Real-world natural passivation phenomena can limit microplastic generation in water

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ABSTRACT
Previous studies using Deionized (DI) water found that household plastic products used in food preparation and storage are a local and immediate source of extremely high quantities of microplastics (MPs) released directly into the human body and the environment. However, DI water is rarely used outside of laboratories. Here, MP release from plastic products exposed to ordinary drinking water was studied. To facilitate this study, the concept of Synthetic drinking water (SDW) was introduced, which involved preparing water in accordance with the WHO standard but modified to mimic the composition of local Tap drinking water (TDW). It was found that the level of MP released from plastics exposed to TDW and SDW are very similar, demonstrating that SDW is an appropriate real-world reference standard to test MP release levels from plastic products. In contrast with the use of DI water, plastics exposed to hot (40–100 °C) SDW and TDW showed the progressive development of a Copper (II) oxide (CuO) passivation film due to the presence of Cu2+ ions in the water samples. Similar passivation films formed on 97% of all food grade plastics. Longitudinal studies of polypropylene products (kettles) exposed to boiling TDW during normal use resulted in the continuous growth of CuO passivation films that ultimately yielded a 99.8% reduction in MP release. Engineered reductions in MP release levels were observed following separate controlled exposures to SDW with elevated Cu2+ levels, yielding denser CuO passivation films. This study underscores the importance of reproducing real world conditions in microplastic studies and also the potential for nature-inspired engineered films to mitigate against the release of MPs and the possibility of sustainable MP-free products.

1. Introduction

Globally, there is a significant dependence on plastics in everyday life that results in around 380 million tons of plastics being produced annually [1]. Concern about the levels of microplastics (MPs) in the environment primarily focussed on plastic waste degradation and contamination of waterways [2–5]. Household plastic products (e.g., plastic bottles, food containers, kettles and teabags [6–11]) have recently been shown to be a local and immediate source of extremely high quantities of MPs, raising concerns about the potential impact on human health. Daily use of plastic-laminated disposable cups [8], polypropylene (PP) baby feeding bottles [10] and plastic teabags [9] have been shown to release in excess of a million MP particles per litre. Direct exposure to hot water (70–100 °C) was reported to be a crucial factor and a robust power-law equation was established to predict the increased level of MP release from plastics at higher temperature [9,10]. These reported levels are 2 to 8 orders of magnitude higher than the levels of MPs in drinking water (mean values ranged from 10−3–103)

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particles per litre reported in a recent WHO study [12]).

Established protocols to investigate MP release from daily-use plastics typically involve the use of Deionized (DI) water [6-8,10,11] or similar purified types of water [9] as a replacement for ordinary drinking water, soup or food. This approach is widely employed to simplify and accelerate the testing process. However, DI or highly purified water is rarely used outside of laboratories. Moreover, it is known that plastic surfaces can be modified by exposure to the environment so that there may be unanticipated consequence for the release of MPs. For example, plastics exposed to water can absorb both organic and inorganic species from the surrounding medium [13–15], resulting in the formation of surface films within seconds to hours [16–18]. Exposure of micro-sized plastics (Polystyrene-PS) to synthetic marine water resulted in the adsorption of salt crystals on the microplastic’s surface [15]. Similarly, immersing Polyamide 6 and vinylidene fluoropolymer in drinking water at room-temperature resulted in the adsorption of macromolecular films [18]. The tendency for film formation depends on the plastic’s surface properties, the exposure temperature and the nature and concentration of the environmental species [13,16,19,20]. The adsorption capacity and subsequent surface film formation can be enhanced at higher temperatures by the increased mobility of molecular species or the swelling of the polymer [21–23].

