

Relationship between land use, seasonality, hydrological conditions, and the adsorption of sulfamethoxazole, ciprofloxacin, and 17 β -estradiol onto polyethylene terephthalate microplastics in a small urban river system, Eastern Cape, South Africa

Edgar Tumwesigye ^a, Chika Felicitas Nnadozie ^a, Frank C. Akamagwuna ^a, Xavier Siwe Noundou ^b, George William Nyakairu ^c and Oghenekaro Nelson Odume ^{a,*}

^a Centre for Environmental Water Quality, Institute for Water Research, Rhodes University, P.O. Box 94, Makhanda, South Africa

^b Department of Pharmaceutical Sciences, School of Pharmacy, Sefako Makgatho Health Sciences University, P.O. Box 218, Medunsa 0204, South Africa

^c Department of Chemistry, Makerere University, Kampala, Uganda

*Corresponding author. E-mail: n.odume@ru.ac.za

 ET, 0000-0001-5548-3255; CFN, 0000-0001-6177-2627; FCA, 0000-0001-8726-3492; XSN, 0000-0002-8667-8351; GWN, 0000-0002-1314-608X; ONO, 0000-0001-5220-3254

ABSTRACT

Microplastics (MPs) are increasingly identified as contaminant vectors in aquatic systems. However, the role of land use, seasonality, and hydrological conditions in contaminant- microplastic (MP) interactions remains underexplored. This study investigated the adsorption of sulfamethoxazole (SMX), ciprofloxacin (CIP), and 17 β -estradiol (E2) onto polyethylene terephthalate (PET) MPs in the Bloukrans River, South Africa, across four land use sites (municipal, wastewater, agriculture, and control) during summer and autumn. PET MPs were deployed *in situ*, retrieved, and analysed for adsorbed contaminants using LC-MS/MS. Sulfamethoxazole adsorption differed significantly by site ($F(3,16) = 4.161$, $p = 0.0234$) and season ($F(1,16) = 7.202$, $p = 0.016$), with adsorption highest at wastewater and agriculture impacted sites, and autumn concentrations exceeding summer by 176.5 ng L⁻¹. CIP adsorption varied significantly only by site ($p = 0.0231$) but not between seasons. E2 adsorption was non-significant ($p > 0.05$) for both sites and seasons. The hydrological analysis indicated that river width significantly influenced CIP, while SMX and E2 showed no hydrological dependence. By addressing the paucity of *in situ* evidence in small urban rivers of Africa, this study demonstrates that land use, seasonality, and hydrological conditions play an important role in influencing the adsorption of the selected compounds by PET MPs.

