Photolysis of Emerging Contaminants Adsorbed onto Plastic in an Aqueous Environment

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Overview

Purpose
To understand the effect of various plastics (PMMA, polystyrene, and polyethylene) and their surface area on the photolysis of emerging contaminants.

Methods
Irradiation of triclosan adsorbed to different plastics in aqueous solution at 300 nm. Samples were analyzed by GC/MS.

Results
An increase of surface area of polyethylene and polymethylmethacrylate increases the rate of emerging contaminant decomposition as a function of time.

Introduction

The accumulation of plastic debris in the environment poses many threats to the environment and human health (1). One way these plastics can cause environmental damage is through the absorption and transfer of potentially toxic compounds to aquatic animals which in turn transfer these toxins to humans when consumed. These toxins are believed to alter basal metabolic rates and increase adipose tissue production in humans (2). Hydrophobic chemicals such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) all accumulate on microplastics. The focus of these studies is to understand how the surface area and type of plastic influence the extent of photolysis (photo-transformation) of emerging contaminants in aqueous solution when irradiated at 300 nm at different times. Triclosan was selected as a model pollutant because it is known to adsorb to plastic in aqueous environments (3).

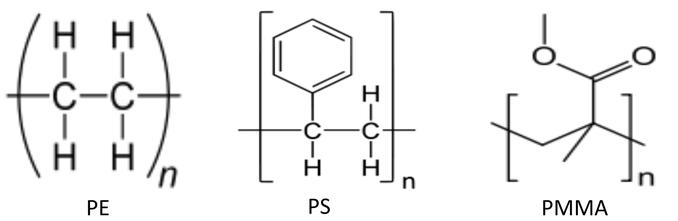
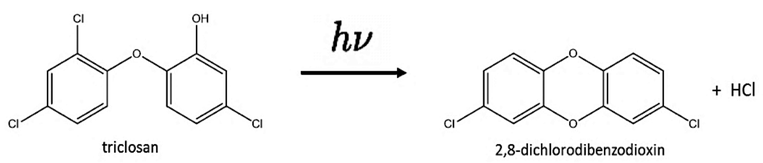


Figure 1: Monomer structures of polyethylene (PE), polymethyl-methacrylate (PMMA) , polystyrene (PS); the three plastics used in this study.



Equation 1: Conversion of triclosan to 2,8-DCDD during photolysis at 300 nm.

Experimental

Photolysis samples were prepared by combining 10 mL of nanopure water, 50 mg of plastic, and 5 µL of 22 mg/mL triclosan in methanol in a 15 mL borosilicate tube. Aqueous triclosan samples without plastic were also prepared as a control. They were placed in a Rayonet Photochemical Reactor and irradiated at various times at a wavelength of 300 nm. All aqueous portions of the samples with and without plastic were extracted by liquid-liquid extraction method with 3 mL of MTBE. The plastics from the irradiated samples were sonicated with 3 mL of MTBE for ten minutes. All extracted samples were stored over dry sodium sulfate until analysis.

Analysis

Samples were analyzed by gas chromatography/mass spectrometry (GC/MS). Mass spectra of the aqueous and plastic extracts were analyzed using an Agilent 6890 GC-MS in positive EI mode. A linear GC gradient was used (32 degrees to 300 degrees) for separation for a total run time of 20.9 minutes. The source temperature was maintained at 280^{o} C. One microliter was injected for analysis.

Results and Discussion

Triclosan is converted to 2,8-dichlorodibenzodioxin (2,8-DCDD) during photolysis (**Equation 1**). Our initial experiments were conducted to see how increasing the surface area of polyethylene (PE) beads irradiated would influence the extent of 2,8-DCDD formation when all other variables were kept constant (concentration of triclosan, total weight of plastic, irradiation time). The **Figure 2** bar graph clearly illustrates that the photo-degradation is increasing with increasing total surface area of the PE particles from 2.8 to 77 cm^2 This increased rate of photolysis is most apparent from 3 to 10 minutes. This is likely because as the surface area is increased, the more triclosan will adsorb on the surface of the beads relative to solution. The data indicates that as irradiation times increase beyond ten minutes that the primary photolysis product, 2,8-DCDD, begins to decompose which leads to low abundances of both triclosan and 2,8-DCDD and thus (m/z 251.9)/(m/z 287.9) abundance ratios that do not reflect the influence of surface area on the photolysis.

Figure 3 is a bar graph that compares the photolysis of triclosan on three different plastics. PMMA was investigated because, like PE, it does not absorb light at 300 nm. Its total surface area (44 mm^2) used in this study is between that of the two PE samples irradiated in this experiment and thus might be expected to yield an (m/z 251.9/ m/z 287.9) ratio that follows the general trend of PE. Here, the ion abundance ratio is seen to increase going from 3 to 10 minutes irradiation times like PE but the photo-degradation of triclosan is more extensive on PMMA than expected, particularly at 10 minutes suggesting that the triclosan may interact with the PMMA surface differently than the PE surface. Two borosilicate vials containing PE with different surface areas (77.8 mm^2 (dark blue) and 13.3 mm^2 (light blue)) were irradiated and analyzed with the vials containing PMMA and PS for comparison.

