

Investigating the Sorption of Pharmaceutical and Personal Care Products on High-Density Polyethylene and Polypropylene Microplastics



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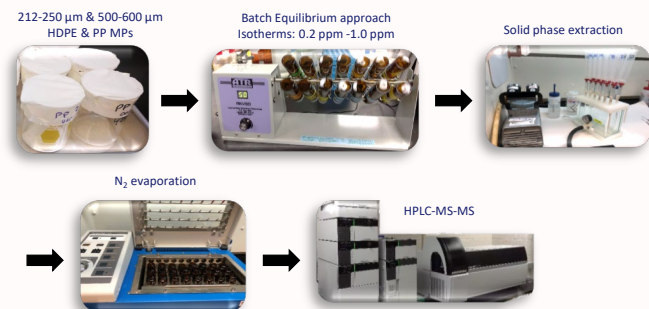
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Abstract: The term “microplastics” refers to plastic particles with a diameter of 5mm or less. Microplastics are capable of sorbing organic contaminants to concentrations magnitudes higher than the surrounding water. One such contaminants class is a group of pharmaceuticals and personal care products (PPCPs). As of now, very little information is known about the sorption behavior of PPCPs on microplastics; therefore, to better understand the interaction between PPCPs and microplastics, their sorption behavior must be studied. The goal of this project is to explore and evaluate the sorption behavior of polar and ionizable PPCPs onto microplastics. The PPCPs in this study were: diphenhydramine, an antihistamine, venlafaxine hydrochloride, an antidepressant, and N, N-diethylmeta-toluamide (DEET), which is an insect repellent

Introduction: Pharmaceuticals and personal care products are a class of organic pollutants that are prevalent in the environment due to their wide use for various purposes by humans, except that they are not as persistent as persistent organic pollutants (POPs). PPCPs also differ from POPs structurally. While most POPs are highly hydrophobic compounds, PPCPs tend to be more structurally diverse and have a wide range of water solubilities due to the presence of polar moieties. In sorption studies, the octanol-water partitioning coefficient, $\log K_{ow}$, which describes the distribution of a compound between a polar phase (water) and a nonpolar phase (octanol) has been used to predict the degree of distribution of compounds from water into microplastics. PPCPs are diverse in their water solubility and many of them are acids or bases and are ionic at environmental pH. The surrounding pH would then be an influencing factor to the sorption by controlling the neutral fraction of the compound. As a result, the sorption behavior of PPCPs may increase or decrease depending on the pH of the surrounding environment. Therefore, a more successful model of K_{ow} that considers the effect of the pH may be needed for a more accurate description for the sorption of PPCPs to MPs.

Methods: A batch equilibrium approach was used to expose polypropylene and polyethylene microplastics to diphenhydramine, venlafaxine and deet in solutions of 50 mL water that were of pH 7.48 ± 0.02 . To extract the PPCPs from solution, a fraction of the 50mL solutions were extracted in acetone using solid phase extraction. The extracts were then evaporated with nitrogen gas and reconstituted in methanol for analysis with the HPLC-MS-MS



Results and Discussion: Per $\log K_{ow}$ standards, venlafaxine, diphenhydramine, and DEET ($\log K_{ow}$ values of 3.28, 3.11, and 2.02, respectively) should be expected to sorb to HDPE and PP MPs. However, experimental results showed that there was no significant sorption detected to HDPE and PP for all three compounds: venlafaxine, diphenhydramine, and DEET. This is due to their pK_a values (diphenhydramine (8.98) and venlafaxine (10.09)) that would make them mostly ionic at a pH of 7.48. As a result, with the PPCPs being ionic and the MPs having hydrophobic structures, there would be no favorable hydrophobic interaction between the PPCPs and the surface of either HDPE or PP that would lead to sorption. DEET, on the other hand, although a non-ionic compound and relatively the least polar of the two other PPCPs, may theoretically be capable of interacting with HDPE and PP. However, it has a relatively high solubility in water, and thus favorably remains in the water phase. As such, $\log K_{ow}$ was shown to be insufficient for predicting and describing the sorption of PPCPs to MPs. $\log D_{ow}$, which is a measure of $\log K_{ow}$ that accounts for the pH dependency of an ionizable compound and is used to measure the distribution of ionized and non-ionized compounds in octanol and water as a function of pH may be a better measure for predicting the sorption of PPCPs to MPs. Given that a wide range of PPCPs are ionizable at environmental pH, only the non-ionized fraction may exhibit sorption to MPs; therefore, by calculating the ratio of the non-ionized fraction of molecules (using $\log D_{ow}$), one can predict the degree of PPCPs sorption to MPs.

Conclusions and Future Work: Sorption was undetectable for PPCPs DEET, diphenhydramine, and venlafaxine to PP and HDPE MPs based on their $\log K_{ow}$ values. Therefore, $\log K_{ow}$ alone may not be a good measure to predict and explain the sorption of relatively polar PPCPs to MPs. $\log D_{ow}$ may present a more accurate method for predicting and explaining the MP sorption of ionic compounds and offer a better model for sorption than $\log K_{ow}$ for polar PPCPs. Future research on MP sorption should focus on utilizing $\log D_{ow}$ to accurately predict the sorption behavior to potential plastic polymers.

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