This study focused on the influence environmental films have on the release of MPs. MP release from plastic products exposed to ordinary drinking water during product life was specifically investigated. While the chemical composition of drinking water varies locally, the WHO has prescribed a drinking water safety standard that sets the recommended allowable concentration ranges for various ions and organics [24]. Using the WHO guidelines as a starting point, the concentration of the constituent ions was supplemental to create a Synthetic drinking water (SDW) that accurately reflects the composition of the local (Dublin, Ireland) Tap drinking water (TDW). The SDW can be modified to mimic the local TDW composition for any location where the water compositional data are known. It was found that the level of MPs released from plastics exposed to local (Dublin, Ireland) TDW and SDW are very similar, demonstrating that SDW is an appropriate real-world reference standard to test MP release levels from plastic products. In contrast with DI water, plastics exposed to hot (40–100 °C) SDW and TDW showed the progressive development of a Copper (II) oxide (CuO) passivation film due to the presence of Cu²⁺ ions in the water samples. Globally, copper is one of the most common elements present in TDW (Fig. S1), which is primarily due to the pervasive use of copper plumbing [25,26]. Calcium is another important element commonly found in TDW. A longitudinal study involving PP kettles showed that the level of MP release decreased with the growth of the CuO passivation layer during normal kettle operation, resulting in a 99.8% reduction in MP release after 2000 boils.

2.2. Preparation of tap drinking water, synthetic drinking water and DI water

The TDW quality was monitored during the whole experiment. Table 1 summarized the main constituents of TDW. To simulate the tap water, SDW was prepared by adding certain amount compounds of CuSO₄·5H₂O (Fisher Scientific), CaCl₂ (Sigma-Aldrich), KCl (VWR Chemicals), Mg(NO₃)₂·6H₂O (VWR Chemicals) and humic acid sodium salt (to simulate organic content, ChemCruz) to DI water, the pH was adjusted to 8.0 using NaOH solution (Acros Organics). The DI water resistivity was 18.2 MΩ·cm throughout.

To study the influence of water types on surface passivation, the concentrations of Cu²⁺ was set as 0.5 mg/L while other ion concentrations were set as shown in Table 1. TDW was collected from a main public drinking-water tap in the campus of Trinity College Dublin and was prefiltered (pore size 0.45 μm, 25 mm, Minisart NY Sartorius) to remove any particulates present in the water supply before the use. To study the specific influence of Cu²⁺ ion concentrations on the passivation of plastic materials and the effect of water temperature SDW with 2 mg/L and 20 mg/L/Cu²⁺ were prepared by adding different amount of CuSO₄ (see Table 1). During the longitudinal study using PP kettles (for P1, P2 and P3), TDW from the same tap was collected and used directly without pre-filtration.

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Table 1

The tap water quality and relevant solubility of potential compound in water scale.

<table>
<thead>
<tr>
<th>Parameters (mg/L, except pH)</th>
<th>TDW</th>
<th>SDW</th>
<th>Drinking water standard-EU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>0.3–0.8</td>
<td>0.5–20</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>7.4–8.5</td>
<td>8.0</td>
<td>NR</td>
</tr>
<tr>
<td>Sodium</td>
<td>4.0–11</td>
<td>4.0</td>
<td>NR</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.9–1.04</td>
<td>1.0</td>
<td>NR</td>
</tr>
<tr>
<td>Calcium</td>
<td>2.1–7.8</td>
<td>2.5</td>
<td>NR</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.9–2.8</td>
<td>1.3</td>
<td>NR</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>8–11</td>
<td>0</td>
<td>NR</td>
</tr>
<tr>
<td>Chloride</td>
<td>10–14</td>
<td>5.4</td>
<td>250</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2.5–6.5</td>
<td>6.4</td>
<td>50</td>
</tr>
<tr>
<td>Sulphate</td>
<td>16–30</td>
<td>0.8–30</td>
<td>NR</td>
</tr>
</tbody>
</table>

NR-no regulation; TDW-tap drinking water; SDW-synthetic drinking water, the concentrations of copper and sulfate are changed for the test of concentrations influence MP release by adding different amount of CuSO₄.
2.3. Study of passivation phenomena in standard plastics

