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Emerging investigator series: release and phototransformation of benzophenone additives from polystyrene plastics exposed to sunlight†

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There are increasing concerns about the human and environmental health impacts of plastic exposure, which include the risks associated with plastic additives. However, despite their presence in most plastic products, the factors governing the release and transformation of chemical additives in the aquatic environment are poorly understood. In this study, we examined the simultaneous release and transformation behavior of four benzophenone-type chemical additives from polystyrene (PS) under natural and accelerated photochemical weathering conditions. Liquid chromatography coupled with high resolution-mass spectrometry (LC-HRMS) quantitatively determined additive concentrations in plastic leachates and identified the formation of phototransformation products. Although the passive release of benzophenones from PS followed a time$^{0.5}$ dependence, the presence of sunlight (active release) altered the concentration of leached benzophenones in solution depending on the relative photostability of the compounds. In accelerated lab-based studies using >300 nm irradiation, a second stage of increased additive release was observed for prolonged irradiation times, an effect ascribed to distinct stages of PS photodegradation. LC-HRMS analysis identified various photodegradation products, including carboxylic acids and hydroxylated species. Quencher experiments indicated that these transformation products were produced by the formation of excited triplet states and hydroxyl radicals generated by benzophenone photoexcitation. Hydroxyl radicals are also likely responsible for the complete mineralization of irradiated benzophenones as evidenced by total organic carbon analysis. This work identifies the impact of photolysis on both additive release and transformation of benzophenones.

Environmental significance

This study investigates the leaching of benzophenone additives from plastics when exposed to sunlight. In contrast to previous studies that have almost exclusively focused on the leaching of parent additives, our research also focused on the identification of phototransformation products. The results revealed that leaching of additives from plastics increases over extended sunlight exposure periods due to the degradation of the polymer matrix. Once in solution, benzophenones undergo phototransformation *via* benzophenone self-sensitization. These results highlight the importance of including phototransformation products to adequately assess additive leaching. The characterization of phototransformation products is also critical to assess potential adverse environmental health impacts associated with additive leaching from plastics.

Introduction

The global use of plastics is expected to rise from 464 Mt in 2020 up to 884 Mt in 2050.[1] This has led to a large accumulation of plastic waste, as roughly 40% of produced plastic has a service lifetime of less than 1 month.[2] At the end of the use-phase, plastics are discarded and often end up in aquatic ecosystems where they can pose significant harm to marine life through organism ingestion, facilitated transport of adsorbed contaminants, the formation of microplastics, and additive leaching.[3–7] However, the potential adverse effects on ecosystems caused by chemical additive leaching from plastics is relatively poorly understood.[2,8] These chemical additives are compounds added to a polymer matrix during plastic manufacturing to improve the performance of the final product.[2,9] Common classes of plastic additives include plasticizers (*e.g.*, phthalates), heat and light scavengers (*e.g.*, benzophenones, benzotriazoles), flame retardants (*e.g.*, organobromines), and antioxidants (*e.g.*, bisphenols).[2,8,10,11]

Since additives are not chemically bound within the polymeric matrix, they can potentially leach from the plastic when

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in contact with water.[2,12,13] This leaching, or release, can take place during the use-phase of the plastic (*e.g.* the migration of additives from food packaging into food) or after the plastic has been disposed.[14–17] A number of recent studies have demonstrated leaching of phthalates, benzophenones, and organotin compounds from plastics.[18–21] Phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), and di-*n*-butyl phthalate (D*n*BP) leach from both polyvinyl chloride and polyethylene plastics into marine and freshwater environments.[18–20] One study found that DEP and DMP were the most dominant phthalates leached from a mixture of polyvinyl chloride microplastics.[20] Benzophenone-3 (BP-3) has also been found to leach from polyethylene fragments, and the associated leachate has been used to study the toxic effects of BP-3 in aquatic organisms.[22,23]

Environmental processes, such as abrasion or exposure to reactive oxygen species, can accelerate the degradation of plastics and increase additive leaching.[24–29] Similarly, previous research has demonstrated that exposing plastics to light can change the release behavior of chemical additives,[21,26] such as organotin additives from polyvinyl chloride and phthalates from commercial polyethylene.[19,21] For example, under UV/visible light irradiation, some organotin additives were not detected in the leachate due to rapid photodegradation.[21] When considering the effects of photolysis on the fate of chemical additives in plastics, the potential for photochemical transformations of the additive either within the plastic or in the surrounding solution must also be taken into account. Most importantly, if an additive undergoes photodegradation, leaching experiments that only assess the parent compound will underestimate overall release rates and concentrations. Thus, to fully understand the environmental risks associated with the presence of additives in plastics, it is important to examine the release and phototransformation as simultaneous processes and to assess the formation of phototransformation products.

Benzophenones are a common class of plastic additives, which act as UV-stabilizers and protect polymers from photodegradation. Benzophenones contain two phenyl rings attached to either side of a central carbonyl bridge. This conjugated structure allows them to efficiently absorb UV light and prevent polymer degradation.[30] Functionalization of the phenyl rings can further enhance the photoprotection mechanism; consequently, numerous benzophenone derivatives are used commercially in personal care products and polymeric materials.[31–34] Their widespread use as additives across a range of industries has led to a significant accumulation of benzophenones in aquatic environments,[30,33–35] where they have been shown to exhibit adverse environmental impacts due to their endocrine disrupting and carcinogenic potential.[36–39] Thus, the leaching of benzophenones from plastics is of concern due to the potential toxicity risk posed to aquatic organisms, including algae, fish, and invertebrates.[40]

Most studies investigating the photochemical fate of benzophenones in surface water have focused on elucidating the photodegradation kinetics by following the loss of the parent compound. In natural waters and at environmentally relevant concentrations (<100 μg L^{-1}), the photodegradation of benzophenones follows first-order kinetics.[41] Furthermore, previous research has shown that indirect photolysis, involving reactions with reactive intermediates (*e.g.* hydroxyl radicals) formed by the photolysis of dissolved organic matter and nitrite, increases the photodegradation rates of benzophenones.[42,43] These studies have also demonstrated that indirect photolysis results in the formation of hydroxylated benzophenone species as a consequence of reactions with hydroxyl radicals and nitrite.[43,44] Benzophenones also have the potential to degrade *via* self-sensitization (*i.e.* formation of benzophenone triplet states); it was shown that self-sensitization of 2,4-dihydroxybenzophenone can result in the formation of singlet oxygen, which contributes to benzophenone degradation.[45]

