Photolysis of Emerging Contaminants on Hydrophilic Plastics

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Overview

Purpose: To study the rate of photolysis of triclosan on hydrophobic and hydrophilic plastic surfaces.

Methods: Triclosan was photoreacted in cellulose and polyethylene aqueous solutions at 300 nm for 0, 5, 10, 15, and 20 minutes. Then, triclosan and the metabolite of triclosan, 2,8-dichlorodibenzoidioxin, were extracted using MTBE solvent. The samples were then analyzed by GC/MS and the abundance ratios were compared.

Results: The rate of photolysis of triclosan was increased on the hydrophobic plastic surface than on the hydrophilic plastic surface.

Introduction

Plastic pollution occurs when plastic debris accumulates in the environment. [1] The decomposition of plastics harms aquatic species and human health as well as negatively impacts the environment. [2] Plastics that degrade into microplastics, which are classified as plastics less than 5 millimeters in length, can be ingested by several marine species causing physical damage and toxic effects to these aquatic animals. Polychlorinated Biphenyls (abbreviated PCBs), triclosan, and other emerging contaminants have been shown to accumulate on microplastics, which enhances toxicity. [3]

In the past, most of our studies have been focused on hydrophobic plastics; however, in this study the goal was to extend our research to hydrophilic plastic surfaces. The purpose of this study was to see if emerging contaminants with limited water solubility such as triclosan absorb onto the surface of hydrophilic plastics and how the interaction between the plastic will affect the rate at which the emerging contaminant triclosan will undergo photolysis.

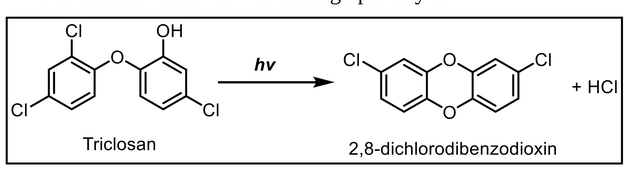

Figure 1: During photolysis at 300 nm, the conversion of triclosan to 2,8-DCDD.

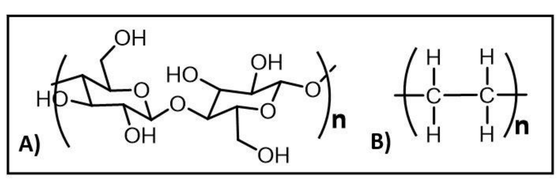

Figure 2: Chemical Structures of **A)** cellulose and **B)** polyethylene.

Methodology

Cellulose plastic was used as the hydrophilic plastic in comparison to the hydrophobic polyethylene plastic sheets. We have found that 5 -chloro-2-(2,4-dichlorophenoxy)phenol (triclosan), which is a relatively hydrophilic compound, will undergo photolysis faster on hydrophobic plastics, specifically polyethylene, than on hydrophilic plastics, specifically cellulose, or in solution alone.

Photolysis samples were prepared by spiking 5 µL of a 22mg/mL solution of triclosan in 10 mL of nanopure water and 50 mg of either cellulose or polyethylene. Control samples were prepared similarly. However, the control contained only water and triclosan excluding the plastic. These samples were irradiated at 0, 5, 10, 15 and 20 minutes in a photoreactor at 300 nm. The photoreactor used was a Rayonet (Southern New England Ultraviolet Co., Branford, CT USA) photoreactor. After being reacted on the photoreactor, the samples were left to sit out for a week and extracted using the Szczuka et al. extraction method.

The aqueous solution in the samples was first prepared for extraction by the addition of 10 mL of NaCl and then spiked with 200 µL of concentrated sulfuric acid. The solution was transferred to a 125 mL separatory funnel and extracted in 3 mL of Methyl tert-butyl ether (MBTE). The plastic was then sonicated in 3 mL MBTE for 10 minutes to isolate triclosan absorbed on the sample. Samples were stored over dry sodium sulfate until analysis using gas chromatography mass spectrometry (GC/MS).

Samples were analyzed using gas chromatography/mass spectrometry. (GC/MS). An Agilent 6890 GC-MS was used in positive EI mode to analyze the aqueous samples in MTBE solvent. A helium mobile phase was used. A gradient from 32 degrees Celsius to 30 degrees Celsius was used to aid separation and decrease run time. The total run time was 20.9 minutes for each set of analyses. The temperature of the source was stabilized at 280 degrees Celsius and one microliter of each sample was injected into the instrument to be analyzed.