To check the influence of water types on passivation, three identical standard PP sheets (exposure size 4.5 cm \( \times \) 4.5 cm, thickness 0.5 mm, Goodfellow) were thoroughly cleaned using DI water. Then the PP sheets were separately exposed to glass beakers filled with three water types (SDW, TDW and DI, 70 mL, \( n = 5 \) for each water type, water preparation see Table 1). The top of each beaker was covered using a glass disk to avoid any potential contamination. Then each beaker was heated using a hotplate until boiling (around 5 mins), and the water was allowed to continue boiling for 5 mins. Finally, the exposed PP sheet was taken out and carefully rinsed using DI water before further characterization of the sheet surface. Following the established protocol [10,28,29], the MPs released into the exposed water were filtered and captured and then the MP release number from per unit area of PP sheet was calculated. (This same protocol was also used to investigate two different copper concentration (pH = 8.0, 2 mg/
L Cu$^{2+}$; pH = 8.0, 20 mg/L Cu$^{2+}$) to assess the influence on the passivation process. A statistical analysis involving one-way ANOVA-test (OriginPro 8.6) was conducted to determine whether there is significant difference between the datasets associated with each water type (SDW, TDW and DI). The null hypothesis ($H_0$) is that there is no difference between the three sets of samples. With a confidence level of 95%, a P value < 0.05 was assumed to be significant (rejecting $H_0$). To check the influence of temperature on the surface passivation phenomenon three identical standard PP sheets (size of 2.5 cm × 5 cm) were thoroughly cleaned using DI water and exposed to glass beaker pre-filled with SDW (20 mg/L Cu$^{2+}$). The beakers were placed in thermal baths, one each at 40 °C, 70 °C and 95 °C, respectively. After 0.5 h, 1 h and 24 h the level of CuO film growth was measured on the surfaces of 95 °C, 70 °C and 40 °C exposed PP sheets, respectively.

The protocol in Fig. 1a was separately repeated using a range of other food-grade polymer samples: polyethylene terephthalate-PET, polyamide-PA, high-density polyethylene-HDPE, low-density polyethylene-LDPE, Polystylene-PS and silicone, standard sheets, size of around 2 cm×2 cm (silicone was provided by RS Ltd. while others were provided by Goodfellow). These sheets were exposed to SDW with 20 mg/L Cu$^{2+}$ (Table 1). After the exposure, the sheets were rinsed using DI water and photographed, following chemical analysis using Raman spectroscopy.

2.4. Study of passivation phenomena in household plastic kettles

Three popular brand-new PP kettles were prepared, P1, P2 and P3 (n = 5 of each product). For P1 and P2, a 200-day test was performed by bring to the boil 0.8 L TDW (no pre-filtering) once per day in accordance with a survey of average kettle users [30] (Fig. S3a). To investigate the MP release from these kettles, an extra boil using DI water was performed on day 1, 3, 4, 5, 7, 10, 20, 30, 50, 70, 90, 110, 130, 150, 175 and 200. For these extra boils, the boiled water sample was collected, filtered and analyzed using the established protocol (Fig. S3b). Meanwhile, the inner surface of P1 and P2 were also photographed (Fig. S3c). After 200 days, the inner passivation layer was carefully taken out and analysed using Raman spectroscopy.

For P3, a higher boil frequency was used to check whether this accelerates the rate of passivation film formation and the suppression of MP release. A one-year test was performed by boiling 0.8 L TDW (no pre-filtering), 6 boils/day, 2000 boils in total. The level of MP release was tested before and after the 2000 boils following the protocol described in Fig. S3b. In addition, to demonstrate the natural occurrence of this passivation phenomenon, a separate study was carried out using PP kettles randomly collected from the Dublin area and their interiors were analysed. In total, 13 used kettles with service durations ranging from 0.5 to 3 years were analysed. Fig. S4 shows a typical used kettle after around 1-year use after experiencing around 1 boil per day. The full details were summarized in Table S1. After rinsing using DI water, a section of the inner surface was carefully removed to conduct physicochemical analysis.

