Polyamide microplastics in wastewater as vectors of cationic pharmaceutical drugs.

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Polyamide microplastics in wastewater as vectors of cationic pharmaceutical drugs

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Abstract

Reported here is the first study to investigate the adsorption of pharmaceutical drugs to microplastics in wastewater. Wastewater is an environmental source of microplastics and pharmaceuticals, which is discharged as treated effluent or combined sewer overflows. In this study, adsorption of cationic pharmaceuticals, with a range of octanol-water distribution coefficients, to polyamide (Nylon 12) microplastics was investigated in real wastewater samples. Significant adsorption was observed for the more hydrophobic pharmaceuticals studied, propranolol, amitriptyline, and fluoxetine, with equilibrium reached within 24 hours. Microplastic-wastewater distribution coefficients for these three pharmaceuticals were 191, 749 and 1,020 L kg^{-1}, respectively. Favourable wastewater conditions for adsorption of pharmaceuticals to polyamide were at pH >7, summer temperatures (20 °C), and no stormwater dilution. Adsorption of the more hydrophilic pharmaceuticals atenolol, pseudoephedrine, metoprolol, and tramadol was ≤7 % under all conditions and considered insignificant. Limited desorption (7-17 %) of propranolol, amitriptyline, and fluoxetine was observed in river water over 24 hours. This suggests that microplastics may be able to transport adsorbed pharmaceuticals for considerable distances after discharge. In simulated gastric fluids their desorption increased to 24-27 % and 40-58 % in cold- and warm-blooded temperatures respectively. The findings demonstrate that wastewater microplastics could act as a vector of pharmaceutical drugs, from wastewater treatment plants to aquatic organisms. However, further research is needed to better appreciate the risks posed by pharmaceuticals adsorbed to microplastics in comparison to other organic particulates found in wastewater.

Keywords: emerging contaminant; adsorption; desorption; environmental chemistry; water pollution; microplastic

1. Introduction

Plastic less than 5 mm in all dimensions are microplastics by definition and have been found in all environmental compartments, travelling far from their original source (Vaughan et al., 2017; Gray et al., 2018; Obbard, 2018; Peeken et al., 2018; Zhang and Liu, 2018; Bollmann et al., 2019). Approximately 80 % of environmental plastic debris originates from land (Jambeck et al., 2015). It was estimated that 4.8 to 12.7 million tonnes of plastics entered the ocean from land in 2010, and municipal wastewater treatment plants (WTPs) are considered a significant contributor of microplastics (Jambeck et al., 2015; Murphy et al., 2016). Sources of microplastics in wastewater include fibres shed from clothing during laundering and those added to personal care products. WTPs typically achieve >95 % removal of microplastics from wastewater (Carr et al., 2016; Murphy et al., 2016; Lares et al., 2018). Nevertheless, significant numbers of microplastics still enter the environment in effluent discharges. For example, a WTP in Glasgow, Scotland, serving a population of 650,000 releases an estimated 65 million microplastic particles in the environment daily (Murphy et al., 2016). Those microplastics removed by WTPs are transferred to sludge which, following anaerobic digestion, are applied to agricultural land as biosolids (Keller et al., 2020; van den Berg et al., 2020), from where they can enter the aquatic environment.

A further source of microplastics in the environment is combined sewer overflows (CSOs). During periods of heavy rainfall, the capacity of combined sewers can be exceeded resulting in the direct discharge of untreated wastewater/stormwater mixtures to watercourses (Botturi et al., 2020). There were >400,000 CSO discharge events in England alone during 2020 resulting in >3,000,000 hours of CSO discharge (Environment Agency, 2020). Greater than 10,000 microplastics/L retained on a 10 µm mesh has been found in untreated wastewater (Simon et al., 2018). Microplastics most abundant in wastewater are polyethylene, polyamide, and polyethylene terephthalate (Sun et al., 2019). Stormwater also contains microplastics from tyres, brakes, and road markings (Liu et al., 2019a). Therefore, CSOs are considered a significant source of microplastics entering rivers and oceans.

An issue of concern is that environmental microplastics have the ability to transport other environmental pollutants that adsorb to their surface (Yu et al., 2019). Pharmaceuticals represent a diverse group of

environmental pollutants found in wastewater which can adsorb to microplastics under varying conditions (Wu et al., 2016; Razanajatovo et al., 2018; Xu et al., 2018; Puckowski et al., 2021). Previous studies have investigated the interactions between pharmaceuticals and microplastics in simple mediums (e.g., 0.01 M calcium chloride - $CaCl_2$) to simulate surface waters (Wu et al., 2016; Razanajatovo et al., 2018; Xu et al., 2018; Elizalde-Velázquez et al., 2020; Puckowski et al., 2021). Only a few studies have investigated pharmaceutical adsorption to microplastics using real matrices (Li et al., 2018; Magadini et al., 2020; Santana-Viera et al., 2021). Furthermore, no previous study has investigated the synergistic behaviour of microplastics and pharmaceuticals in wastewater, despite this being a source of both pollutants.