Although the photodegradation kinetics and toxicity of benzophenone-type additives in aqueous systems are well characterized, their release from plastics and the formation of transformation products remain undetermined. In addition, previous studies on plastic additives typically only focus either on the elucidation of release kinetics or the formation of transformation products despite their potential for simultaneous occurrence (*e.g.* when plastics float on the surface of water bodies). To address these questions, this study investigated the simultaneous leaching and transformation of several benzophenone-type additives from plastics in the presence of light. Four different benzophenones were selected, based on their commercial use and/or expected differences in photostability and UV protection capability. Given the broad range of polymers used to manufacture plastics, we restricted our studies to polystyrene, a hydrophobic polymer frequently used in packaging containers, such as lids, bottles, and trays.[46] Due to its long-term stability in the environment, polystyrene is considered a persistent pollutant and could remain as a source of chemical additives over decades or even centuries.[47] To this end, polystyrene plastic composites containing one of four benzophenones were fabricated and characterized. We then used these materials to compare the release behavior of the benzophenones in the presence and absence of sunlight (active and passive release, respectively) during natural weathering and in accelerated weathering experiments. We also examined direct photodegradation of the benzophenones in solution and identified phototransformation products using liquid chromatography – high-resolution mass spectrometry (LC-HRMS). Due to the hypothesized importance of self-sensitization in the degradation of benzophenones, all experiments were performed in ultrapure water in the absence of a buffer to exclude potential interference from reactive intermediates.

Materials and methods

Materials

All chemicals were used as received without further purification. 4-Chloro-4′-hydroxybenzophenone (4Cl4HBP) and 4-hydroxybenzophenone (4HBP) were purchased from Toronto Research Chemicals, and 2,4-dihydroxybenzophenone (DHBP; commonly referred to as benzophenone-1; BP-1), and 2-hydroxy-4-methoxybenzophenone (MBP; commonly referred to as BP-3) were purchased from Alfa Aesar. Tris (2-chloroethyl) phosphate

(TCEP) was purchased from Millipore-Sigma. Polystyrene (PS, MW = 280 000 Da) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and VWR, respectively. Ultrapure Milli-Q water (18.2 MΩ cm) was used to prepare all aqueous solutions and used in all leaching studies. Liquid chromatography mobile phases were prepared with high-performance liquid chromatography (HPLC) grade methanol, ammonium fluoride, and formic acid purchased from Fisher Scientific.

Synthesis of benzophenone/polystyrene composites. Benzophenone additives were incorporated into the polymer matrix *via* solution blending and casting. In this study a 1% w/w (additive/polymer mass) benzophenone loading was used. The use of a research grade source of PS synthesized by styrene polymerization meant that the concentration of additives could be accurately controlled by solution blending as described in Fig. ESI-1.† In contrast, polystyrene sourced from an industrial source would almost certainly contain a mixture of additives with undisclosed concentrations. Solution blending was used in the present study as a convenient and easily implementable laboratory proxy for blending processes used industrially to incorporate chemical additives into polymers such that the additives are not covalently bound to the polymer matrix. Moreover, solution blending allows accurate control over the loading of benzophenones in the polymer matrix, while also facilitating their uniform dispersion within the polymer (PS) matrix. Additional details of how these composited were synthesized can be found in the ESI (section 'Additional experimental details' and Fig. ESI-1).†

Measuring benzophenones leaching from additive-PS composites

Passive release of benzophenones from additive-PS composites in water. To simulate additive release in aqueous environments, PS composites were cut into 1 × 1 cm^2 pieces (*ca.* 30 mg). Samples were then tethered to a PTFE stir bar (1 cm × 3 mm) with PTFE string to prevent floating and immersed in Milli-Q water (10 mL) in a test tube (pH 7 ± 0.2). After 5 minutes of soaking to remove any surface contaminants, the water was removed and replaced with fresh Milli-Q water. Test tubes were then kept in the dark and the release of benzophenones from these additive-PS composites assessed as a function of time under these passive release conditions.

Active release of benzophenones from additive-PS composites exposed to natural sunlight. Additive-PS composites were prepared in triplicate in quartz test tubes filled with 10 mL of water and sealed with silicone caps, aluminum foil covers, and Teflon tape. All samples were placed outside on a rooftop in Baltimore, MD (39° 19′ W, 76° 37′ N) and sampled at predetermined time intervals from June to August (0, 3 days, 1 week, 2 weeks, 3 weeks, 4 weeks, 6 weeks, and 8 weeks) in 200 μL aliquots. Equivalent dark controls were also prepared, fully wrapped in aluminum foil, and stored outside under a dark box. The timescale over which release was measured was based on previous studies where additive release was monitored on a weekly/biweekly basis over the course of several months.[19,48]

Release of benzophenones during accelerated photolysis of benzophenone-PS composites. Accelerated photodegradation of benzophenone-PS composites was performed in a merry-go-round photochemical reactor (RPR 100, Southern New England Ultraviolet Company, Branford, CT, approximately 4.3 × 10^{16} photons per s) equipped with 16 low pressure mercury lamps (maximum UV light irradiance at 300 nm) and an internal fan to maintain a temperature of 30 °C. Experiments were conducted in borosilicate glass test tubes to exclude UV light below 300 nm. Plastic samples of each benzophenone-PS composite ($n = 2$) were placed in borosilicate test tubes filled with 10 mL of water, sealed with silicone septa, and capped with aluminum foil. Aliquots (200 μL) were sampled at predetermined intervals (0, 2 hours, 6 hours, 12 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 6 days, 8 days, and 10 days). Equivalent dark controls were also prepared in duplicate, completely wrapped in aluminum foil, and stored in a dark drawer at room temperature. All collected aliquots were stored in amber glass vials at 4 °C until analysis.

Photolysis of benzophenones in solution. For the preparation of aqueous stock solutions, each benzophenone was first dissolved in methanol (1 mg mL^{-1}). The volume of the stock solution that was needed to obtain a 10 mg L^{-1} benzophenone solution was then added to a glass bottle and placed under a stream of nitrogen to completely evaporate the methanol. The benzophenone precipitates were then dissolved in ultrapure water using sonication for 30 minutes. Subsequent dilutions in ultrapure water were used to obtain the desired starting benzophenone concentration. Prior to irradiation these solutions were kept in the dark at room temperature to avoid recrystallization of the benzophenones at cold temperatures. Elevated concentrations of benzophenones were used to facilitate the identification of phototransformation products.

Photolysis of benzophenones by natural sunlight. Benzophenone solutions (10 mL) were added to quartz test tubes and sealed with silicone caps, aluminum foil covers, and Teflon tape. All samples were placed outside on a rooftop in Baltimore, MD (39° 19′ W, 76° 37′ N) and sampled at predetermined time intervals from June to August (0, 3 days, 1 week, 2 weeks, 3 weeks, 4 weeks, 6 weeks, and 8 weeks). Aliquots (100 μL) were collected at the same time intervals as those from the benzophenone-PS composites and diluted in ultrapure water. All collected aliquots were stored in amber glass vials at 4 °C until analysis.