2.5. Characterization and determination of the discoloration and passivation layer on the surface of standard plastics and kettles

Multiple techniques were used to characterize and determine the physicochemical properties of the passivation layer formed on the surface of standard plastics and the interior of kettles. Scanning electron microscopy (SEM, Zeiss Ultra Plus) and energy dispersive X-ray (EDX) was performed with an acceleration voltage of 15 kV. The chemical composition of passivation films was also determined by Multiprobe X-Ray photoelectron spectroscopy (XPS, Scienta Omicron) using a mono-energetic Al K-alpha source. A low energy electron flood gun was used during all XPS measurements to compensate for surface charging. Raman spectroscopic testing (Renishaw InVia Raman spectrometer) was also conducted with 532 nm excitation laser and 50% laser intensity. To obtain a large area perspective (mm scale) of the surface roughness of the CuO-films formed in used kettles, contactless optical coherence tomography (OCT, Thorlabs Ganymede) was conducted to analyse the inner surfaces of used kettles under 3D mode.

2.6. Monitoring of water parameter

Following the procedures specified in Standard Methods for the Examination of Water and Wastewater [31], multiple parameters of tap water were monitored. Inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent) analysis was used to test the metal elements concentration, e.g., copper, calcium, magnesium, potassium and sodium in different water types. The pH value was measured by a pH meter (FiveEasy, Mettler Toledo). Other parameters, e.g., nitrate, (bi) carbonate, chloride and sulphate were quantified using Konelabs 20i (Thermo Fisher Scientific).

3. Results

3.1. Water types influence passivation phenomena

As the most widely used plastic in consumer products, polypropylene was chosen to test the level of MP release. Three identical standard PP sheets (4.5 cm × 4.5 cm, thickness 0.5 mm) were thoroughly cleaned and separately exposed to three different water types (SDW, TDW and DI, n = 5 for each water type) that were heated, allowed to boil and then cooled, each step was 5 min duration (Fig. 1a and supporting information section 3). SDW was prepared in accordance with the WHO drinking water guidelines [24] and mimicked the local (Dublin, Ireland) TDW quality. SDW was prepared with a pH of 8.0, and the concentrations of Cu$^{2+}$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and humic acid salt (to simulate organic content) were set at 0.5, 4.0, 1.0, 2.5, 1.3, 5.4, 3.0, 6.4 and 0.11 mg/L, respectively (Table 1 and supporting information section 2). TDW (pH = 8, Cu$^{2+}$ = 0.5 mg/L, and all other ions with similar levels to SDW) was prefilled (pore size 0.45 µm) to remove any particles present in the water supply, while the DI water used had a resistivity of 18.2 MΩ-cm. Fig. 1b shows that the levels of MP release from the three water types are very similar, releasing 3,040 ± 130, 2,590 ± 250 and 2520 ± 550 MPs per cm$^2$ during the exposure to TDW, SDW and DI water, respectively (where ± represents s.d.). A one-way ANOVA-test (OriginPro 8.6) was conducted and found no significant difference (P = 0.12 greater than 0.05) between these datasets. This is consistent with an earlier comparison between prefilled TDW and DI water [10].

There was no visible change in the PP sample after exposure to DI water, however, both the SDW and TDW exposed samples showed evidence of discoloration. AFM images (Fig. 1c–f) showed that the mean roughness of the original PP surface (6.9 nm) was similar to that of DI water exposed PP (6.7 nm), but substantially increased to around 19.0 nm and 17.4 nm, after SDW and TDW exposure, respectively. The increased roughness was due to the presence of particles that coated both SDW and TDW exposed PP sheets. EDX elemental analysis found that copper dominates the spectra of both surfaces, accounting for around 72% and 68% (weight %) of these particles, respectively (Fig. 1g and Table S2). The presence of oxygen and carbon were also confirmed. High-resolution XPS identified the nature of the copper (Fig. 1h and i). XPS peaks at binding energies of around 932, 953 and 940–944 eV are consistent with the well-defined spectra of Cu$_2$P$_{2s/2}$, Cu$_{2p_1/2}$ and shake-up satellite peaks associated with copper (II), respectively [32–34]. The O1s peak at binding energy close to 530 eV is consistent with an oxide O$^{2-}$ ion (Fig. S6) [32]. Raman spectroscopic analysis of these particles closely matched the spectrum of Copper (II) oxide (CuO) (Fig. 1j). The significant peaks at around 288, 335 and 625 cm$^{-1}$, correspond to the well-known A$_g$, B$_1g$ and B$_2g$ vibrations of CuO [35–37]. These data confirmed that the generation and attachment of single-phase CuO particles (around 85–90% of weight contribution, Table S2) on the PP
surface is responsible for the discoloration.