Polystyrene (PS, orange, **Figure 3**) did not show extensive fragmentation because, unlike PE and PMMA, it absorbs 300 nm light so there is less energy available to promote triclosan fragmentation. The total individual ion abundances of both m/z 251.9 and m/z 287.9 decrease at 15 minutes irradiation time for all plastics investigated suggesting that the 2,8-DCDD is absorbing light and decomposing at this point in the experiment as was observed in the experiments described in **Figure 2**.

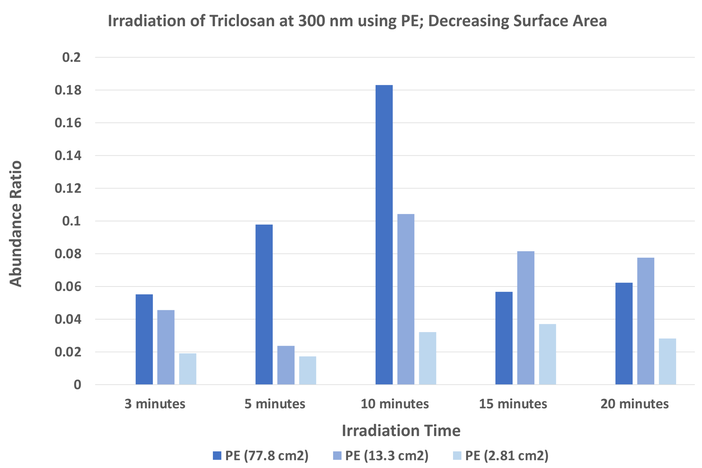


Figure 2: Bar graph of (m/z 251.9)/ (m/z 287.9) ratio versus time irradiated at 300 nm for triclosan and 2,8-DCDD extracted from PE plastic with decreasing surface areas for up to 20 minutes.

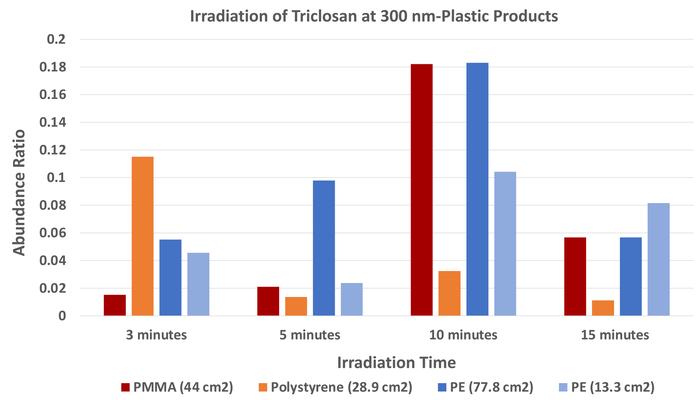


Figure 3: Bar graph of (m/z 251.9)/ (m/z 287.9) ratio versus time irradiated at 300 nm for triclosan and 2,8-DCDD extracted from PE, PMMA, and PS plastic.

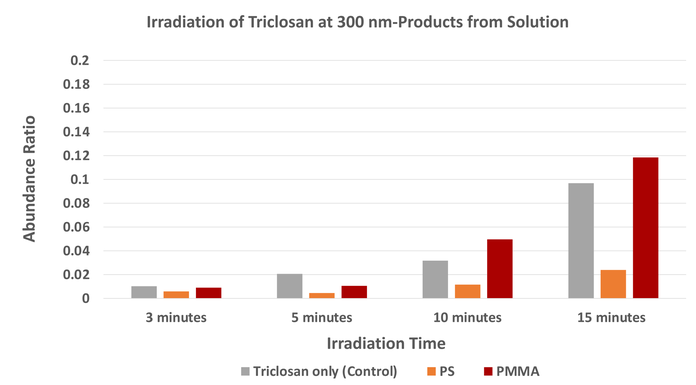


Figure 4: Bar graph of (m/z 251.9)/ (m/z 287.9) ratio versus time irradiated at 300 nm for triclosan and 2,8-DCDD extracted from solution from samples: 1. Triclosan with no plastic (control) 2. PS 3. PMMA.

Conclusion

We have investigated how different types and sizes of plastic influence the photolytic decomposition of the model compound triclosan when irradiated at 300 nm for different times. Studies conducted with polyethylene suggest that as the surface area of the plastic particles is increased, the rate of decomposition increases. Also, polystyrene has relatively low abundance ratios compared to polyethylene because polystyrene is aromatic and is better able to absorb 300 nm light. The results obtained with PMMA suggest that the interactions of triclosan with the particle surface are different than with polyethylene. After 10 minutes, the initial product of the irradiation process began to degrade further.

References

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