Wastewater is a complex matrix with properties and compositions that can vary significantly along the route of transportation and can affect pharmaceutical-microplastics interactions. For example, pH will govern the mechanism of adsorption as most pharmaceuticals are ionisable, with the extent of their ionisation varying with wastewater pH. Therefore, an important property used to predict the environmental fate of pharmaceuticals is the pH dependent octanol-water partition coefficient (log D_{OW}). Pharmaceuticals present in non-ionic form are most likely to have hydrophobic interactions with microplastics (Elizalde-Velázquez et al., 2020; Lin et al., 2020). Charged pharmaceuticals can have electrostatic attraction (or repulsion) to microplastic surfaces. Microplastics are unlike many natural particles as they can be charged electrostatically (Wang et al., 2015; Seidensticker et al., 2018). Li et al (2019) reported pH values at the point of zero charge (pH_{PZC}) for polyamide, polyethylene, polypropylene, polystyrene, and polyvinylchloride microplastics in the range 5.59-5.85. At pH values greater than the pH_{PZC} the microplastic surface has a net negative charge, facilitating interaction with cationic species (Li et al., 2019).

Wastewater temperature is another relevant factor that could influence pharmaceutical adsorption. Tetracycline adsorption to polyamide microplastics increased with increasing water temperature from 15 °C to 40 °C (Lin et al., 2020). Wastewater can also vary in the composition and concentration of dissolved organic matter. Humic acid has been used to simulate different dissolved organic matter concentrations and their effect on pharmaceutical-microplastic interactions (Wu et al., 2016; Xu et al.,

2018). Increasing humic acid concentration reduced the adsorption of 17α-ethinylestradiol to polyethylene microplastics, whereas it had no influence on carbamazepine adsorption (Wu et al., 2016). On the other hand, humic acid significantly enhanced adsorption of the broad-spectrum antibiotic oxytetracycline to polystyrene particles (Zhang et al., 2018). Ionic strength can also influence pharmaceutical-microplastic interactions with some studies reporting a reduction in pharmaceutical adsorption as ionic strength increases (Zhang et al., 2018; Guo et al., 2019a; Guo et al., 2019b; Liu et al., 2019b). This is relevant to CSOs as they can contain salts from road runoff, particularly during winter months.

It is important to consider the fate of pharmaceuticals adsorbed to microplastics once released to the environment. Microplastics can be ingested by a variety of organisms. However, only a few studies have investigated the desorption of pharmaceuticals from microplastics under gastric and intestinal conditions (Razanajatovo et al., 2018; Lin et al., 2020; Liu et al., 2020). Razanajatovo et al (2018) found total desorption of sertraline and propranolol from polyethylene microplastics under simulated gut conditions of 4 % and 8 %, respectively. Liu et al (2020) reported 27-51 % bioaccessibility of atorvastatin and amlodipine from polystyrene microplastics under gastrointestinal conditions. Up to 75 % desorption of tetracycline was observed from polyamide microplastics under gut conditions (Lin et al., 2020). Desorption of pharmaceuticals from wastewater microplastics in the immediate receiving environment (e.g., river water) also needs to be considered.

The aim of this study was to extend the knowledge of pharmaceutical-microplastic interactions to wastewater, and their subsequent desorption. The objectives of the study were to *(i)* investigate the adsorption of cationic pharmaceuticals to polyamide microplastics in wastewater, *(ii)* establish the effect of pH, salinity, stormwater dilution, and temperature on pharmaceutical adsorption, and *(iii)* investigate the desorption of pharmaceuticals from microplastics in river water and gastric fluid conditions of cold- and warm-blooded organisms. Polyamide microplastics were selected for study due to their prevalence in wastewater and adsorption of pharmaceuticals in previous studies (Guo et al., 2019a; Guo et al., 2019b; Sun et al., 2019; Lin et al., 2020). The cationic drugs atenolol, pseudoephedrine, metoprolol, tramadol, propranolol, fluoxetine, and amitriptyline which are commonly

found in wastewater (Petrie et al., 2015), were investigated to represent a broad range of log D_{OW} values (Table 1).

2. Materials and methods

2.1. Materials

Analytical reference standards of acebutolol, amitriptyline hydrochloride, atenolol, carbamazepine, codeine, fluoxetine hydrochloride, propranolol hydrochloride, pseudoephedrine, and tramadol hydrochloride, were purchased from Sigma Aldrich (Gillingham, UK). Acebutolol, carbamazepine, and codeine were utilised as internal standards. High-performance liquid chromatography (HPLC) grade methanol, ammonium formate, and formic acid were purchased from Fisher Scientific (Loughborough, UK). GF/F glass fibre filter papers, 4 mm PVDF 0.45 µm syringe filters, hydrochloric acid (HCl), and sodium hydroxide (NaOH) was also obtained from Fisher Scientific. Ultrapure water was 18.2 MΩ cm^{-1} quality. Sodium azide (NaN_3), sodium chloride (NaCl), and pepsin A were purchased from Sigma Aldrich. Polyamide microplastics (Nylon 12, maximum size – 250 µm and median size – 90 µm) were obtained from Goodfellow Cambridge Limited (Huntingdon, UK; Table 2). Wastewater (50 L) was collected from a septic tank in North-East Scotland during January 2021 and frozen at -20 °C. Stormwater (road runoff, 5 L) was collected following rainfall experienced on three consecutive days in March 2021. River water (5 L) was collected in April 2021.