It was reported that the decomposition of Cu(OH)$_2$ to CuO in aqueous condition occurs at room temperature [38], but substantially speeded up with the temperature reaching 50 °C [39,40]. Given the high temperature during the boiling process (up to 100 °C) and ideal aqueous conditions, the dehydration of Cu(OH)$_2$ is responsible for CuO generation (eq. 1, 2), which results in discoloration. However, at the densities shown in Fig. 1e and f, they have minimal impact on MP release (Fig. 1b). The presence of CuO particles on TDW and SDW exposed samples demonstrates that SDW closely mimics the natural CuO passivation phenomena associated with TDW, whereas DI water fails to reproduce this crucial process that occurs in real world environments.

\[
\text{Cu(OH)}_2(aq) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq) \quad (1)
\]

\[
\text{Cu(OH)}_2(aq) \rightarrow \text{CuO}(s) + \text{H}_2\text{O}(aq) \quad (2)
\]

3.2. Passivation phenomena influence MP release

The CuO-based passivation phenomena is understandable given that Cu$^{2+}$ ions are ubiquitous in drinking water, which is mainly due to the pervasive use of copper plumbing [25,26]. While the CuO particles attached to PP sheets due to a single exposure to hot SDW and TDW have minimal impact on MP release (Fig. 1b), further growth of CuO passivation layer due to longer exposure periods and/or higher Cu$^{2+}$ ions concentrations can dramatically reduce MP release levels. WHO recommends a maximum level of 2 mg/L copper in drinking water while much higher values were reported in some cities (e.g., New South Wales [26], Berlin [41] and many US cities [25]). To simulate this phenomenon and to further investigate the mechanism of CuO film formation, standard PP sheets were exposed to SDW with higher concentrations of Cu$^{2+}$ (2 mg/L and 20 mg/L) following the same protocol (Fig. 1a). After

![Fig. 2. The influence of copper water concentration on CuO film formation and MP release. (a) standard PP sheet before and after exposure to 2 mg/L and 20 mg/L Cu$^{2+}$, SDW using the protocol in Fig. 2a, (b) and (c) AFM images of PP surface exposed to 2 mg/L and 20 mg/L Cu$^{2+}$, respectively, (d) MPs release levels from raw PP (all MP release tests were performed using DI water following protocol in Fig. 1a), 2Cu-PP (PP sheet pre-exposed to 2 mg/L Cu$^{2+}$ SDW, then tested MPs release in DI water following protocol in Fig. 1a), and 20Cu-PP (PP sheet pre-exposed to 20 mg/L Cu$^{2+}$ SDW, then tested MPs release in DI water following protocol in Fig. 1a), respectively. (e) Images of raw plastics and the corresponding surfaces coated with CuO layer (standard silicone, PET, PA, HDPE, LDPE and PS, following the exposure protocol in Fig. 1a, top panel is raw plastic, lower panel is plastic after exposure). (f) Raw PP sheet and PP sheets exposed to SDW at different temperatures with different exposure times. From left to right, raw PP, PP exposed to 40 °C, 70 °C and 95 °C with different durations. The surface coatings in Fig. 2e and f were confirmed as CuO using Raman spectroscopy.](image-url)
a single heat-boil-cool cycle, the surface of PP sheet exposed to 2 mg/L 
Cu\(^{2+}\) (hereafter identified as 2Cu-PP) turned slightly brown while the 
sheet exposed to 20 mg/L Cu\(^{2+}\) (identified as 20Cu-PP) turned 
completely brown due to a denser growth of CuO particles on the PP 
sheet’s surface (Fig. 2a–c and Figs. S7). The 10-fold increase in Cu\(^{2+}\) level 
resulted in a proportional increase in particle density from 2.6 million to 
22.0 million per cm\(^2\) (Fig. 2b, c and Figs. S7, S8). Evidently, Cu\(^{2+}\) ions 
are efficiently transformed into CuO film on the surface of PP plastic.

