

Studies of the Photo-transformation of Emerging Contaminants Adsorbed onto Plastic in an Aqueous Environment

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Overview

Purpose

To understand the effect of plastic surface area (PMMA, polystyrene, and polyethylene) on the photolysis of emerging contaminants.

Methods

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

Results

An increase of surface area of polyethylene 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 our studies is to understand how the surface area and type of plastic influence the extent of photodegradation of emerging contaminants in aqueous solution when irradiated at 300 nm at different times. Triclosan and 1-(4-hydroxyphenyl)nonane were selected as model pollutants for the irradiation studies because they are known to adsorb to plastic in aqueous environments (3). 1-(4-Hydroxyphenyl)nonane produces more decomposition products upon irradiation than triclosan, and therefore we reasoned that it might be a more sensitive probe of the effects of surface area and the polymer structure of the plastic than the triclosan.

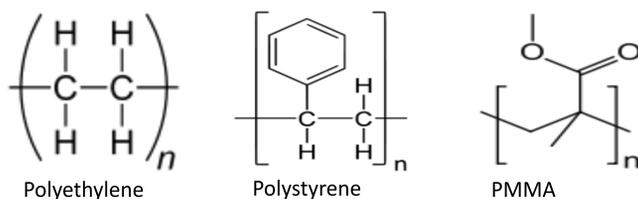
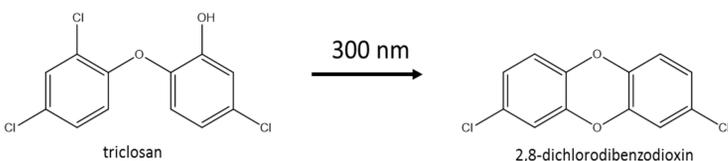


Figure 1: Polyethylene (PE), Polymethylmethacrylate (PMMA), polystyrene (PS), are the three plastics focused on in this study.



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

Experimental

Photolysis samples were prepared by combining 10 mL of nanopure water, 50 mg of plastic, and 5 μ L of 22 mg/mL triclosan in methanol in a 15 mL borosilicate tube. They were placed in a Rayonet Photochemical Reactor and irradiated for a period of 0-20 minutes at a wavelength of 300nm. Photolysis is a form decomposition by light, photons create a chemical reaction that breaks down compounds (4). Aqueous samples without plastic were extracted by liquid-liquid extraction method with 3 mL of MTBE and the plastics from the irradiated samples were sonicated with 3 mL of MTBE for ten minutes then stored with sodium sulfate until instrumental 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 $^{\circ}$ C. One microliter was injected for analysis.

Results and Discussion

Our initial experiments were conducted to see how increasing the surface area of polyethylene (PE) beads irradiated with the triclosan would influence the extent of decomposition when all other variables were kept constant (concentration, total weight of plastic, irradiation time). The Figure 2 bar graph clearly illustrates that irradiation times of three to ten minutes, that the decomposition increasing with increasing the total surface area of the PE particles from 2.8 to 77 cm 2 does in fact lead to an increased rate of photolysis. This is probably because as the surface area is increased, the plastic beads can hold more triclosan. The data indicates that as irradiation times increase beyond ten minutes that the primary photolysis product 2,8-dichlorodibenzodioxin (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.

Triclosan is converted to 2,8-dichlorodibenzodioxin (2,8-DCDD) during photolysis (Equation 1). Figure 3 is bar graph that compares the (m/z 251.9)/(m/z 287.9) abundance ratios taken from the GC/MS analyses of triclosan irradiated at 300 nm in the presence of three different kinds of plastic at four different irradiation times. Two sizes of polyethylene particles, one with a total surface area of 77.8 mm 2 (dark blue) and 13.3 mm 2 (light blue). The (m/z 251.9/m/z 287.9) abundance ratios representing the extent of triclosan decomposition are clearly larger for the PE plastic preparation having more surface area (more and smaller particles) suggesting that the surface interactions with the emerging contaminant are important in promoting the decomposition of the molecule.

Figure 3 is a bar graph that compares the photolysis of triclosan on three different plastics. Polymethylmethacrylate (PMMA) was investigated because, like PE, it does not absorb 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 decomposition 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.

Polystyrene (orange, figure 3) did not show extensive fragmentation because, unlike PE and PMMA, it will absorb 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.

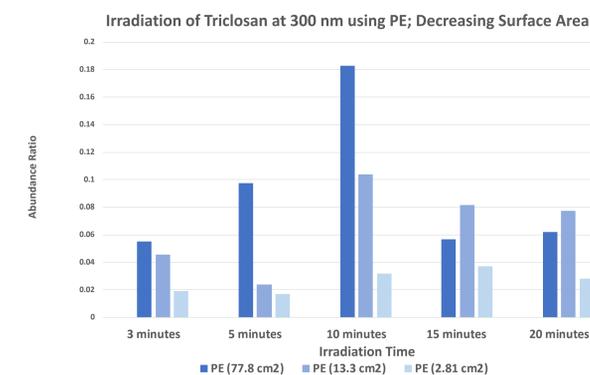


Figure 2: Plot of (m/z 251.9)/(m/z 287.9) ratio versus time irradiated at 300 nm for triclosan and 2,8-DCDD extracted from PE with decreasing surface areas for up to 20 minutes.

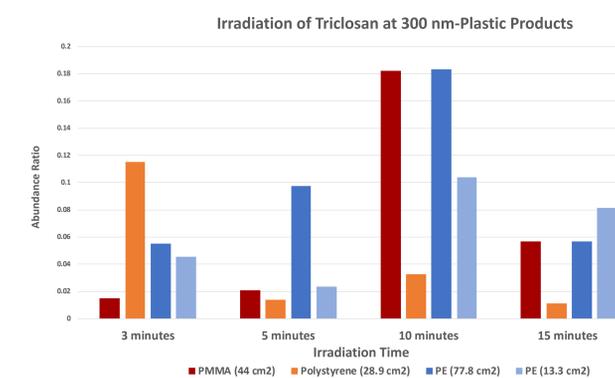


Figure 3: Plot of (m/z 251.9)/(m/z 287.9) ratio versus time irradiated at 300 nm for triclosan and 2,8-DCDD extracted from PE, PMMA, and PS.

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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