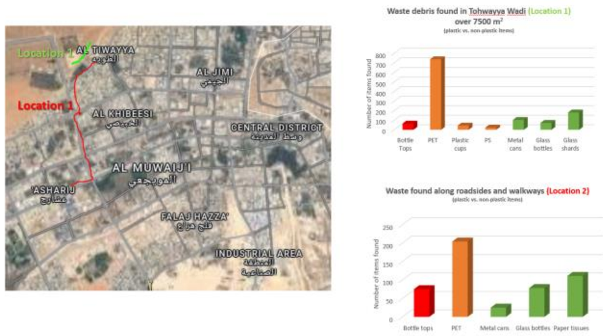

Figure 1. Typical waste items (plastic, glass and metal) found in the open environment at two different locations in Al Ain.

2. Methodology

For this purpose, 500 plastic bottle tops have been collected from 5 sites (100 each) in the Al Ain area, including from Tohwayya Wadi (seasonally water carrying river bed) and the area around Zakher Lake (**Figure 2**). In addition, 50 bottle tops were collected from various locations in Kuwait. The bottle tops are made from PE and PP. In addition, new bottle tops were set out in locations 1 (Tohwayyah Wadi) and 5 (University).

As it was supposed that PE and PP plastics would degrade over time by oxidation, **infrared spectra were performed of all 500 tops (as KBr pellets with Thermo Nicolet Nexus 670 FT-IR and Nexus 670 FT-IR spectrometers).** For this the C=O vibration in the infrared spectrum centered around 1715 cm^{-1} that emerges in the oxidation process was compared to a CH-rocking vibration of the polymer at 718 cm^{-1}. The oxidation process that is accelerated in the presence of light (such as sunlight) is shown in **Figure 5.** So, the intensity of the carbonyl band is an indication of age and of chemical degradation of the PE (and PP) materials. The oxidized polymer can undergo subsequent Norrish type fragmentation reactions (see **Figure 6**). The newly set out bottle tops (at locations 1 and 5) were monitored at fixed times (for location 1 weekly) as to their **weight**. From selected bottle tops samples of **their**

top layer were taken and submitted to IR spectroscopic analysis [Moldovan 2012]**.**

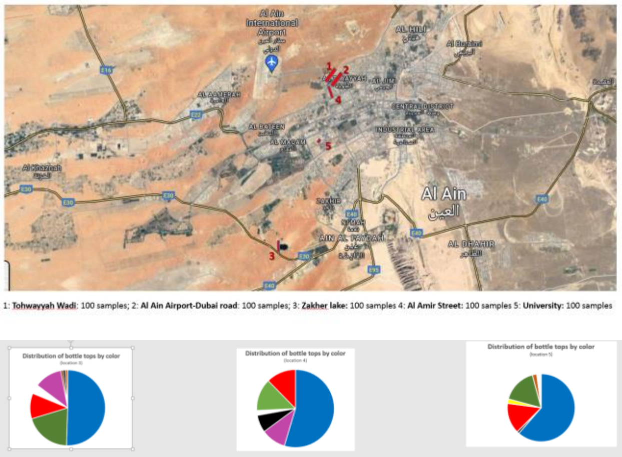

Figure 2. The locations the plastic bottle tops were collected from. Color distribution of the bottle tops collected is also shown.

As it is known that physical properties of plastics can change with weathering [Yildirim 2022], finally, the hardness of selected bottle tops was measured, where the same type of bottle top was submitted to a microhardness test when new, after a number of months and near the end of the study. The newly set out bottle tops were examined for emerging fissures and for changes in their shape. To see changes in the morphology of the plastic tops, a microscope with mounted camera was used. At different times, temperature readings of the top soil at location 5 were performed on a daily basis. Here, a Trister infrared thermometer was used with an initial calibration utilizing a normal immersion glass thermometer. Also, the concentration of plastic bottle tops on the ground was assessed for locations 1 and 2 as shown in Figure 3.

3. Results and Discussion

Plastic tops as macroplastic contaminants in our environment – presence and aging

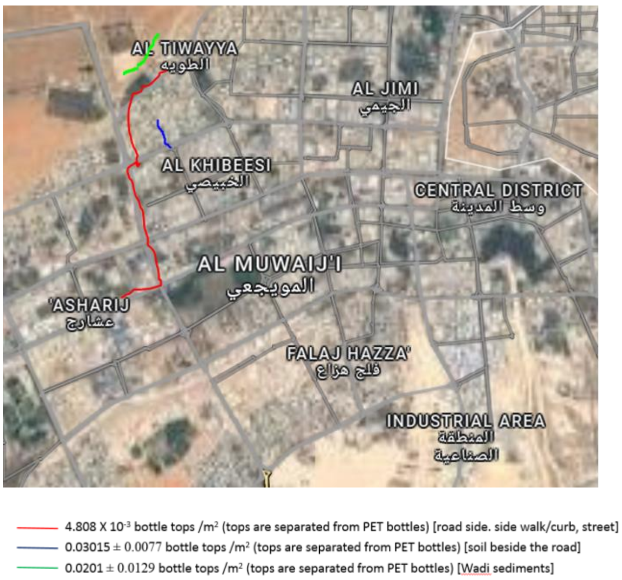

Figure 3. Concentration of bottle tops at locations 1 and 2

An initial assessment of the concentration of bottle tops that were disjoined from the respective plastic (PET bottles) showed a dependence of the concentration on the location. Less bottle tops were found at roadsides or sidewalks where there was road-sweeping activity. A more representative number for the concentration can be found on soils next to roads which incidentally is similar to the concentration of bottle tops on soil sediments in a more secluded Wadi, where nevertheless residents discard their food packaging when finished eating (**Figure 3**).