To assess the influence of the CuO layer growth on MPs release, raw 
PP and the two exposed PP sheets (2Cu-PP and 20Cu-PP) were soaked 
in DI water following the procedure in Fig. 1a. DI water was used to 
measure MP release and to avoid any additional film formation on the 
2Cu-PP and 20Cu-PP sheets. After soaking, the water was collected and 
the MP release levels determined using the established protocol (supporting 
information section 1 and 3) \(^{10}\). Projecting the MP number to the 
exposed PP sheet area, the raw PP released 2,520 ± 550 MPs per cm\(^2\), 
which is consistent with the known high release capacity of PP 
products (such as PP-based food containers \(^{6}\), kettles \(^{11}\) and baby 
feeding bottles \(^{10}\)). For the 2Cu-PP and 20Cu-PP sheets, the release 
levels reduced to 490 ± 200 and 200 ± 110 MPs per cm\(^2\), corresponding 
to 80.6% and 92.1% reductions, respectively (Fig. 2d), demonstrating the 
ability of naturally formed CuO layers to limit MP releases. A one-
way ANOVA-test (OriginPro 8.6) confirmed the significant difference 
(\(P = 0.0000003 < 0.05\)) between these datasets. Evidently, a single 5-
min boil with relatively high concentration of Cu\(^{2+}\) ions (20 mg/L) 
can substantially affect MP release. Although a single boil in SDW with 
low concentration of Cu\(^{2+}\) ions (0.5 mg/L) similar to that found in 
(Dublin, Ireland) TDW had an insignificant influence on MP release 
(Fig. 1b), the accumulated growth of CuO layer during prolonged 
exposure dramatically reduced the levels of MP release (see below).

3.3. Passivation phenomena for food-grade plastics during different daily 
scenarios

To test whether this CuO passivation phenomenon was unique to PP, 
the protocol in Fig. 1a was repeated separately using a range of other 
standard food-grade polymer sheets (polyethylene terephthalate (PET), 
polyamide (PA), high-density polyethylene (HDPE), low-density poly-
ethylene (LDPE), Polystyrene (PS) and silicone), exposed to SDW with 
20 mg/L Cu\(^{2+}\). Fig. 2e showed that all test samples were coated with a 
CuO layer after a single exposure. Combining with PP, these CuO-film-
forming plastics account for over 97% of total market share of the 
plastics used in food packaging \(^{42}\).

To simulate the temperature and agitation levels plastics experience 
during food preparation (e.g., around 40–75 °C for dishwashers and 
during 91–96 °C for coffee machines without boiling), plastic sheets 
(standard PP) were exposed to turbulence-free SDW containing 20 mg/L 
Cu\(^{2+}\) at three commonly used temperatures (95 °C, 70 °C and 40 °C, 
temperature sustained using thermal baths). After 0.5 h, 1 h and 24 h, 
significant growth of CuO film was found on the surface of PP sheets at 
95 °C, 70 °C and 40 °C, respectively (Fig. 2f). The enhanced growth of 
CuO films at higher temperatures is likely due to the higher trans-
formation rate of Cu\(^{2+}\) to CuO, which is consistent with previous reports 
about copper compound reactions \(^{39,40}\). Though more study is 
needed, it is evident that this passivation phenomenon is ubiquitous 
for most plastics used in food preparation.