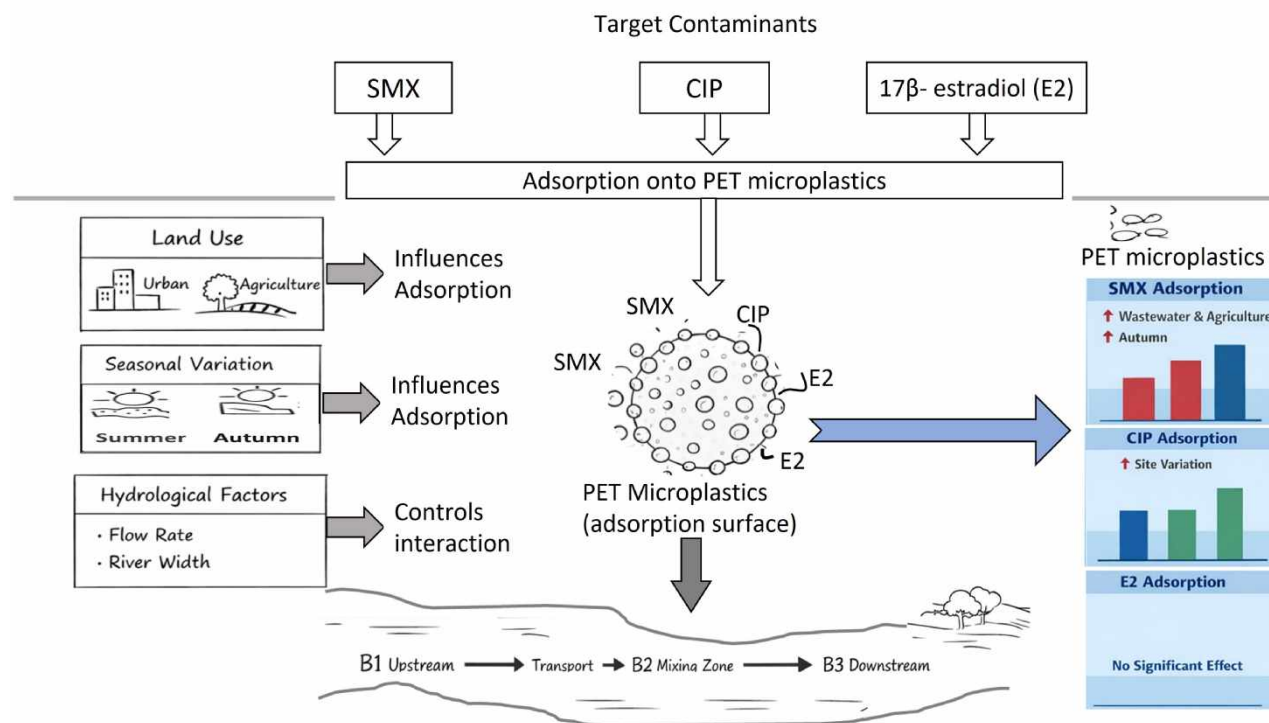
Key words: hydrological conditions, microplastics, sulfamethoxazole, urban river systems, land use

HIGHLIGHTS

- Land use significantly influenced SMX and CIP adsorption.
- Seasonality affected SMX but had little impact on CIP and E2.
- Interaction effects were relevant only for SMX, where autumn adsorption at the municipal discharge site was consistently higher.
- Model comparison supported mixed-effects and GLM frameworks for site heterogeneity and skewed residuals.

GRAPHICAL ABSTRACT

Drivers of adsorption of SMX, CIP, and E2 onto PET microplastics in an urban river systems



1. INTRODUCTION

Microplastics (MPs) are defined as plastic particles with diameters less than 5 mm (Wang *et al.* 2021). Scientists agree that they have emerged as ubiquitous environmental contaminants of global concern due to their mobility, persistence, and potential to bioaccumulate in aquatic ecosystems (Hale *et al.* 2020; Ziani *et al.* 2023). Among the various types of microplastics, polyethylene terephthalate (PET) is one of the most widely produced polymers worldwide (Parolini *et al.* 2020; Gola *et al.* 2021). They are light in weight and have very low production costs, hence they are one of the best candidates for single-use plastic (Piccardo *et al.* 2020). Microplastics not only pose direct physical risks to aquatic organisms in freshwater systems, but also act as vectors of various chemical contaminants, including pharmaceutical chemicals and endocrine-disrupting compounds (EDCs) (Atugoda *et al.* 2021; Puckowski *et al.* 2021; Santos *et al.* 2021). The adsorption potential of MPs is due to their diverse functional groups, which facilitate their interactions with different chemical pollutants (Lo *et al.* 2019).

Organic chemical contaminants such as sulfamethoxazole (SMX), ciprofloxacin (CIP), and 17β-estradiol (E2) have been detected globally in aquatic ecosystems and have been recognised for their potential adverse effects on aquatic organisms and human health (Guo *et al.* 2018; Munzhelele *et al.* 2024). SMX and CIP are widely used antibiotics, frequently detected in surface waters due to incomplete removal by wastewater treatment plants, and runoffs from agricultural lands (Munzhelele *et al.* 2024). E2, a natural estrogen hormone, is a key endocrine-disrupting chemical (EDC) which, if present in waters, can impair development, reproductive functions, and fertility in mammals, including humans and non-humans, even at trace concentrations (Gonsioroski *et al.* 2020). Various physicochemical processes influence the environmental fate, including adsorption onto particulate matter such as microplastics (Rochman *et al.* 2013; Turner & Holmes 2015).