Accelerated photolysis of benzophenones. Photolysis was performed in the same merry-go-round photochemical reactor emitting 300 nm light used to irradiate benzophenone-PS composites. Borosilicate tubes were used to exclude wavelengths <300 nm. After addition of benzophenone solutions (5 mg L^{-1}; 10 mL total volume), the borosilicate tubes were sealed and capped with aluminum foil. Dark controls were prepared similarly but completely wrapped in aluminum foil and stored at room temperature in a dark cabinet to prevent light exposure. Radical scavenging experiments were performed using 26 mM isopropanol (hydroxyl radical)[49] and 2.2 mM sorbic acid (excited triplet state quencher).[50] Aliquots were collected at predetermined time intervals and stored in the dark at 4 °C until analysis. For UV-vis and total organic carbon measurements which required larger sample volumes, two replicate tubes for each irradiation time were prepared, removed from the photoreactor, and combined.

It should be noted that throughout our studies we used a small volume of water (10 mL) to increase the concentration of additive released and thereby facilitate quantification. However, even under these conditions the highest additive concentration measured in solution was only 30 $\mu g\ L^{-1}$. This was observed for MBP release during accelerated weathering studies where we observed ≈ 12 μg MBP per g PS (see Fig. 4). Since the mass of PS coupons was ≈30 mg, this corresponds to a MBP concentration of ≈30 $\mu g\ L^{-1}$, almost 300 times less than the solubility limit of MBP (8.8 $mg\ L^{-1}$). Additive release can therefore be assumed to occur into an infinity dilute solution of MBP, conditions where release behavior has been modelled.

Quantification of benzophenone concentrations and identification of their phototransformation products. The concentrations of benzophenones released from the PS composites during passive or active release were determined using liquid chromatography-high resolution mass spectrometry (LC-HRMS) (Q Exactive HF; Thermo Fisher Scientific) in electrospray ionization (ESI) negative ion mode. For chromatographic separation of the benzophenones and any potential transformation products (TPs), a Hydro-RP (C18; 150 × 1 mm, 4 μm, 80 Å) column and a gradient mobile phase method were used. The initial conditions of the eluents were 95% 1 mM ammonium fluoride (pH 7.1) and 5% methanol from 0–2 min, followed by a linear change of methanol to 95% from 2–12 min, continued 95% methanol from 12–21 min, and ending with a return to 5% methanol from 21–30 min. Sample injection volume was 10 μL and the flow rate was set to 75 $\mu L\ min^{-1}$. Data dependent acquisition was used to collect MS2 spectra as follows: a full scan (100 to 700 *m*/*z*) was conducted followed by MS2 for the 5 most abundant ions with a resolution of 30 000, an isolation window of 1.0 *m*/*z*, and normalized collision energies of 30, 50, and 70 eV. Concentrations of released additives were determined using an external calibration curve (6 points). Laboratory blanks and analytical blanks were run with every batch to exclude potential background contamination. Target analytes were absent in all blanks. LC-HRMS was also used to identify the presence of transformation products (TPs) in collected leachates and photolysis solutions. The proposed formulas of TPs were initially assessed with CompoundDiscoverer software (Version 3.2, Thermo Scientific). Identity and structures of proposed formulas were elucidated *via* chromatogram dd-MS^2 analysis using Thermo Xcalibur QualBrowser software.

HPLC-UV was used to assess kinetics and determine the concentrations of benzophenones as a function of irradiation time in photodegradation experiments conducted in the absence of PS. Chromatographic separation of the parent additive and individual TPs was achieved by injection of 25 μL sample onto an Acclaim 120 column (Thermo Scientific; 4.6 × 100 mm, 5 μm, 120 A). An isocratic mobile phase method using varying proportions of methanol and 0.1% formic acid was employed at a flow rate of 0.600 $mL\ min^{-1}$ for a run time between 8 and 12 minutes with a column temperature of 20 °C. The settings of the UV detector were optimized based on the UV-vis spectrum of the parent compound. A 3D field plot was also acquired for all samples from 200 to 600 nm. Quantification of the benzophenones was achieved with an external calibration curve (6 points). Complementary UV-visible spectra and dissolved total organic carbon (TOC) measurements were collected to analyze changes in the absorption profiles and mineralization extent of benzophenones during photolysis. Further details are provided in the ESI (section 'Additional experimental details').†

Results and discussion

Transformation of benzophenone-PS composites due to sunlight exposure

After 30 days exposure to sunlight, visible changes to PS composites were dependent on the benzophenone additive (see Fig. 1). Composites containing DHBP and MBP showed no visible changes in color or material characteristics between light exposed and control (dark) samples (Fig. 1a and b, respectively). In contrast, composites containing 4HBP and 4Cl4HBP (Fig. 1c and d) appeared yellowed, and 4Cl4HBP-containing PS samples were embrittled and fragmented. This photooxidative yellowing and embrittlement of polystyrene following light exposure has been described previously.[47,51–53] In the presence of sunlight, the phenyl rings of polystyrene undergo excitation, leading to the formation of free radicals within the polymer chain that react with oxygen and result in chain scission or crosslinking.[54,55] The addition of UV stabilizers, like benzophenone, prevents this degradation by preferentially absorbing incident UV radiation and converting the energy into a less damaging form (*e.g.*, heat).[10] The presence of the hydroxyl group adjacent to the carbonyl chromophore in DHBP and MBP allows for rapid nonradiative transitions and thereby reduces photodegradation of the plastic.[56] This nonradiative decay process involves a sequence of enol–keto tautomerizations that promotes nonadiabatic energy transfer from the excited state and subsequent vibrational cooling. However, in the case of 4Cl4HBP and 4HBP, lack of a neighboring hydroxyl group to the carbonyl bridge prevents dissipation of the UV energy as heat.[57] Instead, excited states of 4Cl4HBP and 4HBP are more likely to transfer energy to the polymer chains and cause PS degradation. Moreover, previous results from Khaled *et al.* indicate that photodegradation of polymer additives can actually accelerate PS degradation.[58,59] In this respect, the enhanced yellowing seen in the exposed 4Cl4HBP composites may be due to the reactions of halogenated photoproducts or radicals which have also been previously detected during the degradation of PS containing organobromine flame retardants.[58,59] Our results therefore indicate that the use of halogenated benzophenones as additives should be avoided.

