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Aged microplastics enhance adsorption of pharmaceuticals

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Plastic pollution is an increasing environmental concern with increasing understanding of the nature and extent of the issue (*1*). Microplastics (< 5 mm in all dimensions (*2*)) often co-exist with aquatic pollutants, including pharmaceuticals. Pharmaceutical ecotoxicity and the adsorption potential of microplastics is worrisome from an environmental and human health perspective, particularly relating to the potential of particles entering the food chain.

The mismanagement of solid wastes contributes to plastic contamination. In 2018, only 32% of post-consumer plastic waste was recycled, and 25% was sent to landfill (*3*). Plastic particles can enter freshwater systems in a wide range of sizes. In the aquatic environment, plastic debris is exposed to continuous photo-oxidation and/or mechanical abrasion that can lead plastics to be broken-down into smaller particles (*4*).

Microplastics are divided into two different types, primary and secondary microplastics. Primary microplastics are plastic particles, including pre-production pellets, manufactured to microplastic size; despite recent regulations prohibiting their use, they are still commonly found in legacy personal care products (*5*). The most abundant microplastics in the environment (*6*) are secondary microplastics, produced by physical, chemical, and/or biological degradation of larger plastic materials (*2*).

Artificially aged microplastics

Microparticles of polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyamide (PA), polystyrene (PS), and polyvinyl chloride (PVC) are widely detected in freshwater environments (*7*). Two sizes of these polymers were investigated, described as 'small' (median size < 33 µm) and 'large' (median size 95-157 µm). Virgin microplastics were artificially aged in the laboratory by subjecting them to light and heat to evaluate how the photo and thermal oxidation processes affect microplastic interactions with pharmaceuticals.

Pharmaceuticals as the adsorbate

Pharmaceuticals are widely reported in freshwater environments, especially those with high prescription rates and/or low biodegradability (8, 9). Ibuprofen, carbamazepine, fluoxetine, ofloxacin, and venlafaxine were selected for this study due to their environmental relevance. The chemical parameters considered were toxicity to aquatic organisms (i.e. the water flea, *Daphnia magna*), prescription rate, and persistence in freshwater. Those selected cover a range of hydrophobicities.

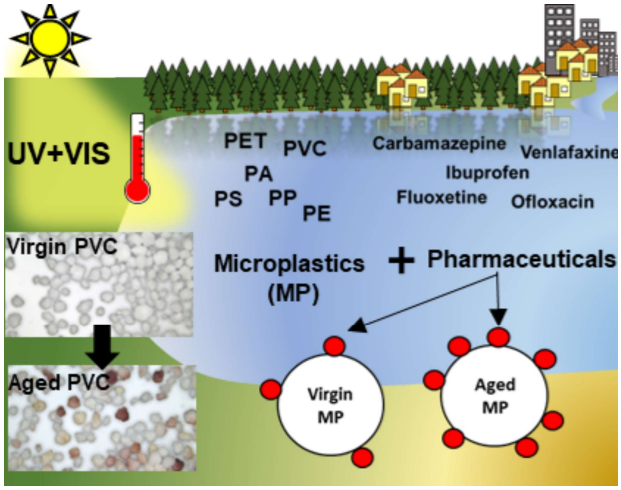

Figure 1. *Environmental interaction due to the co-occurrence of micropollutants, such as microplastics and pharmaceuticals in the aquatic environment.*

Recent adsorption studies focused on the adsorption of organic compounds onto virgin plastic particles, which have been reported to adsorb a range of aquatic contaminants, from natural toxins (*10*) to toxic metals (*11*). However, in the environment, microplastics are exposed to a variety of degradation processes that can impact the adsorption behaviour of the microplastics (**Figure 1**). This study investigated how ageing microplastics affects the adsorption potential of water contaminants. Results demonstrated a significant increase of the concentration of pharmaceuticals adsorbed by aged microplastics when compared to virgin microplastics (**Figure 2**). Exposure of polymers to ultraviolet radiation causes photooxidative degradation which breaks down the polymer chains which, in turn, generates free radicals (*12*). The presence of radicals, including carbonyl radicals, can enhance the adsorption of organic compounds onto microplastics.

The type of the microplastic is also a determinant for pharmaceutical adsorption behaviour and susceptibility to degradation. Each microplastic investigated responded differently after ultraviolet and visible light exposure. A yellowing developed for aged PS and PA microparticles, while a brown-reddish colour formed for aged PVC. Plastic

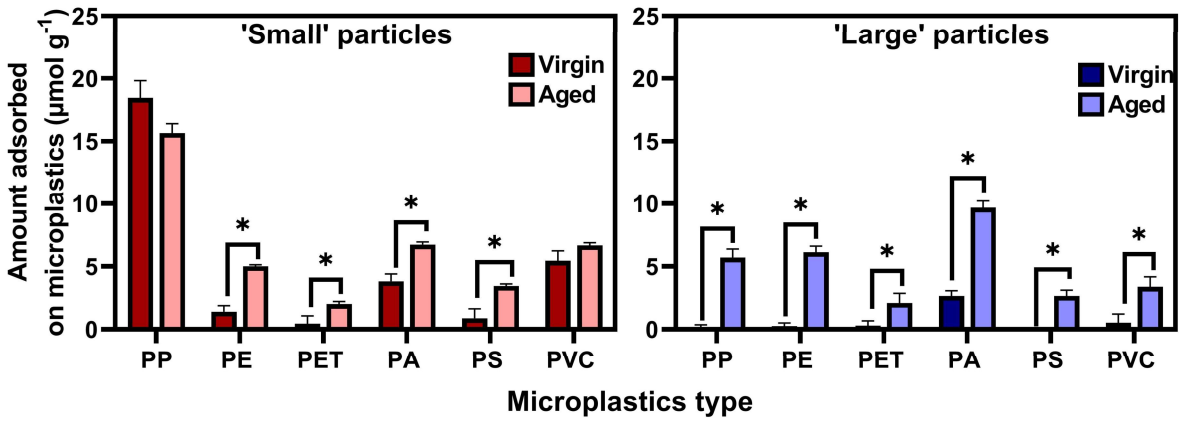

Figure 2. *Adsorption of pharmaceuticals onto 'small' and 'large' polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyamide, polystyrene (PA), and polyvinyl chloride (PVC). *Significant difference between the virgin and aged particles, t-test $p < 0.05$.*

degradation is often associated with a colour change; however, this does not occur for all plastics. Aged particles of PP, PE, and PET did not change colour. In contact with a mixture of pharmaceuticals, PP, PA, and PVC showed greater pharmaceutical adsorption compared to PS, PE, and PET. Concerningly, PP is the most widely produced plastic, primarily used for single-use items, and the most reported in freshwater (*7*).

Pharmaceutical hydrophobicity was identified as a driving factor for microplastic interaction. In a mixture containing ibuprofen, carbamazepine, fluoxetine, ofloxacin, and venlafaxine, fluoxetine demonstrated the greatest rate of adsorption onto microplastics. Fluoxetine was the most hydrophobic pharmaceutical in this study. It is also reported to have the greatest ecotoxicological effect on the water quality indicator organism, *Daphnia magna*.

This investigation showed that polymer composition, microplastic weathering, and the pharmaceuticals' hydrophobicity are key factors affecting the adsorption of pharmaceuticals onto microplastics. Research is ongoing to further understand if microplastics are a vector or a sink for pollutants such as fluoxetine.

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