Interactions between MPs and organic chemical compounds in freshwater systems are very complex, partly governed by factors, including but not limited to hydrophobicity, physicochemical properties of the pollutants, and the surface characteristics of the MPs (Guo *et al.* 2019; Wang *et al.* 2020). However, the role of spatial factors, particularly land use practices, seasonal variability, and hydrological conditions in influencing these interactions remains poorly studied and understood, particularly in the context of small urban rivers in developing regions like sub-Saharan Africa (Guo & Wang 2019; Fu *et al.* 2021). Urban rivers often receive a complex mixture of contaminants from domestic sewage, industrial

effluents, stormwater runoff, and agricultural drainage, which vary spatially and temporally, depending on land use and climatic conditions (Ashley *et al.* 2005).

Spatial factors such as land use influence the type and quantities of pollutants entering river systems. Urbanised regions contribute high loads of organic chemical residues into rivers due to dense human populations and extensive wastewater discharges (Wen *et al.* 2017; Brindha & Schneider 2019). Agricultural lands contribute pesticides, veterinary drugs, and nutrients whose combined effects may be synergistic or antagonistic (Boxall *et al.* 2012). Additionally, seasonality governs hydrological conditions such as water velocity, depth, width, temperature, and sediment load, affecting the fate of organic chemical contaminants (Van *et al.* 2012; Filella & Turner 2018). For instance, enhanced water runoffs can increase pollutant inputs but dilute contaminant concentrations, while dry seasons may concentrate pollutants (Amelia *et al.* 2021).

High flow rates due to increased rainfall can lead to the resuspension of sediments and MPs, enhancing their interactions with dissolved organic chemical contaminants (Owowenu *et al.* 2023). Similarly, low flow conditions may promote the settling and accumulation of MPs and contaminants in riverbed sediments, potentially creating hotspots for adsorption and ecological exposure. Hence, the combination of these factors in freshwater systems can affect the distribution, abundance, and interactions of microplastics with organic chemical pollutants, ultimately influencing the overall adsorption processes in the environment (Guo & Wang 2019; Fu *et al.* 2021).

The Eastern Cape province of South Africa provides an ideal case study for investigating these dynamics due to its diverse land use, seasonal rainfall patterns, and socio-economic challenges related to water quality management (Odume *et al.* 2022). Small urban rivers, especially the Bloukrans River systems, are frequently impacted by untreated or partially treated wastewater, informal settlements around Grahamstown, agricultural activities in the Belmont valley, and Grahamstown municipal operations, resulting in complex pollution dynamics (Gqomfa *et al.* 2023). Despite the increasing research studies on microplastic (MP) pollution in South African aquatic environments, there remains a significant knowledge gap regarding how local land use, seasonality, and hydrological conditions affect the interaction between microplastics, pharmaceuticals, and EDCs (Selwe *et al.* 2022; Li *et al.* 2025). Additionally, many of the studies on the vector effect of MPs have mainly been in laboratory settings, which do not represent environmental realism (Sun *et al.* 2020; Zhang *et al.* 2021). Addressing these knowledge gaps is critical for developing targeted management and mitigation strategies that account for pollution sources, spatial-temporal variability, and environmental conditions.

Therefore, this study hypothesises that the adsorption of SMX, CIP, and E2 onto PET microplastics in a small urban river system is significantly influenced by land use patterns, seasonal changes, and hydrological conditions. It further hypothesised that the interaction between land use characteristics and hydrological dynamics plays a key role in shaping the spatial and temporal adsorption patterns of these chemicals. To test these hypotheses, the specific objectives of the study were to: (1) investigate the spatial and temporal variations of the concentrations of SMX, CIP, and E2 adsorbed onto PET microplastics, and (2) examine the influence of physical river properties, including water flow rate, velocity, depth, and channel width, on the adsorption potential of PET microplastics for the targeted contaminants. By linking in-situ contaminant-microplastic interactions with urban land use and seasonal flow regimes, this work provides new insights into the ecological risks of pharmaceuticals and endocrine disruptors in microplastic-polluted freshwater systems.