2.2. Adsorption experiments

The same wastewater was used in all experiments and did not contain detectable levels of any of the studied pharmaceuticals. Wastewater was defrosted overnight, filtered through GF/F filters, and treated with 0.2 g L^{-1} sodium azide to limit microbial activity. Wastewater volumes of 20 mL had 50 mg of polyamide microplastic added in 50 mL conical flasks. This is similar to previous studies (Xu et al., 2018; Guo et al., 2019a; Guo et al., 2019b; Lin et al., 2020; Liu et al., 2020). These were kept in the dark and mixed at 175 rpm using an orbital shaker (Cole-Palmer, Staffordshire, UK). The wastewater temperature was 20 °C. Samples were mixed for one hour prior to spiking with pharmaceuticals. Pharmaceutical spiking concentration of 0.5 mg L^{-1} was used to establish uptake kinetics and establish equilibrium time. This gave pharmaceutical-microplastic ratios similar to other studies (Wu et al., 2016;

Razanajatovo et al., 2018; Xu et al., 2018; Guo et al., 2019a). Samples were collected at 0, 0.5, 1, 2, 3, 4, 6, 16, 24, 40 and 48 hours. Pharmaceutical concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1 and 2 mg L^{-1} were used in the adsorption isotherm experiments. The linear (1), Freundlich (2) and Langmuir (3) isotherms were used to model the data:

$$q_e = K_d C_e \quad (1)$$

$$q_e = K_F C_e{}^{1/n} \quad (2)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (3)$$

q_e (mg kg^{-1}) is the adsorbed pharmaceutical concentration and C_e (mg L^{-1}) is the remaining pharmaceutical concentrations in wastewater, K_d (L kg^{-1}) is the distribution coefficient between the microplastic and wastewater, K_F [(mg kg^{-1})(mg $L^{-1})^n$] and n are the Freundlich constants, K_L is the Langmuir constant (L mg^{-1}), and q_{max} (mg kg^{-1}) is the estimated maximum adsorption capacity. The uptake kinetics were fitted using the pseudo-second order model:

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

t (hours) is the mixing time and K_2 (kg mg^{-1} h^{-1}) is the equilibrium rate constant.

Wastewater pH was adjusted to 3, 6, 7, 8 and 11 using HCl or NaOH to investigate the effect on pharmaceutical adsorption. Varying composition of wastewater:stormwater (100:0, 75:25, 50:50, 25:75, and 0:100) were prepared to investigate the influence of stormwater dilution on pharmaceutical adsorption. Salinity concentrations of 0, 1, 2, 3, and 4 g L^{-1} NaCl in 50:50 wastewater:stormwater were investigated. Experiments were also conducted in wastewater at 20 °C and 5 °C, respectively. All samples were collected following 24 hours of mixing. Equivalent experiments without microplastic to evaluate any pharmaceutical losses to glassware were utilised for all experiments. All experiments were performed in triplicate.

The effect of pH, dilution of wastewater with stormwater, and NaCl addition to pharmaceutical adsorption to polyamide microplastics were analysed using one-way ANOVA followed by Tukey's multiple comparison tests; the effect of temperature was analysed by unpaired t-tests followed by

160 Welch's correction. The statistical analysis was performed using Prism v.9.0.1 (GraphPad Software,
161 USA). A *p*-value of <0.05 was considered significant.

162 **2.3. Desorption experiments**

163 Adsorption experiments were conducted in wastewater at 20 °C using 2 mg L^{-1} pharmaceutical
164 concentrations, mixed at 175 rpm and collected after 24 hours. Samples were filtered through GF/F
165 filters following adsorption equilibrium, and the filtrate collected to assess pharmaceutical adsorption.
166 The retained microplastics were then transferred to a flask containing 20 mL desorption medium which
167 included river water and simulated gastric fluids. Simulated gastric fluids were prepared using 3.2 g L^{-1}
168 pepsin A in 100 mM NaCl and adjusted to pH 2 using HCl (Liu et al., 2020). River water and 'cold-
169 blooded' gastric fluid was maintained at 20 °C, whereas 'warm-blooded' gastric fluid was maintained
170 at 37 °C. Samples were collected at 1, 2, 3, 4, and 24 hours. All desorption experiments were conducted
171 in triplicate.

172 **2.4. Analytical methods**

173 All samples were passed through 0.45 µm PVDF filters and spiked with 1 mg L^{-1} of acebutolol,
174 carbamazepine and codeine as internal standards. PVDF filters were selected as they achieved superior
175 analyte recoveries over nylon, PTFE, and cellulose acetate filters (Figure S1). Any samples containing
176 NaCl were diluted by 50 % in ultrapure water prior to addition of the internal standards. Analysis was
177 performed by HPLC-tandem mass spectrometry (MS/MS). Separation was performed on a 100 x 2.1
178 mm Kinetex 5 µm C18 column (Phenomenex, Cheshire, UK) using an Agilent 1260 Infinity Series
179 HPLC (Cheadle, UK).

180 A gradient elution of 10 mM ammonium formate in water containing 0.1 % formic acid (mobile phase
181 A) and 10 mM ammonium formate in methanol containing 0.1 % formic acid (mobile phase B) was
182 used. Initial conditions of 80 % A was maintained for 0.5 minutes before reducing to 20 % over 9.5
183 minutes. This was maintained for 3.5 minutes before returning to starting conditions over 0.1 minute.
184 Re-equilibration of the column was achieved over 6.4 minutes. The column temperature was 25 °C and
185 the injection volume was 2 µL. Quantification was by internal standard calibration prepared in
186 wastewater. The calibration ranged from 0.01 to 2.5 mg L^{-1}, with 1 mg L^{-1} internal standard. The MS/MS

was an Agilent 6420 triple quadrupole operated in multiple reaction monitoring mode (MRM). Details of the MRM transitions are outlined (Table S1).

