Investigations into the Reactivity of Microplastics in Water

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Abstract

Microplastics, plastic pieces less than 5 mm, are a significant part of the plastic pollution in surface waters. Given the massive, global extent of this pollution, it is important to understand the chemical reactivity of microplastics in water. This study used radiation chemistry techniques to explore the transformations of plastics in water. Adsorption experiments were also conducted with microplastics and other model water contaminants. When water mixtures are exposed to gamma radiation, radicals that are prominent in nature, namely the hydroxyl radicals (•OH), are created. The reported irradiation experiments were done to simulate stagnant waters. Water mixtures containing either polyethylene (PE) or polyethylene terephthalate (PET) in closed containers were exposed to different irradiation dose rates and doses. Caffeine, dodecane and benzophenone, commonly occurring pollutants, were used as model compounds in microplastic adsorption experiments. Infrared and Raman spectroscopies along with GC-MS and LC-MS were the main techniques used to assess the changes to the microplastics. A few compounds, such as dodecane and 2-dodecanone, were detected in the water/PE mixtures after exposure to the radicals. The surface chemistry of the microplastics was mostly unchanged, even after high doses of irradiation. Adsorption experiments showed that caffeine does not adsorb to PE or PET, dodecane strongly adsorbs to PE, and benzophenone partly adsorbs. The natural •OH-mediated breakdown of caffeine was not affected by the presence of PE. Even though benzophenone adsorbs to PE, the degradation rate of benzophenone in solution did not change in the presence of PE microplastics.

Figure 1. Magnified polyethylene microplastics isolated from water (left) and common plastic pollution in water (right).

Radiation Chemistry

The OH radical is one of the most common and powerful oxidants in nature. Hydroxyl radicals are formed in the lab using radiation sources. When water is subjected to gamma rays, OH radicals and other species are produced:

H_2O -\/\/\/\/→ $[0.28]{}^{\bullet}OH + [0.06]\,H^{\bullet} + [0.27]e_{aq}^{-} + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H^{+}_{aq}$

Hydroxyl radicals are also created with UV light and H_2O_2. PE and PET were exposed to both types of radiation, and therefore, OH radicals, to simulate natural transformations. The figures below are the instruments that create the radicals.

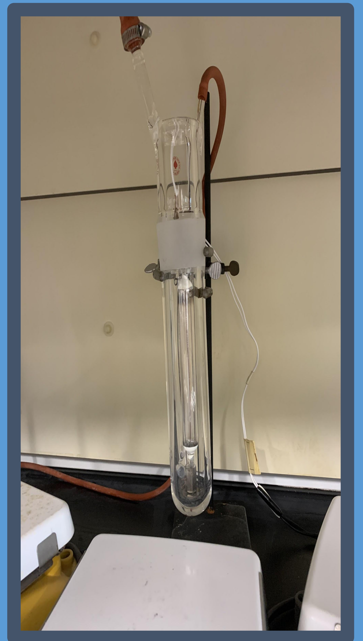


Figure 2. UV lamp at Valparaiso University.

Figure: 3. Gamma Irradiator at Idaho National Labs.

Microplastics undergo slow transformations in the environment

Reactivity is dependent on environmental conditions, such as oxygen levels and amount of sunlight.

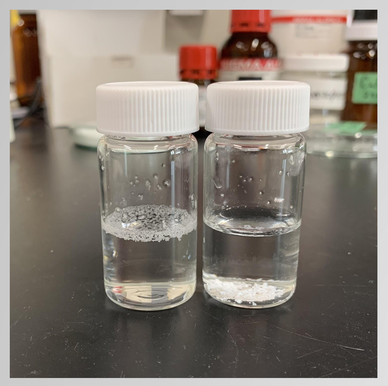


Figure 4. Polyethylene, PE (left) and polyethylene terephthalate, PET (right).