Figure 4 is very important as it shows how oxidized the bottle tops are that have been collected. 36% of the tops from location 5 showed an intensity ratio of 1 and above 39% of the tops show an intensity ratio of 0.9 and above. Bottle tops with an intensity ratio of 1 and above are so brittle that they can be easily crushed into a powder with mortar and pestle. The bottle tops sampled from the other locations were similarly oxidized.

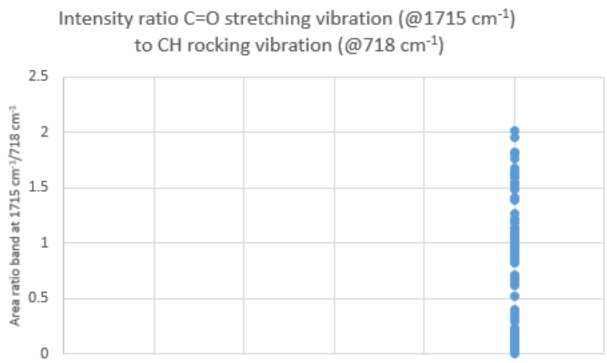

Figure 4. Aging in form of oxidation as expressed by the intensity ratio of the vibration in the infrared spectrum of the plastic at 1715 cm^{-1} and the vibration at 718 cm^{-1}, used as a surface oxidation index (compilation of data of 100 bottle tops from location 5).

The oxidation of the PE and PP plastics occurs through the general pathway shown in **Figure 5**. The oxidation affects the near order of the polymer chains. It is not clear whether it is the oxidation alone or also potential chain cleavage reactions of Norrish type 1 and Norrish type 2 (see **Figure 6**) that affect the crystallinity of the plastic.

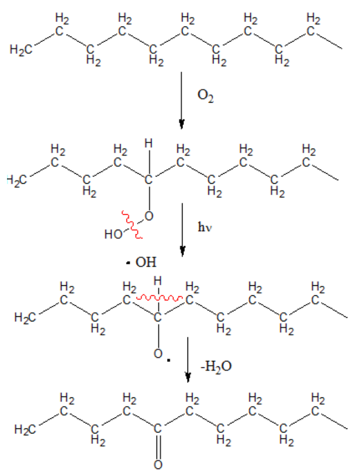

Figure 5. Likely mechanistic pathway in the oxidation of polythene.

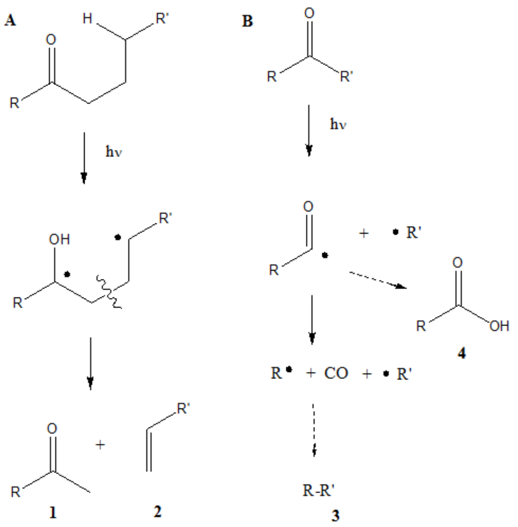

Figure 6. Photochemical Norrish Type 1 (B) and Norrish Type 2 (A) reactions that lead to bond cleavage α- and β- to the carbonyl group of ketones. In our experiments it was shown that the signal for carbonyl group in the plastic was building over time. This would speak for unreacted A/B as well as for Norrish type 1 (B) reaction.

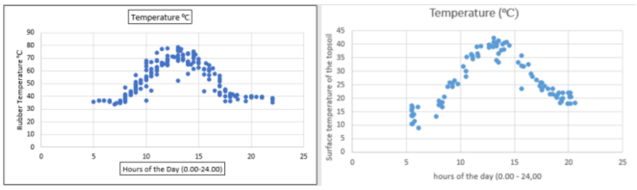

Figure 7. Topsoil surface temperatures in a.) July/August and b.) January (location 5)

Topsoil temperatures in the Al Ain area can top 70 ºC (**Figure 7**). While PE has a melting point of above 100 ºC, softening can happen at lower temperatures. It is expected that due to the softening and hardening as well as through expansion and contraction in the day/night cycle in the summer months, bottle tops can warp (bottle top type Mai Dubai) or develop centered fissures (bottle top type HCM). This physical degradation goes hand in hand with the chemical degradation through oxidation (see above) which leads to an overall hardening of the plastic tops. In compression tests it was seen that for a typical HCM bottle top, the hardness values were in the range of 5.009 to 5.477 HV with an average value of 5.303 HV. However, for the HCM bottle top exposed to the outdoors (Sept.-Feb.) the hardness values were in the range of 5.816 to 6.187 HV with an average value of 6.037 HV. Similarly, a pristine Mai Dubai bottle top had hardness values of 4.575 to 5.034 HV with an average value of 4.818 HV, after 3 months exposure hardness values were in the range of 5.419 to 5.848 HV with an average value of 5.597 HV.