To ensure the quality of data obtained, wastewater spiked with known concentrations of pharmaceuticals as quality control samples were analysed every 12 samples as well as blanks (non-spiked wastewater). Standard tolerances of deviation in retention time were adhered to. The recovery of pharmaceuticals through PVDF filters was also verified for each of the different samples analysed.

3. Results and discussion

3.1. Adsorption kinetics of pharmaceuticals to polyamide microplastics in wastewater

Adsorbed pharmaceutical concentrations were determined by the concentration difference in the liquid phase of samples with and without microplastic. Equilibrium of propranolol, amitriptyline, and fluoxetine was achieved within 24 hours (Figure 1). Therefore, in subsequent investigations all samples were collected following 24 hours of mixing to ensure equilibrium was established. This agrees with previous adsorption studies of pharmaceuticals to microplastics in simple water mediums (Xu et al., 2018; Liu et al., 2019b; Feng et al., 2020; Puckowski et al., 2021). Mixing for 24 hours is also relevant for the sewer residence time of wastewater prior to reaching WTP for treatment (Petrie et al., 2019).

Propranolol, amitriptyline, and fluoxetine adsorption fitted to the pseudo-second order kinetic model. Coefficients of determination (r^2) were ≥0.981 (Table 3); suggesting that ≥98.1 % of the variability in the dataset was explained by the estimated regression line. As can be observed in Figure 1 and Table 3, both the calculated and experimental values of q_e compare well. The data fitted to the pseudo-second order model suggesting chemical adsorption over a physical process (e.g., Van der Waal forces) dominates the interactions between the pharmaceuticals and microplastic. This agrees with previous research which has found pharmaceutical adsorption to microplastics fits the pseudo-second order model (Xu et al., 2018; Liu et al., 2020; Yu et al., 2020).

The adsorption of atenolol, pseudoephedrine, tramadol, and metoprolol was ≤7 % of the spiked concentration. The method precision (filtration and LC-MS/MS analysis) for the selected pharmaceuticals in wastewater was ~5 %. Therefore, a difference in liquid phase concentration between

samples with and without microplastic could not be established. Preliminary studies investigating higher microplastic to pharmaceutical ratios also revealed no significant adsorption. These pharmaceuticals all had log D_{OW} values ≤0.58 in the wastewater (pH 7.6; Table 1). The log D_{OW} values for propranolol, amitriptyline, and fluoxetine were 1.65, 3.11 and 1.85, respectively (Table 1). However, the calculated and theoretical q_e values followed fluoxetine>amitriptyline>propranolol (Figure 1; Table 3). A previous study found that log D_{OW} alone was insufficient to predict the adsorption of pharmaceuticals to other substrates such as sludge (Hörsing et al., 2011).

3.2. Pharmaceutical adsorption isotherms to polyamide microplastic

The linear, Freundlich and Langmuir isotherms were used to model the equilibrium data (Figure S2). The linear model demonstrated r^2 values ≥0.990 and partition coefficients (K_d) values of 191, 749 and 1,020 L kg^{-1} for propranolol, amitriptyline, and fluoxetine, respectively (Table 1). Previous research on microplastics has found a range of K_d values for propranolol. Puckowski et al (2021) reported K_d values of 1.3-2.4 L kg^{-1} for polyethylene, polypropylene, and polyvinylchloride at microplastic concentrations of 100 g L^{-1}. On the other hand, Razanajatovo et al (2018) reported a K_d value of 2,300±2,790 L kg^{-1} for polyethylene at 0.2 g L^{-1}. This study utilised a microplastic concentration of 2.5 g L^{-1}. To the best of our knowledge this is the first study to report the adsorption of both amitriptyline and fluoxetine to microplastics. Their higher adsorption is attributed to their greater hydrophobicity and log D_{ow} values (Table 1).

Adsorption of propranolol, amitriptyline and fluoxetine fitted to the Freundlich isotherm with r^2 values ≥0.988 (Table 3). The Freundlich isotherm has been used to model pharmaceutical adsorption to microplastics numerous times in the literature (Li et al., 2018; Zhang et al., 2018; Guo et al., 2019a; Guo et al 2019b). It describes adsorption to heterogenous surfaces by the occupancy of high energy sites followed by low energy sites (Tourinho et al., 2019). Fitting to the Freundlich isotherm indicates multilayer adsorption to the microplastic surface (Liu et al., 2019b). The curvature of the Freundlich isotherm is described by the n values. A value of 1 signifies that relative adsorption was identical across the concentration range tested. The n values were 1.04, 1.09 and 1.00 for propranolol, amitriptyline, and fluoxetine (Table 3).

The Langmuir isotherm assumes a homogenous adsorbent surface covered by a monolayer of adsorbate molecules, and a finite number of adsorption sites. The equilibrium data also fitted the Langmuir isotherm with similar r^2 values (0.988-0.998) across the concentration range studied (Table 3). Li et al (2018) found that the adsorption of antibiotics to microplastics could fit the Langmuir and Freundlich isotherms, and the isotherm which had the better fit was both antibiotic and microplastic specific. Other studies have found that pharmaceutical adsorption was better described using the Langmuir isotherm over the Freundlich isotherm (Liu et al., 2019a; Liu et al., 2019b; Feng et al., 2020; Lin et al., 2020).