3.4. Passivation phenomena for plastic kettles

To determine the effectiveness of this passivation layer to limit MP 
release in real world-consumer products, PP kettles were studied because 
they are the most widely used household appliances. Two types of 
brand-new popular kettles (P1 and P2, \(n = 5\) of each type) were chosen 
to undergo a 200-day test by boiling 0.8 L TDW (heated for 2 mins, boil 
for 20 s and emptied) once per day in accordance with a survey of kettle 
users \(^{30}\). During the 200-day testing period the water composition 
varied but remained within the WHO recommended range: Cu\(^{2+}\) levels 
were 0.3–0.8 mg/L with pH 7.4–8.5 (Greater Dublin Area, supporting 
information section 2). At the start of the study both kettles released 
50–60 million MPs per L (Fig. 3a). During the first 10 days, the MP levels 
from both products were higher than ten million particles/L. From day 
10 to day 20, the release levels dropped sharply to 2,382,000 ± 70,000 
and 5,223,000 ± 394,000 for P1 and P2, respectively. Although there 
were daily fluctuations in the levels of MP release, after day 200, P2 
released 1,694,000 ± 112,000 particles/L, with similar levels observed 
from P1. Optical images of the kettle interiors show that in the first 10 
days there were no significant colour change. However, after day 20 
significant discolouration occurred below the water level mark, which 
continued to darken and turned to deep brown/black at day 200 (Fig. 3b 
and Fig. S3c). The observed reduction in MP releases was due to the 
growth of CuO-based passivation films (determined using Raman spec-
troscopy) and is consistent with that found for standard plastics samples 
using SDW (Fig. 2).

To demonstrate the natural occurrence of this passivation phenom-
enon, used PP kettles were randomly collected and their interiors ana-
lyzed (13 used kettles, service duration 0.5–3 years, collected from the 
Dublin area, Table S1). Physicochemical analysis confirmed the growth 
of CuO-based films with thicknesses varying locally from 1.5 to 30 \(\mu\)m 
observed inside all used kettles, regardless of user habits, kettle styles 
and service durations (Fig. 3c–f and Table S1 and Figs. S4, S5 and S10). 
Control tests confirmed that kettles do not release elemental copper and 
that TDW is the dominant contributor to CuO film formation (supporting 
information section 5).

An additional MP release test using kettle product 3 (P3, \(n = 5\), 6 
boils/day, 2000 boils in total) showed MP levels that dropped from 
around 31.4 million MPs/L to 64,000 MPs/L, which is equivalent to the 
drop from around 30,000 MPs per cm\(^2\) to 70 MPs per cm\(^2\) (projecting the 
MP number to per unit area of kettles, Fig. 3a and supporting informa-
tion section 4). The substantial suppression (99.8% reduction) is 
consistent with the results obtained using standard PP sheets. In addi-
tion, these results confirmed that high numbers of boils accelerate the 
passivation film growth and achieve a greater level of suppression of MP 
release.

4. Discussion

This study shows the importance of using the Synthetic drinking 
water (SDW) approach to reproduce real-world conditions reflected 
through the composition of local Tap drinking water (TDW). Through 
this approach, researchers can tune SDW to mimic their local conditions 
and to make improved predictions about the behaviour of plastics and 
indeed any other material exposed to local TDW. SDW also provides a 
rational platform through which researchers can systematically explore 
the effects of increased level of minerals, additives and impurities on 
the behaviour of materials to which it is exposed. Crucially, using SDW 
avoids potentially misleading results that are a direct consequence of 
using DI water or other purified forms of water when trying to simulate 
the effects of local drinking water.