Figure 8 shows the weight loss of plastic tops resting in the environment. It was found that pristine and undamaged plastic tops can retain their weight for many months. Oxidation of plastic should lead to weight gain. However, concomitantly running Norrish type fragmentation reactions may lead to weight loss. Here, there could be two possibilities: a) the layers that are oxidized in the plastic body are but few; b.) oxidation and fragmentation balance each other out.

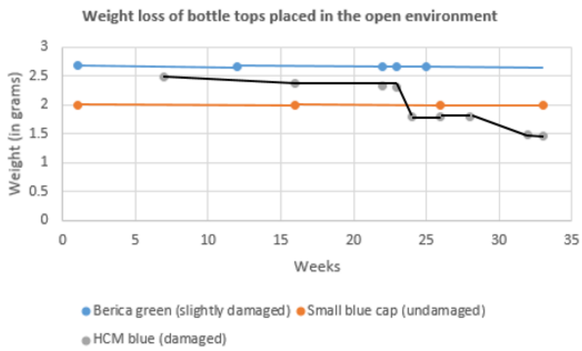

Figure 8. Weight loss of differently artificially damaged bottle tops placed in location 5. The bottle tops were damaged by filing.

Damaged bottle tops lose weight more quickly due to fragmentation that can happen with a minimal application of pressure. Important to note is that while the microplastic fragments may be distributed through the wind, it is equally likely that they are buried in position, in the soil.

4. Conclusions

A significant concentration of loose bottle tops can be found in the open environment of Al Ain City. On average, the bottle tops collected from five different locations of Al Ain City show significant oxidation of their surface. This indicates that many bottle tops have been resting in the open environment for a long time (> 1 year). The climate – high temperatures in the summer and many days without appreciable cloud cover – is amenable to the oxidative degradation of plastic materials. Oxidative degradation of the bottle tops leads to increased hardness, which makes the bottle tops more brittle. Thus, they can break more easily with sudden shock (ie., sudden application of force). There are bottle tops that deform (warp) with the temperature differences (day/night) in the summer. There are bottle tops that develop fissures with these temperature differences (environmental stress cracking). Intact (undamaged) bottle tops can remain in the environment for many years without being a source of microplastics due to fragmentation. Fragmentations need sudden shocks (eg., through being run over by a car). However, damaged bottle tops degrade/oxidize more quickly and can fragment more easily (eg., through blown sand). It may be that very old and oxidatively degraded bottle tops shed microplastics due to expansion-contraction of the material body during night/day cycles. The microplastics then come to lie concentrically around the main body. This last phenomenon needs further research.

References

Chamas A., Moon H., Zheng J., Qiu Y., Tabassum, T., Jang J.-H., Abu-Omar M., Scott, S.L. and Suh, S. (2020), Degradation rates of plastics in the environment, *ACS Sustainable Chemical Engineering*, **8**, 3494-3511.

Habib R.Z., Ramachandran T., Hamed F., Al Kindi R., Mourad A.I. and Thiemann, T. (2022a), Microplastic in an arid region: identification, quantification and characterization on and along-side roads in Al Ain, Abu Dhabi, United Arab Emirates, *Journal of Environmental Protection* (JEP), **13**, 671-688.

Habib R.Z., Al Kendi R., Ghebremedhin F., Elkashlan M., Iftikhar S.H., Poulose V., Ramachandran T., Mourad A.H.-I., Hamed F. and Thiemann, T. (2022), Tire and rubber particles in the environment – a case study from a hot arid region, *Frontiers in Environmental Science - Toxicology, Pollution and the Environment*, **10**, 1009802.

Huang D., Xu Y., Lei F., Yu X., Ouyang, Z., Chen Y., Jia H. and Guo, X. (2021), Degradation of polyethylene plastic in soil and effects on microbial community composition, *Journal of Hazardous Materials*, **2021**, *416*, 126173.

Moldovan A., Patachia S., Buican R. and Tierean M. (2012), Characterization of polyoleflin wastes by FTIR spectroscopy,

Bulletin of the Transilvania University Brasov, Series I, **5** (54), 65– 72.

Yildirim F.F., Hicyilmaz A.S. and Yildirim K. (2022), The effects of the weathering methods on the properties of the ABS, ASA and PMMA polymers *Polymer Testing*, **107**, 107484.