3.3. Effect of changing wastewater characteristics on pharmaceutical adsorption

Wastewater pH had the greatest effect on pharmaceutical adsorption to polyamide microplastic, influencing both the charge of the pharmaceuticals and the microplastic. Greatest adsorption of propranolol, amitriptyline, and fluoxetine occurred at pH 11 (Figure 2A). At pH 11 these pharmaceuticals are present in non-ionic form (Figure S3). This suggests hydrophobic interactions are likely to account for the higher adsorption. This agrees with Elizalde-Velázquez et al (2020) who found higher adsorption of the anionic pharmaceuticals when present in non-ionic form (at pH 3). However, at pH 11 tramadol has a log D_{OW} value of 2.39 (Figure S4), but no appreciable adsorption was observed.

At pH values in the typical range for wastewater (pH 6-8), the pharmaceuticals were >98 % ionised and in cationic form (Figure S3). This facilitates electrostatic attraction with negatively charged adsorbents. Greater adsorption of fluoxetine and amitriptyline was achieved at pH 7 and 8 than at pH 6. However, it should be noted that atenolol, pseudoephedrine, metoprolol, and tramadol are all positively charged at these pH values, but no adsorption was observed. Interestingly, negligible pharmaceutical adsorption occurred at pH 3 (Figure 2A). Li et al (2019) reports polyamide as having a pH_{PZC} value of 5.82 which may explain the lower adsorption at pH 6 than pH 7 and 8. At pH values below the pH_{PZC} value the microplastic surface is positively charged. Therefore, electrostatic repulsion will occur with the positively charged pharmaceuticals at pH 3 (Figure S3).

Dilution of wastewater with stormwater was used to assess pharmaceutical-microplastic interactions during storm events. Interestingly, reduced adsorption of fluoxetine was found in diluted wastewater (Figure 2B). It is postulated that the higher concentration of dissolved organic species can act as a bridge

between the pharmaceutical and the microplastic. Previous studies report complexation between cationic species and deprotonated locations on bulk dissolved organics such as humic acid (Sun et al., 2010; Zhang et al., 2018). Humic acid has been found to adsorb to other microplastics polymer types such as polystyrene (Fadare et al., 2019). The adsorption of oxytetracycline to polystyrene particles is enhanced by humic acid (Zhang et al., 2018). However, increasing the proportion of stormwater in wastewater:stormwater mixtures from 25 % did not result in any further reduction in amitriptyline and fluoxetine adsorption (Figure 2B). On the other hand, propranolol adsorption was reduced when the proportion of stormwater increased beyond 25% (Figure 2B).

The addition of NaCl up to 4 g L^{-1} in a 50:50 wastewater:stormwater mixture had little effect on amitriptyline and fluoxetine adsorption (Figure 2C). Several studies report that NaCl has a negligible effect on pharmaceutical adsorption to microplastics (Wu et al., 2016; Xu et al., 2018; Lin et al., 2020). However, a 37 % reduction of propranolol adsorption was observed with the addition of 1 g L^{-1} NaCl. No further reduction was observed with increasing NaCl concentration (Figure 2C). A similar observation was found for sulfamethoxazole adsorption to polyamide microplastics (Guo et al., 2019a). Na^+ can result in a charge shielding effect on the microplastic surface (Lu et al., 2018), reducing electrostatic interactions between the microplastic and the charged pharmaceutical. On the other hand, Puckowski et al (2021) found that increasing ionic strength using $CaCl_2$ significantly reduced propranolol adsorption to polyethylene, polypropylene, and polyvinylchloride microplastics. This is likely to be due to the divalent cation Ca^{2+} reversing the microplastic charge resulting in repulsion of propranolol.

The influence of wastewater temperature was assessed using wastewater incubated at 20 °C and 5 °C. At 5 °C the adsorption of propranolol, amitriptyline, and fluoxetine was reduced by 58 %, 62 %, and 57 %, respectively (Figure 3). It is hypothesised that the lower adsorption is a result of reduced adsorption kinetics at 5 °C, not reaching equilibrium within 24 h. Nevertheless, the observation is valid considering typical sewer residence times being ≤24 hours (Petrie et al., 2019). Tetracycline has also shown increased adsorption to polyamide microplastic with increasing temperature from 15 °C to 40 °C (Lin et al., 2020). Wastewater temperature can decrease to 8-15 °C during winter in temperate

294 climates (Zhou et al., 2018). This can reduce further to <5 °C in treatment processes with long residence
295 times such as lagoons (Hoang et al., 2014; Delatolla et al., 2019).