Release of benzophenones from PS

Passive release in the dark. The concentration of all four benzophenones leached from plastics in the dark (Fig. 2) can be well fit by a $t^{0.5}$ dependence (solid lines), indicative of an additive release process involving Fickian diffusion where the diffusion rate of the additive within the polymer is much greater than the polymer relaxation time.[60] The rate and total amount of

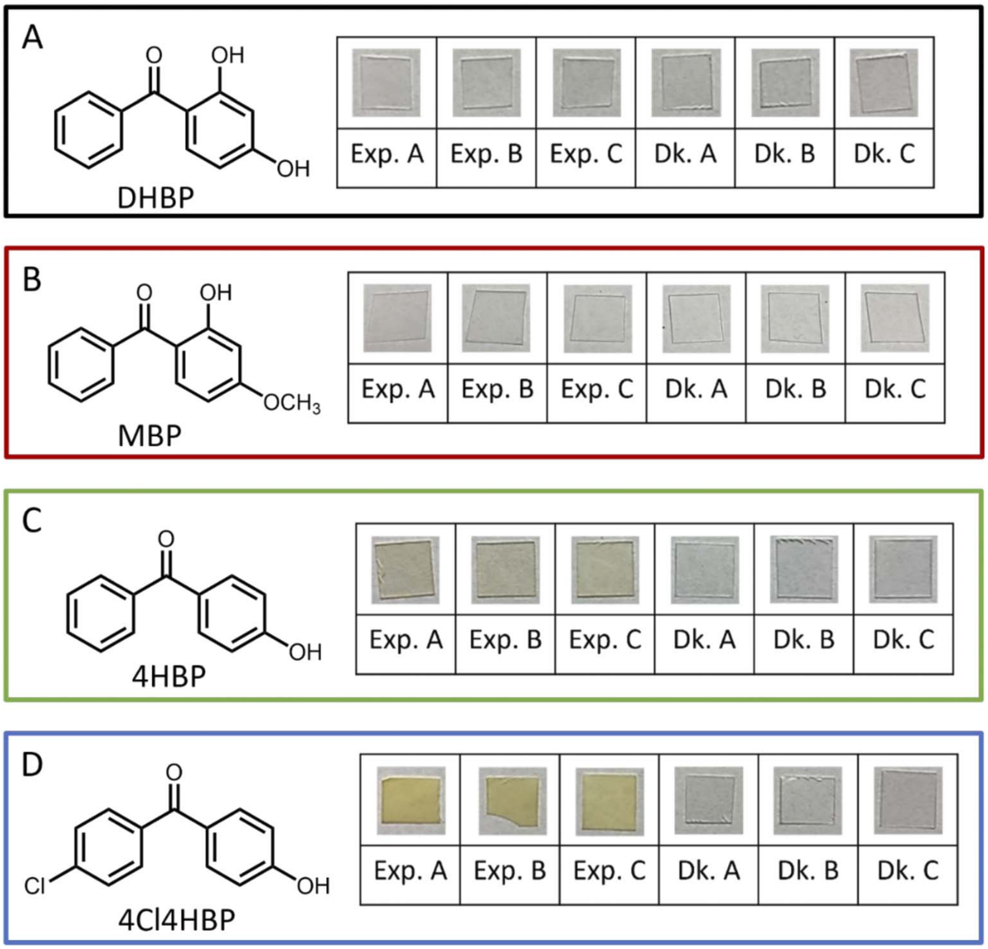

Fig. 1 Images of PS composites containing 1 w/w% (A) DHBP, (B) MBP, (C) 4HBP, and (D) 4Cl4HBP after exposure to natural sunlight (indicated by Exp.) for 30 days or kept under dark conditions (indicated by Dk). A, B, and C represent replicates.

additive released in the dark (approx. 8 μg benzophenone per g PS by week 8) was similar for all four benzophenones. Since the MW (molecular weight) and solubilities of the four benzophenones are all similar (MWs ranging from ∼210–260 amu and log P (partition coefficient) values ranging from 3.1 to 3.7,[61] the observation of similar release rates suggest that under passive conditions, the structural differences between the four benzophenones do not lead to significantly different physicochemical interactions with the PS matrix that would impact their leaching behavior. Additive leaching rates depend on the MW of the additive because this directly impacts their average diffusion rate through a polymer matrix, while the partition coefficient P provides a measure of the additive's preference to dissolve in water as compared to the more hydrophobic PS.

Active release during photolysis. In contrast to the similarity between the passive benzophenone release profiles, leaching profiles of the different benzophenones during exposure to natural sunlight varied widely. For composites containing 4Cl4HBP and 4HBP, leached concentrations during the first 3 days of sunlight exposure were similar to those observed in the dark, but thereafter over the remaining 8 weeks there was a steady decrease (Fig. 2). For composites containing DHBP, there was an increase in release over the first 7 days of sunlight exposure compared to the passive release scenario. Like 4Cl4HBP and 4HBP, for more prolonged exposure times this was followed by a slow but steady decrease in benzophenone concentration in solution. In contrast, MBP-containing PS composites released nearly double the concentration of benzophenone when exposed to sunlight, reaching a concentration of approximately 17 μg per g PS by week 3 (Fig. 2B). Moreover, the concentration of MBP leached into solution increased monotonically with increasing irradiation time, in marked contrast to the behavior of the other three benzophenones.

The photolysis of benzophenones in solution (crosses in Fig. 2) provides a rationale for the differences in release behavior shown in Fig. 2. Specifically, concentrations of DHBP, 4HBP, and 4Cl4HBP all decreased as a function of sunlight exposure time. In contrast, no significant decrease in MBP was observed over the course of 8 weeks sunlight exposure. Thus, for DHBP, 4HBP, and 4Cl4HBP photo-induced release from PS is accompanied by the concurrent photodegradation of the parent compound once it enters solution. In contrast, MBP is photochemically stable in natural sunlight over the 8 week time course of these experiments and consequently the MBP concentration increases as PS photolysis increases the MBP