Results/Discussion

Triclosan undergoes photolysis to form the metabolite 2,8-dichlorodibenzodioxin. **Figure 1** describes this photolysis reaction. Our hypothesis was to see whether triclosan undergoes photolysis faster forming a larger 2,8-dichlorodibenzodioxin to triclosan ratio of abundance on hydrophobic surfaces than on hydrophilic surfaces. Due to the nature of the surface of polar hydrophilic plastics, it is hypothesized that water competes with triclosan for the surface of cellulose because of cellulose's hydrophilic nature and thus the rate of photolysis is slower than on a hydrophobic plastic such as polyethylene.

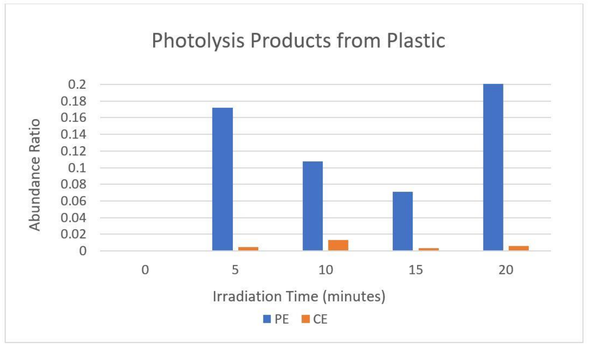

Figure 3: Bar graph showing (m/z 251.9) / (m/z 287.9) ratio versus time of triclosan and 2,9-DCDD for polyethylene and cellulose irradiated from zero to 20 minutes extracted from the plastic.

Figure 4: Bar graph showing (m/z 251.9) / (m/z 287.9) ratio versus time of triclosan and 2,9-DCDD for polyethylene and cellulose irradiated from zero to 20 minutes extracted from the aqueous solution.

Figure 2 shows the different surfaces of **A)** cellulose and **B)** Polyethylene. As shown in the figure, cellulose is much more hydrophilic due to its polar hydroxyl groups than polyethylene which is made up of simple long carbon chains. Thus, triclosan will be able to absorb to the surface of polyethylene faster than cellulose.

The abundance ratios in **figure 3** were collected via Gas Chromatography Mass Spectroscopy and show the ratio of (m/z 251.9) to (m/z 287.9). The metabolite 2,8-dichlorodibenzodioxin has a m/z peak at 251.9 and triclosan has a m/z peak at 287.9. Therefore, the higher abundance ratio in figure 3 shows the faster rate of photolysis. Polyethylene has an abundance ratio significantly higher than cellulose at 5, 10, 15, and 20 minutes.

Figure 4 shows the abundance ratios similarly to figure 3; however, in figure 4 the abundance ratios represent the triclosan and 2,8-dichlorodibenzodioxin accumulating in the aqueous solutions surrounding the plastic when it was irradiated. The abundance ratios are greater in polyethylene samples than in cellulose samples except at the 15-minute irradiation time. Overall, in figure 4 the abundance ratios are smaller compared to the plastic. This is consistent with our previous studies suggesting that triclosan undergoes photolysis faster on surfaces than in aqueous solution alone.

At the fifteen-minute irradiation time that is when 2,8-dichlorodibenzodioxin is likely to decompose and form another byproduct. This is why the abundance ratios at the fifteen-minute mark are smaller in both the photolysis from plastic and the photolysis from water extractions.

Conclusion

Here we photodegraded 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan) in the presence of a hydrophilic plastic (cellulose) and a hydrophobic plastic (polyethylene) at 300nm for 0, 5, 10, 15, and 20 minutes. This was performed for the purpose of investigating how the surface interactions between the substrate, triclosan, and the surface of the plastic affects the product formation process and the rate of the chemical reaction. Our studies found that triclosan photodegrades faster in the presence of hydrophobic surfaces (polyethylene) than on hydrophilic surfaces. This is most likely due to the fact that water competes with triclosan on hydrophilic plastic surfaces due to its polar surface.

References

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