296 **3.4. Desorption of pharmaceuticals from polyamide microplastics**

297 Desorption studies were conducted in river water (pH 7.4) and simulated gastric fluids (pH 2). Those
298 studies in river water were to establish pharmaceutical desorption upon discharge to the environment.
299 Desorption of propranolol, amitriptyline, and fluoxetine proceeded quickly (Figure 4). Both
300 amitriptyline and fluoxetine reached equilibrium within 24 hours. Total desorption at 24 hours was
301 17±3 %, 8±1 %, and 7±1 % for propranolol, amitriptyline, and fluoxetine, respectively, in river water.
302 Higher desorption of propranolol is attributed to its weaker interactions with the microplastic, as noted
303 from the isotherm data. Although a notable amount of the studied pharmaceuticals was released from
304 the microplastic in river water, significant levels remain adsorbed to the microplastic. This suggests that
305 pharmaceuticals can be transported with microplastics for considerable distances from their point of
306 discharge into the environment. Low desorption of atorvastatin and amlodipine was previously
307 observed from polystyrene microplastics in simulated seawater (Liu et al., 2020). To the best of our
308 knowledge this is the first study to evaluate the desorption of pharmaceuticals from microplastics in
309 river water.

310 Intentional and unintentional consumption of microplastics can result in organisms exposed to adsorbed
311 pharmaceuticals. Desorption studies were undertaken in simulated gastric fluids at 20 °C and 37 °C to
312 mimic cold- and warm-blooded organisms. At both 20 °C and 37 °C, desorption was rapid within the
313 first hour which then slowed and did not appear to reach equilibrium after 24 hours (Figure 4). Liu et
314 al (2020) reported a fast desorption of atorvastatin and amlodipine in gastric fluid over 2 hours followed
315 by a slow phase that can take months before equilibrium would be reached. Nevertheless, it is relevant
316 to consider the desorption during the likely retention time within stomach conditions. Several studies
317 consider a 2-hour exposure time in gastric fluid (Tao et al., 2010; Wang et al., 2011; Liu et al., 2020).

318 Desorption of propranolol, amitriptyline, and fluoxetine at 20 °C was 26±3 %, 27±2 %, and 24±1 %
319 after 2 hours (Figure 4). At 37 °C this was increased to 58±5 %, 52±5 %, and 40±4 %. Desorption was
320 considerably greater in gastric fluids than river water (pH 7.4). The desorption observed is not surprising

considering the gastric fluid had a pH of 2, and no interactions of the pharmaceuticals with the microplastic was found under acidic conditions previously (Figure 4). Enhanced desorption at pH 2 may be due to the surface charge of the microplastic becoming positively charged, leading to repulsion of the now similarly charged pharmaceuticals. A previous study found a less notable difference in desorption of atorvastatin and amlodipine from polystyrene microplastics at cold- and warm-blooded temperatures (Liu et al., 2020). Lin et al (2020) found 6 % higher desorption of tetracycline from polyamide microplastics in simulated gut conditions between 37 °C and 27 °C. Razanajatovo et al (2018) investigated the desorption of the antidepressant sertraline and propranolol from microplastics under simulated gut conditions. Lower desorption of the more hydrophobic pharmaceutical (sertraline) was observed, similar to the general trend in this study, however, this observation requires further research.

The findings demonstrate that propranolol, amitriptyline, and fluoxetine adsorb to polyamide microplastics in wastewater under various conditions, and their desorption behaviour suggests they could pose a risk to exposed aquatic organisms. Further research is needed on the role of other organic particulates found in wastewater as vectors of pharmaceuticals drugs in comparison to and when mixed with microplastics. It has been found that triclosan preferentially adsorbs to microplastics over a natural substrate (soil) (Chen et al., 2021). However, Koelmans et al (2016) concluded that the amount of hydrophobic organic pollutants like polychlorinated biphenyls and polyaromatic hydrocarbons adsorbed to microplastics is likely to be low compared to other particulates found in natural environments. Other than microplastics, cationic pharmaceuticals are known to adsorb to negatively charged natural substrates with high cation exchange capacities such as clay (Droge and Goss, 2013). Therefore, studies which assess the adsorption of cationic pharmaceuticals to other substrates present in wastewater, and the fate of these substrates in the environment is needed to appreciate the relative role of wastewater microplastics as vectors of cationic pharmaceuticals.

4. Conclusions and future research

The more hydrophobic pharmaceuticals (log D_{OW} ≥1.65) adsorbed to polyamide (Nylon 12) microplastics in wastewater at pH 7.6 and fitted pseudo-second order kinetics (r^2 ≥0.981). Equilibrium

time was reached with 24 hours and is relevant considering typical sewer hydraulic retention times. Linear and Freundlich isotherms were suitable to describe amitriptyline and fluoxetine adsorption with r^2 values ≥0.990. Propranolol adsorption fitted moderately better to the Langmuir isotherm over the Freundlich isotherm. Wastewater conditions which favoured pharmaceutical adsorption to microplastics were pH >7, summer wastewater temperatures (20 °C) and no dilution with stormwater. Exposure of pharmaceutical loaded microplastics to simulated stomach conditions of warm-blooded organisms revealed >50 % desorption of propranolol, amitriptyline, and fluoxetine was possible. Further studies are now needed on the adsorption and desorption of pharmaceuticals to and from other particulates found in wastewater to better understand the importance of wastewater microplastics as vectors of pharmaceutical drugs.