In this paper, we identified the importance of the levels of Cu\(^{2+}\) ions 
in water and their role in the formation CuO film coatings on plastics. 
This natural passivation phenomenon occurs following routine exposure 
of plastics to drinking water and film formation is enhanced at higher 
water temperatures. These CuO films were shown to be remarkably 
efficient in reducing the level of MP release, with reductions of up to 
99.8% occurring even under the most aggressive boiling conditions. This 
suppression phenomenon is particularly important for plastic products, 
such as kettles, where the CuO film is allowed to build up over time. This 
study also found that repeated rinsing fails to remove the CuO passiv-
ation layer. For these reasons, MP release studies based on DI water 
significantly over-estimated the actual levels of release during the 
product service life. Based on above results (Fig. 2b–d) it is also 
reasonable to expect that the nature of the passivation film will depend
Fig. 3. CuO-based passivation layer in kettles. (a) Long-term test of the correlation between number of times brought to the boil and MPs release level. 3 kettle products and TDW were used in this test. (b) Typical optical images of the interior of kettle P2 with the increase of number of boils. (c) SEM image of typical CuO-based passivation layer from a used kettle (U-1 in Table S1). (d) and (e) EDX mapping of element Cu and O on the passivation layer from the used kettle, respectively. (f) Optical coherence tomography (OCT) test for the 3D image of passivation layer from the used kettle, unit-mm. To benefit the test, part of passivation film was carefully removed using DI water. Red box area in (f) is CuO film while whiter circle area is film removed part, details see Fig. S9. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
on the actual concentrations of the different species found in tap drinking water. By tuning the composition of the SDW further it is possible to engineer a range of nature-inspired passivation films.

The suitability of these films for MP-free food preparation and storage applications will depend on film adhesion strength, mechanical robustness, and more importantly, its chemical resilience and safety. Copper is an essential element for the human body that supports the proper functioning of many important enzyme systems [43]. However, high concentration of copper (around 4–8 mg/L) in drinking water can cause the gastrointestinal symptoms, such as nausea, vomiting and/or abdominal pain [44]. Due to the potential toxicity, WHO suggests that no more than 2 mg/L of Cu is permissible in drinking water to protect against the adverse effect of copper [45], although published data show copper concentration in some regions (such as New South Wales, Australia [26]) that are higher than the recommended safe level (Fig. S1). For this reason, it is crucial to ensure that CuO-based coating film is not an additional source of copper due to the potential leaching. To test this, we exposed CuO coated surfaces to repeated boiling process (100 °C and water turbulence) and rinses and observed that the micron sized feature that comprise the film are unaffected and that there is no evidence of the leaching of CuO particles into the boiled water. These observations are consistent with a previous report of high-temperature resistance and zero-leaching performance of CuO [46,47]. However, the daily use plastics endure even more severe conditions, such as the repeated mechanical cleaning and vigorous shaking so that further study will be required to fully assess the leaching potential of these CuO films.

To date, little is known about the detailed PP degradation processes that occur during boiling. In general, it is known that PP is susceptible to oxidation [48]. It was also reported that during boiling PP is very susceptible to thermal degradation [11]. The thermal-oxidative environment and extreme turbulence associated with boiling water are considered to be ideal conditions for the release of high numbers of MPs [11]. The presence of the CuO passivation film acts as a barrier layer to minimise direct contact between the plastic and the reactive water environment. Though further study is clearly required to fully understand the origin of the MP reduction mechanism, the learnings from this work represent an important advance in the development of microplastic-free plastics and future work will focus on exploiting these insights in combination with established plastic coating technologies.

5. Conclusions

This study focused on the influence of environmental factors on the formation of passivation film that impact on the release of MPs. It was found that these environmental factors can be explored via the use of SDW concept, so that SDW is an appropriate real-world reference standard to test MP release levels from plastic products. In contrast with the use of DI water, plastics exposed to hot (40–100 °C) SDW and TDW showed the progressive development of a Copper (II) oxide (CuO) passivation film due to the presence of Cu²⁺ ions in the water samples. Similar passivation films formed on 97% of all food grade plastics. Engineered reductions in MP release levels were observed following separate controlled exposures to SDW with elevated Cu²⁺ levels, yielding denser CuO passivation films. This study underscores the importance of reproducing real world conditions in microplastic studies and the potential for nature-inspired engineered films to mitigate against and perhaps even prevent the release of MPs entirely.

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 associated with this article can be found in another file (9 Figures and 2 Tables).

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.132466.

References