2. MATERIALS AND METHODS

2.1. Study area and site selection

The study was conducted in the Bloukrans River, a tributary of the Kowie River in the Eastern Cape Province of South Africa. Data were collected between December 2021 and June 2022 (Figure 1). The catchment covers approximately 220 Km², with the river extending ~ 40 km (Dalu *et al.* 2019).

Four sampling sites were established to represent dominant land use types within the catchment (Table 1). Site selection was guided by the prevalence of municipal, WWTWs, and agricultural activities, given their hydrological influence and potential role as sources of contaminants. An additional site was selected in the adjacent Palmiet River, with minimal anthropogenic disturbances.

Site B1 is located on the upper reaches of the Bloukrans River on the outskirts of Grahamstown/Makhanda, near Fort England Psychiatric Hospital. The site is mainly polluted by stormwater from informal settlements on the city's outskirts. Visible at the site are solid waste, grey water, and urban debris coming directly from the city. Site B2 is immediately

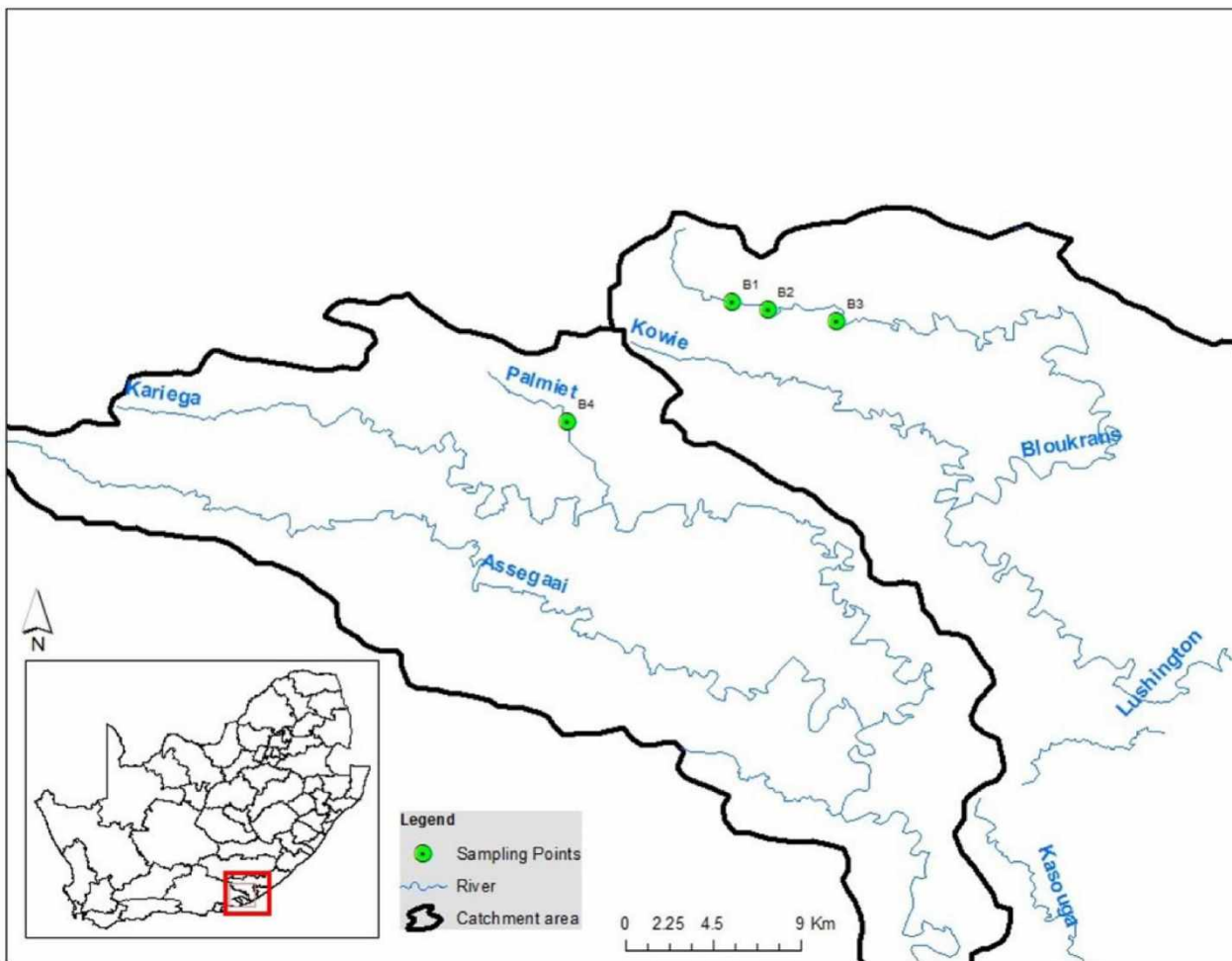


Figure 1 | Map of the Bloukrans River catchment showing the location of the experimental sampling sites along the Bloukrans and Palmiet Rivers. Site B1 (Bloukrans River upstream site: Municipal waste refuse impacted area), Site B2 (downstream of discharge point of the WWTW site), Site B3 (Bloukrans River agricultural impacted site), Site B4 (Palmiet River, control site).

Table 1 | Names and geo-coordinates of the experimental study sites in the Bloukrans and Palmiet River (control, least-impacted site)

Experimental Site No	Land use type	Site Name	Latitude	Longitude
B1	Municipal waste refuse impacted area	Upper stream Bloukrans River	–33.3144	26.5517
B2	Wastewater Treatment Works impacted area (WWTWs)	Middle stream Bloukrans River	–33.3697	26.5682
B3	Agriculture-impacted area	Lower stream Bloukrans River	–33.3237	26.5999
B4	Control site (least impacted area)	Palmiet River	–33.3697	26.4758

downstream of the discharge point of the Belmont Valley Wastewater Treatment Works (WWTW) and receives treated wastewater effluent. Site B3 is further downstream of Site B2 and is surrounded by irrigated commercial crop farms and livestock operations. The main pollution source at Site B3 is runoff from cultivation and grazing activities. The site was chosen as an example of a location impacted by agricultural activities. Although B4 is not part of the Bloukrans River continuum, it shares comparable catchment-scale hydrological and geomorphological characteristics. Site numbering, therefore, reflects the overall study design rather than a continuous downstream sequence (Table S1).