•OH →

What happens to the microplastics (MPs)?
*analyze water
*analyze MPs

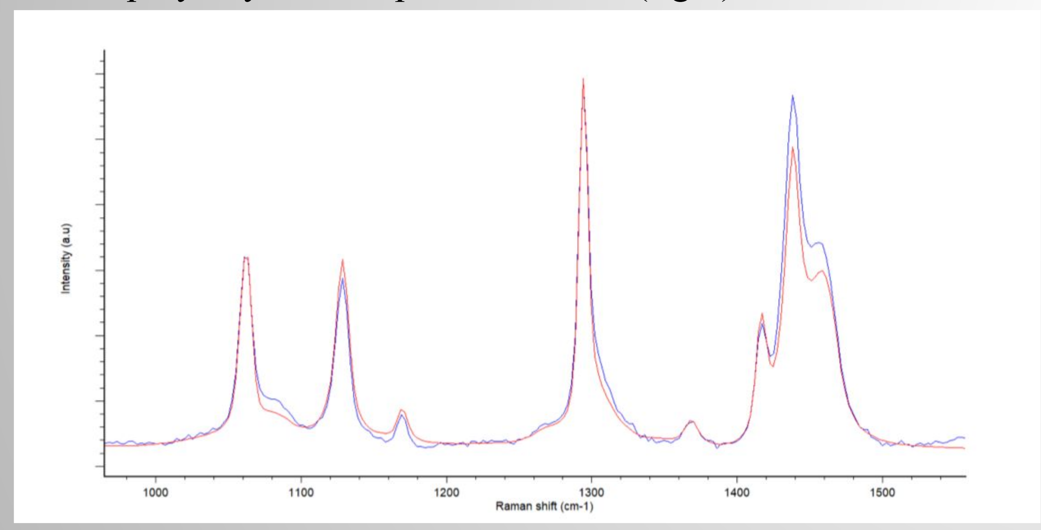


Figure 5: Raman spectra of PE and gamma irradiated PE (2.1 MGy, closed vessel).

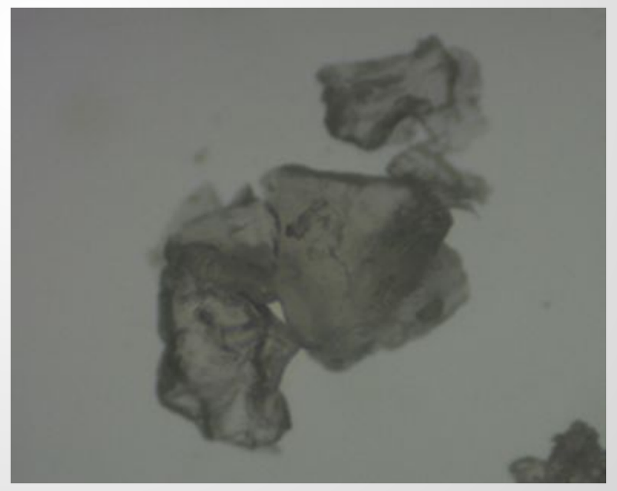


Figure 6. Magnified stereomicroscopic view of irradiated polyethylene microplastics.

Some of the compounds detected in water:
*Dodecane
*2-Dodecanone
*Tridecane
*Hexadecane

Microplastics interact with numerous compounds in the environment

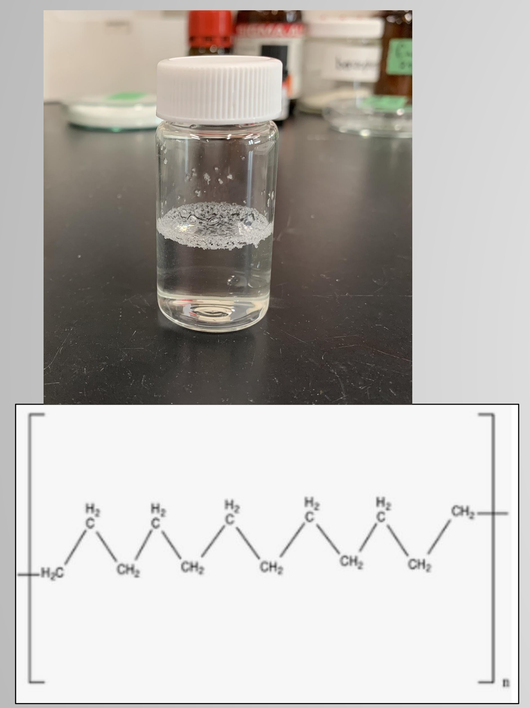


Figure 7. PE in vial (top) and molecular structure (bottom).

Model contaminants: caffeine, benzophenone, and dodecane →

How much contaminant ends up on the surface of the plastic?
How much remains in the water?

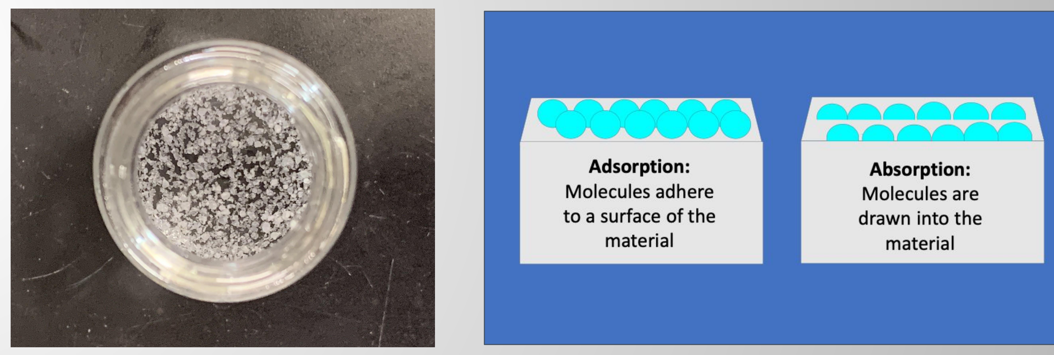


Figure 8. View from top of PE - water mixture.