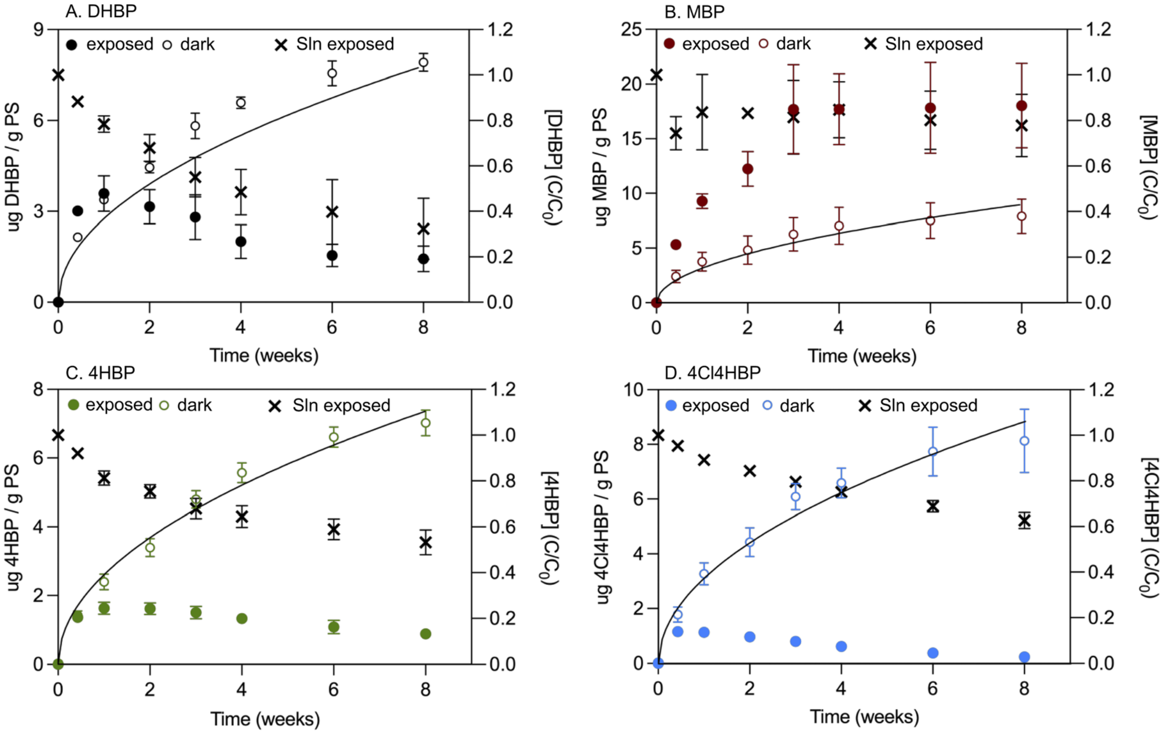

Fig. 2 Concentration of (A) DHBP, (B) MBP, (C) 4HBP, and (D) 4Cl4HBP detected in the leachate solutions of 1 w/w% benzophenone-PS composites ($n = 3$) suspended in water and exposed to sunlight (closed circles) for 8 weeks or kept under dark conditions (open circles). Overlaid is the photodegradation kinetics of the additives in solution (10 mg L^{-1}) exposed to the same sunlight conditions (labeled as Sln exposed and indicated with black crosses) and collected at the same times as the aliquots from the benzophenone-PS composites. The solid lines in each plot represent the best fit data for the passive release of benzophenones from PS using a kinetic model where the rate of release is proportional to release time $(t)^{0.5}$. Note the different *y*-axis scale for MBP as compared to the other three BP additives. It should be noted that the exposure time represents the time span of sunlight exposure.

release rate. Indeed, a comparison of the MBP released passively (dark) and actively (as a result of photolysis) reveals that the rate and quantity of MBP being released during polymer photodegradation roughly doubles. Comparing the results shown in Fig. 1 and 2 it is apparent that the different photostabilities of benzophenones influence not only the concentrations of the released parent compound during photolysis but also the UV protection that they provide to PS.

Active release of additives from PS composites during accelerated photochemical weathering

To understand the longer-term behavior of active additive release, accelerated photodegradation of additive composites was investigated using a Rayonet photochemical reactor (see Experimental section for details†). In these experiments, the additive-PS composites were exposed to >300 nm wavelength light for up to 10 days. In these studies, initial experiments were performed with PS containing the photostable, flame-retardant additive TCEP (Experimental details for TCEP are provided in the ESI section 'Additional experimental details'†). The release of TCEP serves as a "tracer" to evaluate the effect of light-induced polymer degradation on additive release without the complications caused by photodegradation. Fig. 3 shows the passive (dark) and activated (light-exposed) release of TCEP from a 1 w/w% TCEP-PS composite. A comparison of the active and passive TCEP release profiles reveals that polymer photodegradation results in an approximately 10-fold increase in total TCEP released during the first day. However, for irradiation times between 1–4 days, little if any additional TCEP is released. This active release behavior of TCEP over the first 4 days of irradiation is similar to the active release profile of MBP over the course of 8 week exposure to natural sunlight (Fig. 2b); a time period over which MBP was photostable. This similarity in active release profiles for TCEP over 4 days of accelerated

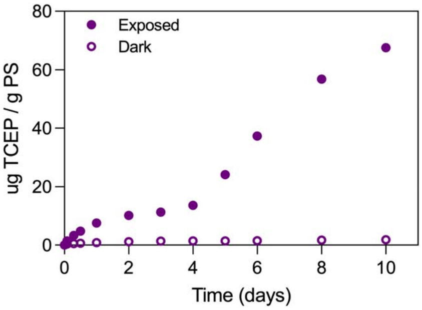

Fig. 3 Concentration of TCEP detected in the leachate of a 1 w/w% TCEP-PS composite suspended in water and exposed to UV$_{>300\text{nm}}$ irradiation (closed circles) or under dark conditions (open circles).

photochemical weathering to MBP over 8 weeks exposure to natural sunlight suggests that accelerated photolysis in the Rayonet photoreactor is providing an approximately 20-fold increase in the rate of PS photolysis.

For more prolonged (>4 days) exposures to >300 nm light, Fig. 3 shows that TCEP release begins again with a release rate (≈10 μg TCEP per g PS per day) that remains roughly constant for irradiation times between 4–10 days. In contrast, there is no increase in the TCEP released from PS during passive experiments. We ascribe this non-linear behavior in active TCEP release kinetics to different stages of PS degradation. During the initial stages of PS photodegradation (<4 days) the enhanced rate of TCEP release compared to passive release in the dark is a consequence of direct oxidative photochemical reactions within the PS. This process leads to the release of some polymer fragments as well as TCEP and the creation of a cross-linked surface layer containing oxygen-containing photoproducts.[62] This newly formed surface layer is more photostable than the native PS and thereby prevents further TCEP release for a period of time (2–4 days in Fig. 3). However, for more prolonged light exposures (4–10 days), this photo-oxidized layer starts to break down, resulting in the formation of microcracks and possible polymer fragmentation that provide a higher surface area for additive release.[63] This idea of a two-step photodegradation process is supported by previous studies that have identified two distinct phases of PS degradation, one associated with the initial decomposition of photolabile PS structures, and the second with the photolysis of oxidation products, such as hydroperoxides.[64] This basic mechanism of PS photodegradation followed by embrittlement/fragmentation of the surface oxidized layer has also been invoked to explain the formation of microplastics during the irradiation of PS microbeads.[65]

Fig. 4 shows the released additive concentrations in solution for the four different PS-benzophenone composites when they are exposed to the same accelerated photolysis conditions used for TCEP-PS composites. For each benzophenone-PS composite, there is a rapid initial increase in the concentration of benzophenone detected in solution due to the photodegradation of the native PS, analogous to what is seen in Fig. 2 and 3. For intermediate irradiation times, the benzophenone concentration decreases, an effect that can be rationalized by the data shown in Fig. 2 and 3, wherein additive release slowed and the dominant process is photodegradation of the benzophenones released into solution. The absolute concentration of 4HBP and 4ClHBP, the additives that provide the least UV protection to PS (Fig. 1) is the smallest amongst the four benzophenones. This underscores the general inverse correlation observed in Fig. 1 and 2 between the protective capabilities of the benzophenones and the concentration of benzophenones released during