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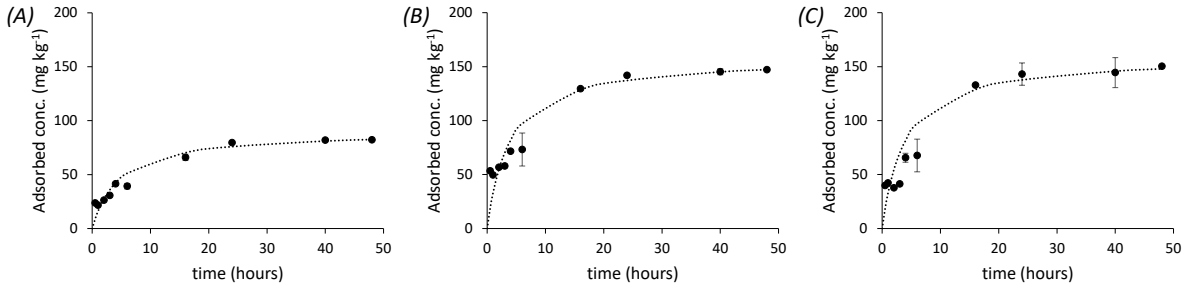


Figure 1. Adsorbed concentration of propranolol *(A)*, amitriptyline *(B)*, and fluoxetine *(C)* to polyamide microplastics in wastewater over 48 hours. The dashed line represents the pseudo-second order model.

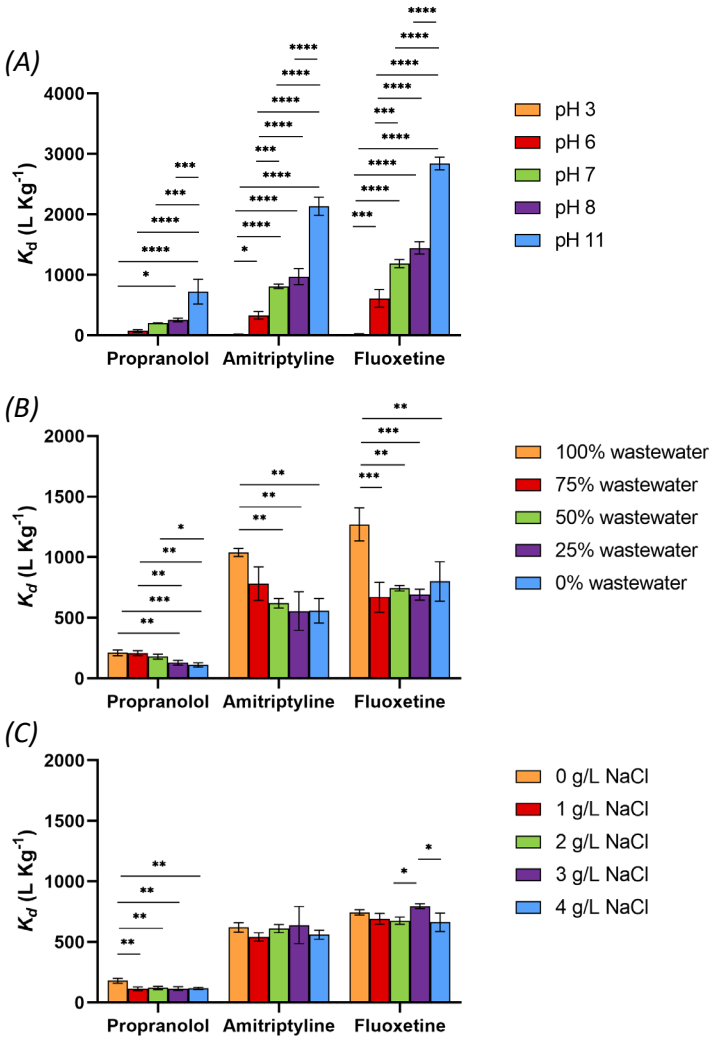


Figure 2. Influence of pH *(A)*, dilution of wastewater with stormwater *(B)* and NaCl addition *(C)* to pharmaceutical adsorption to polyamide microplastics. The investigation of NaCl to pharmaceutical adsorption was conducted in 50:50 wastewater:stormwater. The asterisks represent significant differences where *p<0.05, ** p<0.01, *** p<0.001, and **** p<0.0001 based on one-way ANOVA followed by Tukey's post-hoc correction. See Table S2 for the p-values.

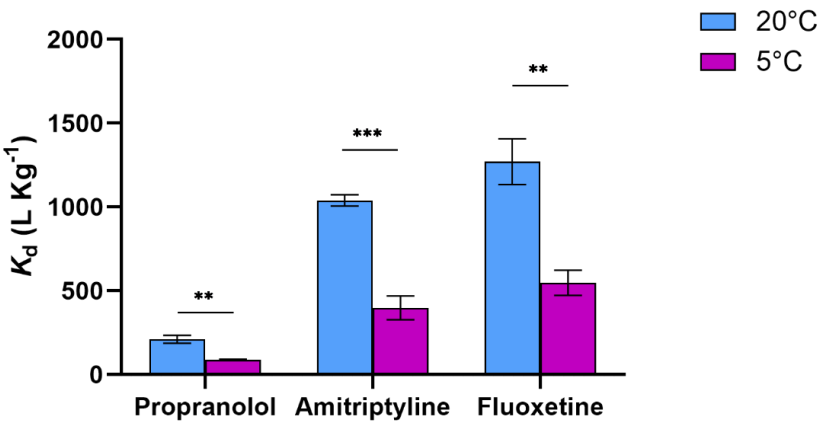


Figure 3. Effect of wastewater temperature (20 °C *versus* 5 °C) on propranolol, amitriptyline, and fluoxetine adsorption to polyamide microplastics over 24 hours. The asterisks represent significant differences where ** $p<0.01$, *** $p<0.001$, and based on unpaired *t*-tests followed by Welch's correction. See Table S2 for the *p*-values.