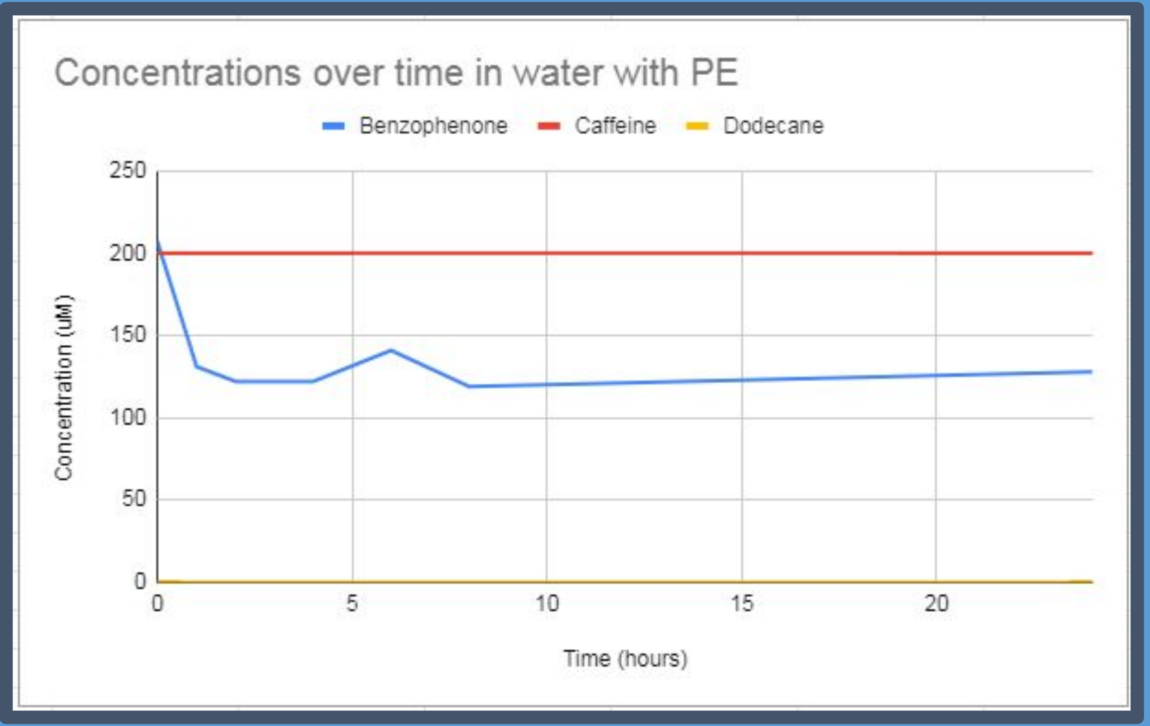


Figure 9. Absorbance of compounds with PE over time.