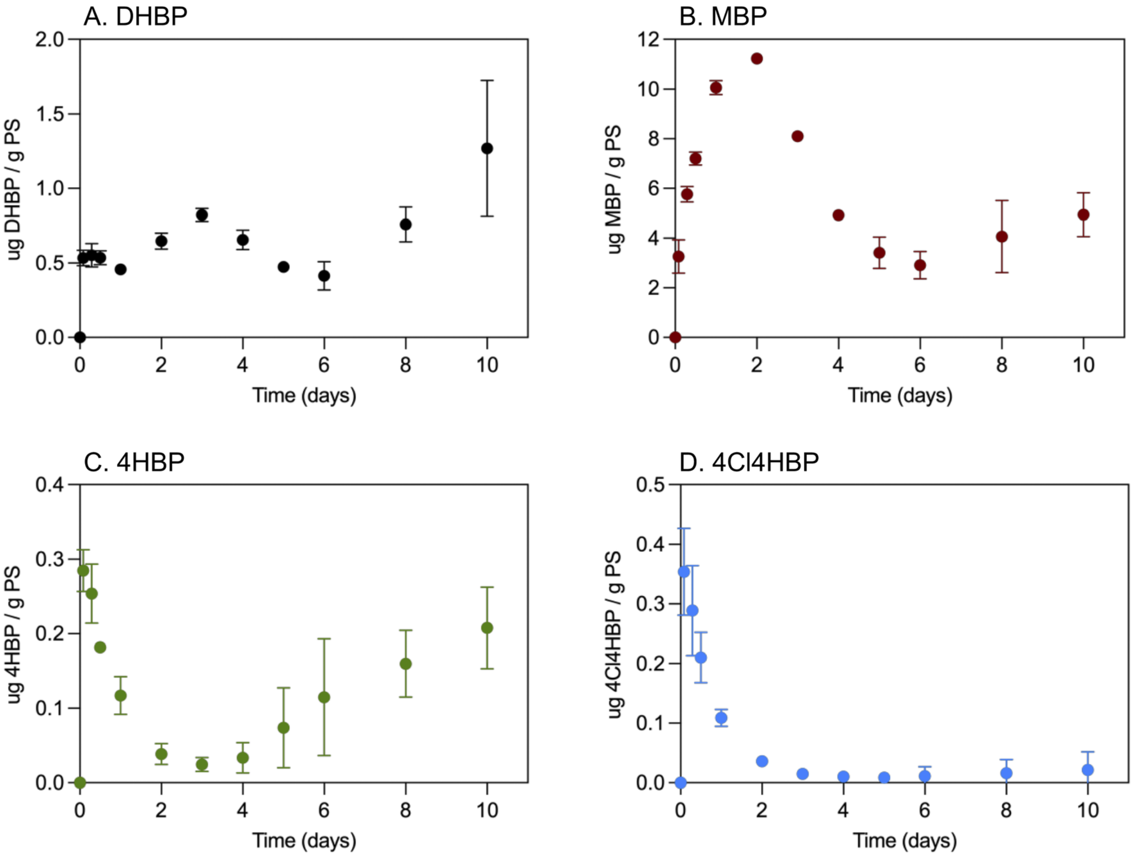

Fig. 4 Concentration of (A) DHBP, (B) MBP, (C) 4HBP, and (D) 4Cl4HBP detected in the leachate of 1 w/w% benzophenone-PS composites ($n = 2$) suspended in water and exposed to $UV_{>300nm}$ irradiation.

photolysis. Fig. 4 also shows that there is a second increase in benzophenone release that occurs for more prolonged irradiation times (>4 days). This effect can be rationalized by the changes to the PS that occur during irradiation, and which were invoked to explain the TCEP release behavior (Fig. 3). The magnitude of this secondary increase is dependent on the benzophenone's properties. Thus, the largest absolute increase in benzophenone concentration is observed for the most UV-protecting and photostable benzophenone (MBP).

Kinetic models used to estimate additive leaching described in literature often only include terms for release and loss due to abiotic or biotic pathways when predicting additive concentration at a given time, while ignoring photolysis.[66] The changes in the release profile of the photostable additive TCEP (Fig. 3) and the benzophenones (Fig. 2 and 4) highlight how photolysis alters the release rates and concentrations of polymer additives. Moreover, to fully assess the risks associated with chemical additives, it is crucial to determine the nature of potential products formed during the photodegradation of the parent additive. To complement the information on benzophenone release kinetics from benzophenone-PS composites, we therefore conducted additional experiments to elucidate the photolysis mechanisms and identify phototransformation products of the various benzophenones in solution.

Photodegradation mechanisms of benzophenones in solution

Benzophenones can undergo direct photolysis once leached from polymers into surface waters, since their light absorbance overlaps with the solar spectrum (Fig. ESI-2†). Due to their absorption peak maxima around 295 nm, we conducted photolysis experiments using $UV_{>300nm}$ light. Although the contribution from this wavelength range around 300 nm to the sunlight spectrum is small, it still constitutes a measurable flux of photons that reaches Earth's surface.[67] In these experiments, we used the same Rayonet photoreactor equipped with UV_{300nm} bulbs used in the accelerated PS photodegradation experiment to increase the rate of benzophenone photolysis and assess the fate of benzophenones under extended sunlight exposures. Under these conditions, all benzophenones photodegraded to approximately 50% of their initial concentrations after 12 hours; after 36 hours, DHBP, 4HBP, and 4Cl4HBP were completely degraded (Fig. ESI-3†). In contrast, the concentration of MBP only decreased by 80% after 36 hours, in accord with the relative photostability of MBP compared to the other three benzophenones observed in sunlight (Fig. 2).

To investigate the mechanism of benzophenone photolysis and assess the contribution of reactive intermediates formed by self-excitation of benzophenones in the photodegradation process, radical scavengers were employed. Isopropyl alcohol and sorbic acid were selected as scavengers for any hydroxyl radicals and excited triplet states of benzophenones produced during photolysis, respectively.[49,50] Fig. ESI-3† shows that the photodegradation of all four benzophenones at UV_{300nm} was significantly slower in the presence of isopropyl alcohol or sorbic acid compared to photodegradation in the absence of scavengers. Specifically, DHBP, 4HBP, and 4Cl4HBP only degraded to ≈40% of their initial values after 36 hours in the presence of isopropyl alcohol or sorbic acid as compared to complete degradation without scavengers. For MBP, the presence of isopropyl alcohol or sorbic acid led to a loss of about 10–20% over 36 hours, whereas 80% MBP parent loss was observed in the absence of scavengers (Fig. ESI-3†).