2.2. Microplastic sourcing

PET fragments were sourced from the Grahamstown Recycling Centre (GRC), crushed into small pieces of approximately ≤ 5 mm using a metallic blender, and subsequently sorted to yield particles of size range 2 mm ≤ 5 mm using stainless metallic sieves. The MPs were pre-washed with 75% ethanol and sterile ultrapure water to disinfect and remove residual contaminants on their surfaces.

2.3. Microplastic characterisation

The Fourier transform infrared spectrophotometer (A Perkin Elmer FT-IR two universal ATR) was used to confirm the basic structural units of the PET MPs polymer used in this study (Fig. S1). Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX) (Quanta 250, FEI, USA) was used to inspect the surface morphology of the MPs before and after retrieval to establish the potential adsorptive characteristics of the MPs. Secondary electron images (SE), Backscattered Electron images (BE), and energy-dispersive X-ray data (EDS) were collected in high vacuum on a Tescan Vega 2 Scanning Electron Microscope with a W-filament. Energy Dispersive X-ray data was collected on an Oxford INCA Penta-FET-X3 Si (Li) detector, at 20.00 kV. Samples were coated with sputtered gold.

2.4. Selection of targeted compounds, standards, and reagents used for this study

Target analytes were selected based on previous studies in the Bloukrans River (Farounbi & Ngqwala 2020; Vumazonke *et al.* 2020). The selection was further based on their detection frequency in freshwaters elsewhere in South Africa (Ngqwala & Muchesa 2020; Ncube *et al.* 2021). The selected target analytes and their respective internal standards are presented in Table S2. SMX, CIP, E2, and their isotopically labelled internal standards in their crystalline form were purchased from Toronto Research Chemicals Inc. (North York, Ontario, Canada). Acetonitrile (HPLC grade) and methanol (HPLC grade) were obtained from Sigma Aldrich, Gauteng, South Africa. Milli-Q water was used to prepare aqueous solutions for all chemicals. All standard stock solutions were prepared in methanol at a concentration of 1,000 mgL⁻¹.