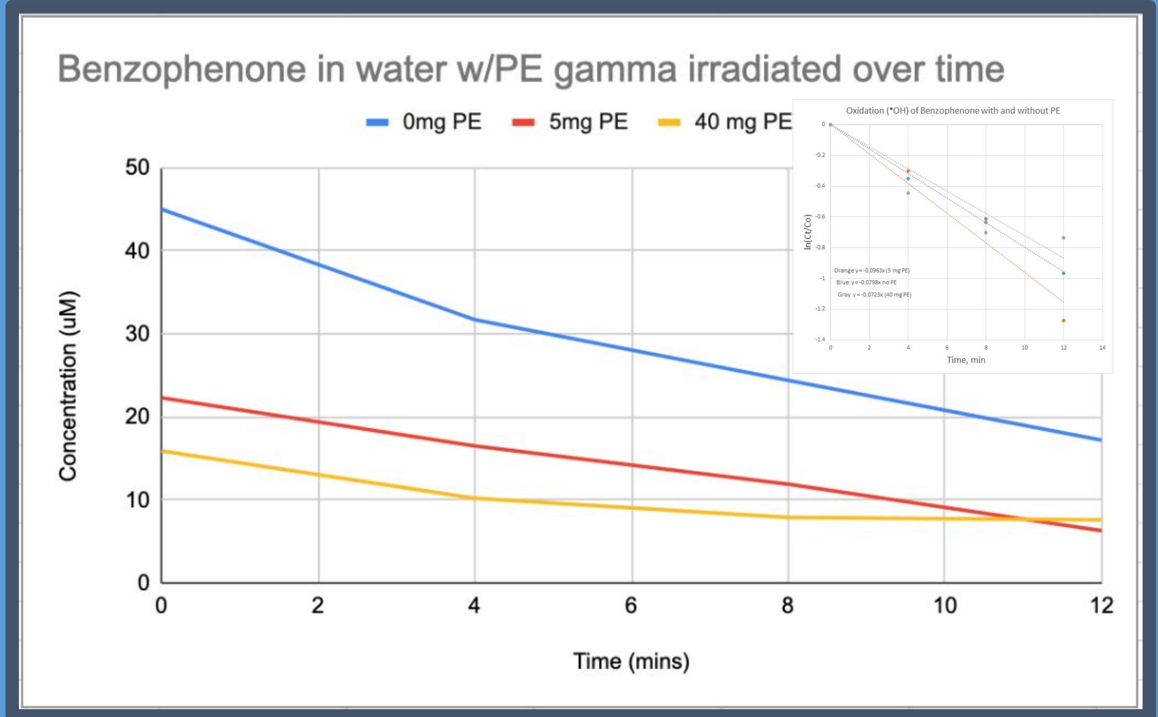
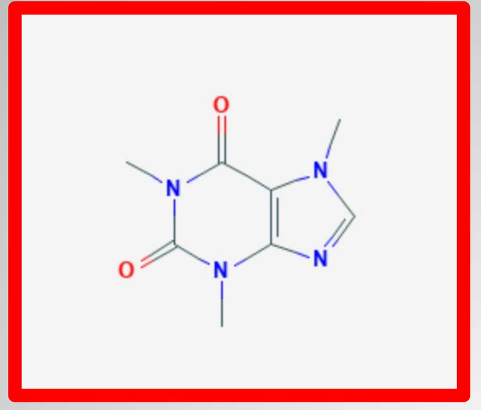
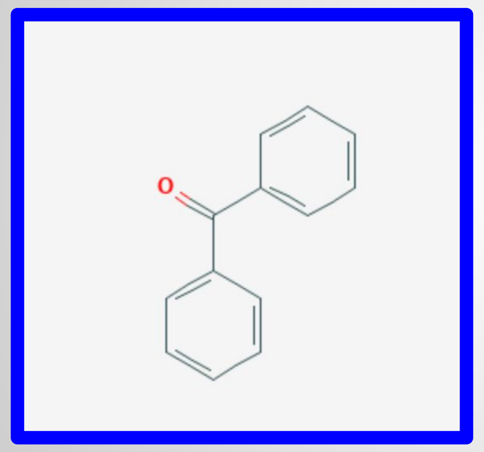


Figure 10. Change in concentration of Benzophenone with and without PE using gamma irradiation.

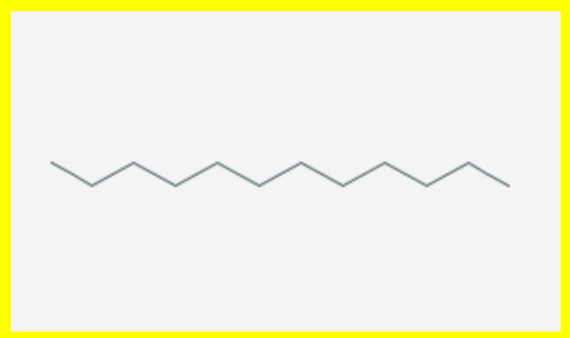
Why were these compounds chosen?



Caffeine is a common molecule present in many beverages. It enters surface waters through treated wastewater.



Benzophenone is a common molecule used as an additive for plastics, sunglasses, food flavorings, lipsticks, and more.



Dodecane is a common hydrocarbon, and was a product detected in our radiation experiments. It is representative of fuel compounds.

Adsorption Experiments and Results

Solutions of caffeine, benzophenone, and dodecane were combined with polyethylene or PET microplastics and the concentrations were measured over time (see *Figure 9*). These adsorption experiments were done to determine if these contaminants adhere to the microplastics. For both PE and PET, caffeine did not adsorb. Benzophenone adsorbed to PE and less to PET. Dodecane was fully adsorbent with PE.
Solutions of caffeine and benzophenone were then irradiated with OH radicals and then with 5 and 40 mg of PE (see *Figure 10*) to determine if the microplastics influence the reactivity of these compounds. *Figure 10* shows the change in solution concentration of benzophenone is not affected by the presence of the PE microplastics.

In the low oxygen conditions of our gamma radiolysis, both PE and PET undergo very little change. This suggests that in real world stagnant water conditions, these microplastics are resistant to OH radical-induced chemical transformations. Adsorption and desorption of other compounds in the water are expected and may affect chemical reactivity.

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