These results highlight that reactive species significantly contribute to the photodegradation of the benzophenones. Since these experiments were conducted in ultrapure water and at wavelengths ($UV_{>300nm}$) our results indicate that direct photolysis produces excited triplet states of benzophenones *via* photoexcitation.[57] In the presence of sorbic acid, these excited triplet states relax back to form the chemically inert ground state benzophenone molecules. The excited triplet states of the benzophenones may also form hydroxyl radicals *via* reaction with dissolved oxygen present in water, which are preferentially scavenged by isopropanol. Suppression of benzophenone degradation was observed in the presence of either scavenger, which suggests that both reactive pathways (formation of hydroxyl radicals and excited triplet states) contribute to the overall photodegradation process. This assertion agrees with results obtained by Zhang, *et al.*, who suggested that photodegradation of benzophenones may generate photoproducts that act as photosensitizers and facilitate degradation of the parent compounds.[57] Specifically, production of photoproducts containing a common aromatic ketone structure were suggested to undergo additional photoexcitation to a triplet state that produces reactive oxygen species. However, in contrast to previous studies that demonstrate the involvement of singlet oxygen,[57] our results also indicate the formation of hydroxyl radicals. The formation of hydroxyl radicals during photolysis is supported by the formation of hydroxylated phototransformation products discussed below. It is interesting to note that in contrast to our results, Zhang *et al.* only observed self-sensitization for DHBP but not for MBP. This can most likely be attributed to these experiments having been conducted at 365 nm, a wavelength at which DHBP shows a substantially higher absorption compared to MBP (Fig. 6).

Identification of transformation products formed during the photolysis of benzophenones

Identification of phototransformation products (TPs) revealed the formation of a range of hydroxylated and carboxylic acid species during photolysis of the four benzophenones (see Table ESI-1 and Fig. ESI-4–ESI-19†). The loss of parent benzophenones and formation of selected TPs was determined as a function of $UV_{>300nm}$ irradiation time (Fig. 5). During the photolysis of DHBP and MBP, the formation of TP-229 ($C_{13}H_9O_4$) and TP-243 ($C_{14}H_{11}O_4$) indicates a mass increase of 16 amu, respectively, and suggests the formation of hydroxylated DHBP and MBP species. The formation of these hydroxylated products clearly supports the formation of hydroxyl radicals during photolysis as suggested by the scavenger experiments described in Fig. ESI-3.† For MBP, an additional TP (MBP TP-213; $C_{13}H_9O_3$) with a retention time and fragmentation pattern matching that of DHBP was observed (Fig. ESI-12

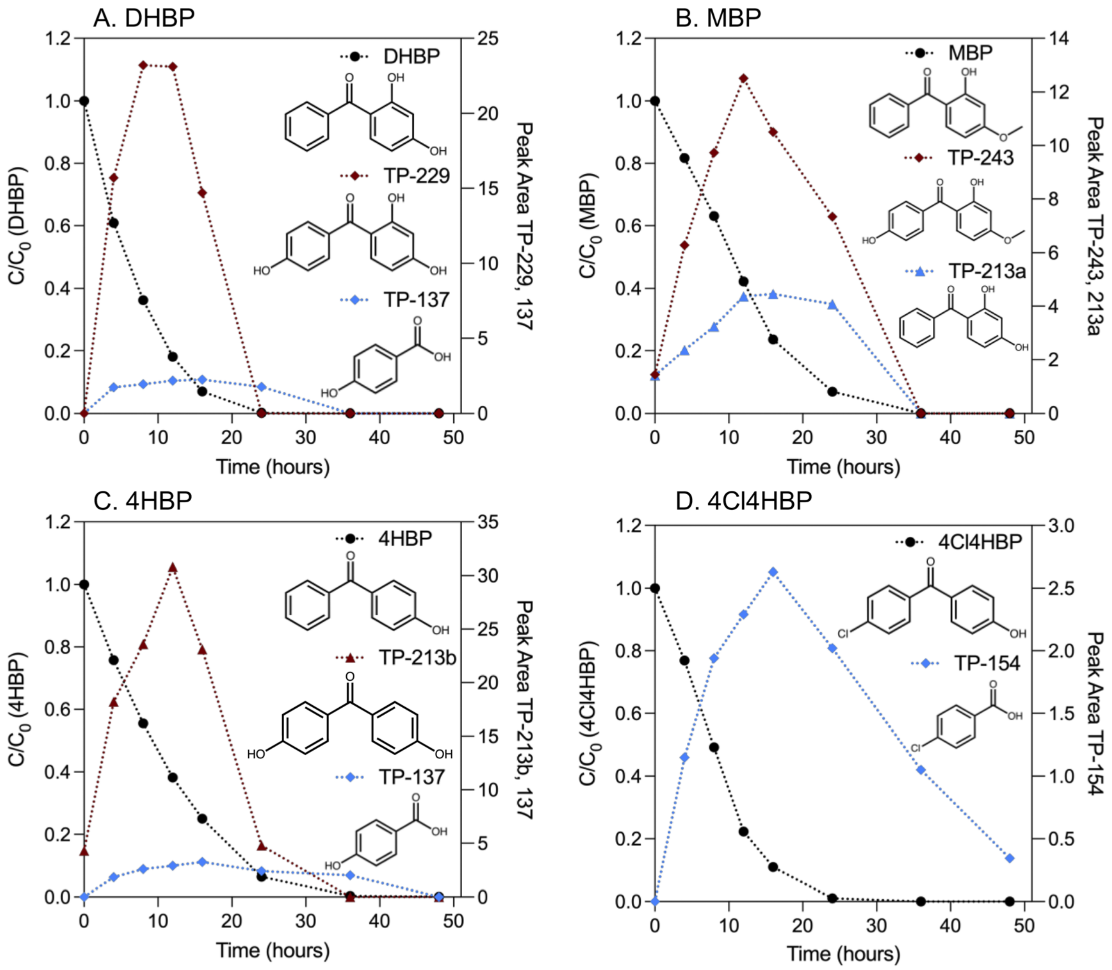

Fig. 5 Photodegradation of (A) DHBP, (B) MBP, (C) 4HBP, and (D) 4Cl4HBP, including the formation and subsequent loss of phototransformation products as a function of UV$_{>300nm}$ irradiation time. The relative concentration of each species is represented by the peak area for the principal ion (negative mode) associated with each species. For 4Cl4HBP formation of TP137 (4-hydroxy benzoic acid) was observed but at very low abundances (data not shown).

and Table ESI-1†). This TP indicates that MBP can be transformed into DHBP *via* cleavage of the ether group. Interestingly, a TP with a mass increase of 16 amu was also observed for 4HBP (4HBP TP-213; $C_{13}H_9O_3$), resulting in the same molecular weight as DHBP and MBP TP-213. However, in comparison to DHBP and MBP TP-213, the LC-HRMS retention time differed slightly (15.09 *vs.* 15.46 min for 4HBP TP-213 and DHBP/MBP TP-213, respectively) and we also observed differences in the MS^2 fragmentation pattern (Fig. ESI-12 and ESI-16†). As such, 4HBP TP-213 is likely an isomer of DHBP/MBP TP213. The fragmentation pattern, specifically the detection of a fragment at m/z 93 ($C_6H_5O^-$) indicates a hydroxylation reaction at the unsubstituted aromatic ring of the parent compound, likely resulting in the formation of 4,4′-dihydroxybenzophenone.