2.5. Experimental design

2.5.1. Microplastic deployment

In-situ deployment of the MPs followed a method used by Magadini *et al.* (2020) with adjustments. PET MPs pellets of a size range 2 mm ≤ 5 mm were used. Before deployment, the PET MPs and all glassware were washed with ethanol (75%) and air dried. An artificially made stainless steel mesh bag with an approximate pore size of 100 μ m was used to house the MPs. One big mesh bag containing three infuser bags with the PET MPs pellets was deployed seasonally per site, starting with 20th January 2022 for the summer season and 7th April 2022 for the autumn season. In total, 12 infusers containing PET MPs were deployed per season. The mesh bags containing the MPs were tightly sealed and labelled according to the retrieval period. The bags were submerged approximately 60 cm below the water surface at each experimental site. The GPS coordinates, date, surface water temperature, time, river width, water depth, and water flow rate were recorded at the time of each deployment.

2.5.2. Microplastics retrieval

Four mesh bags containing PET MPs were retrieved per retrieval event on days 7, 14, and 35 during the dry and wet seasons. The retrieved mesh bags containing PET were placed into cooler boxes containing ice (previously maintained at 4 °C) and transported back to the water quality laboratory of the Institute for Water Research (IWR), Rhodes University. Before extraction, the samples were stored in a refrigerator maintained at 2 °C, and analysis was done within 24–48 hours after each retrieval.

2.6. Hydrological variables

Measurements for flow velocity, river width, and water depth were taken during each deployment and retrieval event. Water depth and river width were measured using a tape and a dip stick. Water velocity was measured *in situ* using a Marsh-McBirney Flo-Mate 2000 portable electromagnetic flow meter. The water flow rate was subsequently calculated using the measured water velocities and river cross-sectional area values.

2.7. Treatment of the PET microplastics after retrieval

At the laboratory, the MPs were removed from the stainless-steel mesh bags and washed with 100 mL of the filtered surface water from the respective study site to dislodge any environmental particles attached. Each sample was immersed in Milli-Q water for 30 minutes. The samples were then transferred into separate vials containing 5 mL of a 1:1 methanol: acetonitrile solution for 10 hours to extract the analytes of interest from PET particles. A 1 mL portion of each extract was centrifuged using the universal 320R at 12,500 revolutions per minute (RPM) for 30 minutes. The supernatant extract was filtered through a 0.2 µm syringe filter.

2.8. Liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis and data acquisition

The analysis of the extracts was carried out in multiple reaction monitoring mode with a Dionex Ultimate3000 UHPLC (Thermo Fisher Scientific, Sunnyvale, CA, USA) on a Speed core-HPLC SP18-030526 polar C18 column (100 × 3.0 mm, 2.6 µm) (Fortis Technologies, Neston, CH64-3UG, United Kingdom). The binary mobile phase comprised acetonitrile and water, each adjusted with 0.1% formic acid (V/V). A method used by [Nantaba *et al.* \(2020\)](#) was adopted without modification. Each analysis started with a 5-minute equilibration of the column at 15% acetonitrile. The mobile phase gradient was ramped at a flow rate of 0.4 mL/min (held for 5 minutes) starting from 15% to 50% acetonitrile in 2 minutes (held for 2 min, then ramped to 80% acetonitrile in 3 minutes and finally to 15% in 3 minutes (held for 3 minutes). The injection volume for each sample was 5 µL, whereas the column and autosampler temperature was maintained at 40 °C and 4 °C, respectively.