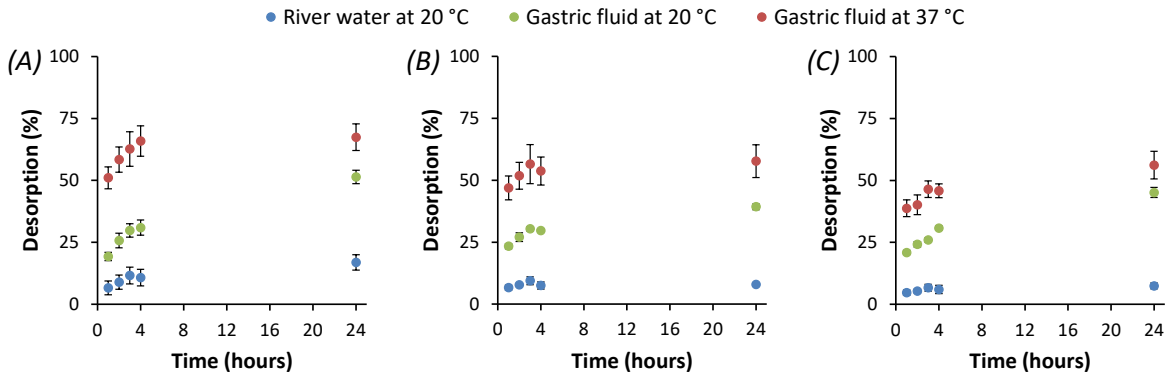


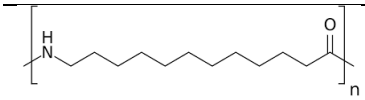
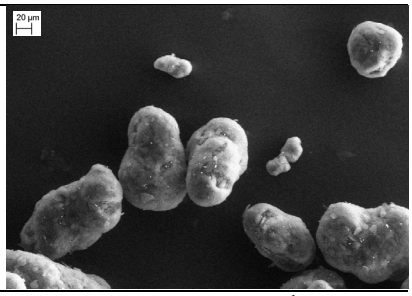
Figure 4. Desorption of propranolol *(A)*, amitriptyline *(B)*, and fluoxetine *(C)* from polyamide microplastics in river water and gastric fluids at 20 °C and 37 °C.

547 Table 1. Pharmaceutical properties at pH 7.6

Pharmaceutical	**Therapeutic group**	**Molecular mass (g mol^{-1})**	***pK$_a$***	**Log *D$_{OW}$*[a]**	**Ionisation (%)[b]**	**Charge[b]**
Atenolol	Betablocker	266.34	9.67	-1.91	99.1	+
Pseudoephedrine	Decongestant	165.23	10.30	-1.81	98.8	+
Metoprolol	Betablocker	267.36	9.67	-0.19	99.1	+
Tramadol	Analgesic	263.38	9.41	0.58	97.7	+
Propranolol	Betablocker	259.34	9.42	1.65	99.1	+
Fluoxetine	Antidepressant	309.33	9.80	1.85	99.4	+
Amitriptyline	Antidepressant	277.40	9.40	3.11	99.3	+

548 [a]Log D_{OW} = Log K_{OW} - Log(1+10$^{(pKa\text{-pH})}$) calculated using Log K_{OW} values obtained from Pubchem
549 (2021)
550 [b]Values taken from ChemAxon (2021)

551 Table 2. Polyamide microplastic properties

Monomer	Size (µm)[a]	Density (g cm^{-3})	pH$_{PZC}$	SEM image[b]
	90 (d_{50}) 250 (max.)	1.13-1.41[c]	5.82[d]	

552 [a]As detailed by the manufacturer [b]500 x magnification [c]British Plastic Federation (2020) [d]Li et al.,
553 (2019)
554 Key: pH$_{PZC}$, pH value at the point of zero charge; SEM, scanning electron microscopy; d_{50}, median size
555

556

557 Table 3. Calculated kinetics and isotherm data for propranolol, amitriptyline, and fluoxetine with
558 polyamide microplastics in wastewater

Model	Type	Parameter	Pharmaceutical drug		
			Propranolol	**Amitriptyline**	**Fluoxetine**
Kinetics	Pseudo-second order	q_e (mg kg^{-1})	90.4	159	168
		K_2 (kg mg^{-1} h^{-1})	2.42 x 10^{-3}	1.65 x 10^{-3}	1.07 x 10^{-3}
		r^2	0.990	0.991	0.981
Isotherm	Linear	K_d (L kg^{-1})	191	749	1.02 x 10^3
		r^2	0.990	0.997	0.996
	Freundlich	K_f [(mg kg^{-1})(mg L^{-1})$^{1/n}$]	198	732	1.02 x 10^3
		n	1.04	1.09	1.00
		r^2	0.988	0.998	0.996
	Langmuir	q_{max} (mg kg^{-1})	1.21 x 10^4	3.03 x 10^3	7.84 x 10^4
		K_L (L mg^{-1})	0.0166	0.297	0.0131
		r^2	0.988	0.998	0.996

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560