During the photodegradation of 4HBP, an additional TP with a retention time of 5.10 minutes (4HBP TP-137; $C_7H_5O_3$) was observed. Using a reference standard, this compound was identified as 4-hydroxybenzoic acid (Fig. ESI-15†). 4-Hydroxybenzoic acid was also confirmed as a TP for 4Cl4HBP and DHBP. For 4Cl4HBP, a second TP at 11.70 minutes (4Cl4HBP TP-154; $C_7H_4O_2Cl$), attributable to the formation of 4-chlorobenzoic acid was observed and confirmed using a reference standard (Fig. ESI-18†). The formation of these carboxylic acids during direct photolysis of 4Cl4HBP and 4HBP indicates that a key step of photodegradation involves photoinduced homolytic cleavage of the carbonyl bridge. As indicated by the results of the experiments conducted in the presence of scavengers (Fig. ESI-3†), the formation of these TPs can be partially attributed to the formation of reactive benzophenone species. The production of carboxylic acids is likely a direct result of the formation of excited triplet states formed during photolysis of the benzophenones, while formation of hydroxyl radicals from these excited states is likely responsible for the hydroxylated species.

LC-HRMS analysis indicated that all TPs are themselves transformed further under extended light exposure (Fig. 5) to form secondary TPs. This is also supported by the fact that none of the TPs were detected in leaching experiments with plastics containing individual benzophenones that were exposed to sunlight or simulated UV light. UV-vis spectroscopy demonstrated that this transformation is associated with the loss of all

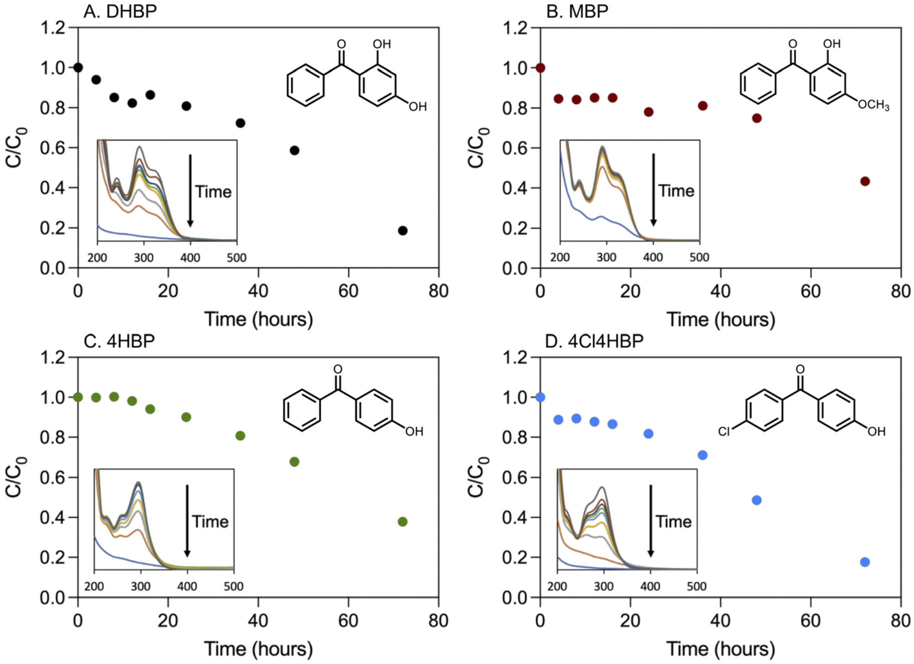

Fig. 6 Change (C/C_0) of total dissolved carbon as a function of $UV_{>300nm}$ irradiation time of (A) DHBP, (B) MBP, (C) 4HBP, and (D) 4Cl4HBP in ultrapure water in borosilicate test tubes (10 mg L^{-1} solution for each benzophenone). The inset plots are the corresponding UV-visible spectrum collected at each timepoint.

UV active chromophores (Fig. 6), suggesting a breakdown of the aromatic rings. To determine if this degradation potentially results in the mineralization of benzophenones, samples were also analyzed for total organic carbon (TOC). For all four benzophenones, TOC decreased by at least 50% within 72 hours of light irradiation (Fig. 6). Lowest TOC removal was observed for MBP, which agrees with its relative photostability compared to the other benzophenones (Fig. 2 and 4). Analogous to the results obtained by the sunlight photodegradation experiments performed in solution, the results also highlight the lower photostability of DHBP compared to MBP despite their similar UV protection capabilities (Fig. 1). The significant loss of TOC during photolysis of all benzophenones indicates that volatile carbon-containing species (*e.g.* CO_2) are ultimately formed during photodegradation, most likely as a result of a sequence of reaction steps involving highly reactive and oxidizing species such as hydroxyl radicals.

Conclusions

This study highlights the impact of natural sunlight on the release of additives from plastics. For benzophenones that are relatively photostable, photolysis increases the leaching rate due to photodegradation of the PS matrix. For more photolabile benzophenones, release kinetics reflect an initial increase in concentration due to polymer photodegradation followed by a steady decrease caused by photodegradation of the benzophenones released into solution. Accelerated photolysis experiments revealed that the release of additives such as benzophenones evolves in response to changes in the PS matrix that occur as a function of light exposure. A comparison between the UV stability afforded to PS by different benzophenones and their active release profiles during photolysis reveals that the concentration of parent compound present in solution is governed by their relative photostabilities as opposed to their UV protecting properties.

Our results also highlight the importance of phototransformation products that are formed once benzophenones are released into the surrounding solution. We were able to show that the phototransformation of benzophenones likely ultimately results in their detoxification due to the observed photomineralization when exposed to sunlight for extended time periods. This can be explained by benzophenone self-sensitization that results in the formation of reactive intermediates, including excited triplet states and hydroxyl radicals. Considering that all our experiments were conducted in ultrapure water, future studies examining release and transformation behavior in more complex environments (*i.e.* alkaline or acidic pH, salinity) and the presence of other matrix constituents such as natural organic matter and major ions are warranted. Most importantly, our study demonstrates that to fully understand the environmental and human health impact of chemical additives used in plastics, it is necessary to understand the effects of photolysis in terms of its impact on both additive release from the polymer matrix as well as the phototransformation reactions that can occur upon release into solution. This is particularly important for the holistic assessment of environmental exposures, considering that additive leaching can be substantially underestimated when phototransformation reactions are not taken into consideration.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its ESI files.† Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors have no conflict of interest to declare.

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