Mass spectrometric analysis of the targeted adsorbed analytes was carried out using a triple quadrupole time of flight mass spectrometer (Bruker Compact QToF, Bremen, Germany) equipped with an electron spray ionisation (ESI) source, the positive mode only (ESI⁺). The ESI-source parameters were set in a positive mode: the nebuliser pressure was set to 3.0 bar, and the capillary voltage was 2,000V. The temperature and flow rate of the drying gas were set at 220 °C and 9.0L/min, respectively. End of plate offset 300 V. An *m/z* scan range of 50 *m/z* to 1,000 *m/z* was analysed, and MS² spectra were recorded in data-acquisition mode, selecting the three most intense precursor ions for the acquisition of MS² spectra at a collision energy of 3.0 eV and transfer time of 80 µs.

2.9. Compound identification and data processing

The raw data were converted to mzXML format using the Bruker Compass software (Bruker, Bremen, Germany). The resulting mzXML files were processed in MZmine 2.53 using a modified method described by [Pluskal *et al.* \(2010\)](#). Mass lists were created using the mass detection module with a noise level of 1,000 counts for MS¹ and 100 counts for MS²/*m/z* tolerance with mass tolerances of 10 ppm. The chromatogram builder module creates peak lists with a minimum retention time (min), a minimum peak height of 3,000 counts, and an *m/z* tolerance of 20 ppm. The peak lists were deconvoluted using the local minimum search algorithm with the following parameters: chromatographic threshold of 0.01%, search minimum in the retention time range of 0.2 min, absolute minimum height of 3,000 counts, and peak duration range of 0.05–3 min. For MS² scan pairing, the *m/z* range was set to 0.01 and the retention time range to 0.2. Next, the deconvoluted peak lists were aligned using the Join aligner module with an *m/z* tolerance of 20 ppm, a retention time tolerance of 0.1 min, weighting by *m/z*, and retention time set to 75 and 25, respectively. The aligned peaks list was then subjected to gap-filling and filtered to exclude all features present without associated MS² spectra, and peak IDs were resent, followed by the export of a .csv table and mgf file.

2.10. Analytical quality control

Quality control procedures were applied throughout MP deployment, extraction, and LC-MS/MS analysis to ensure data reliability. Procedural blanks (pre-cleaned PET MPs) and field blanks deployed alongside samples were included in each analytical batch to assess contamination. Target analytes in blanks were consistently below the method detection limits. Method accuracy and extraction efficiency were evaluated using blank MP spike recoveries. Clean PET MPs were spiked with known concentrations of SXM, CIP, and E2 before extraction and analysed following the same procedure as the samples. Recoveries are expressed as mean recovery (%) ± relative standard deviation (RSD).

Matrix effects associated with river-exposed MPs were assessed using sample MP spike recoveries. Deployed PET MPs were spiked with known amounts of the target analytes, and native concentrations measured in unspiked samples were subtracted before recovery calculation. Sample spike recoveries as mean recovery (%) ± RSD. Isotopically labelled internal

standards were added to all samples, blanks, and calibration standards before extraction to correct for extraction losses and ionisation variability. Analytical precision was evaluated using replicate extraction and injections, with RSDs <10%. Calibration curves were linear over the investigated ranges ($R^2 \geq 0.9909$). Data were accepted only when spike recoveries were within 80–120% and all QC criteria were met. Additional quality-control information is provided in the supplementary information.

2.11. Statistical analysis

Statistical analysis was performed using the R programming environment (R Core Team 2025) to test the influence of land use patterns, seasonal changes, and hydrological drivers on the adsorption of SMX, CIP, and E2 onto PET MPs. Before analysis, the data were captured and prepared in Excel (Microsoft 2010 Office) and exported to the R software package, version 4.4.3 (2025-02-28 ucrt). The normality of the data was tested using the Shapiro-Wilk normality test (Table S7). Since most variables violated the assumption of normality ($p < 0.05$), non-parametric tests were applied. Specifically, the Kruskal-Wallis test was used for multi-group comparisons, followed by pairwise Wilcoxon rank-sum tests with p -value adjustment to identify significant differences between groups (Tables S8–S10). Box plots were used to visualise contaminant adsorption concentrations across land-use types and seasons. Two-way analysis of variance (ANOVA) was used to test for the overall effects of site, season, and their interaction on adsorption. Where statistically significant differences were detected, Tukey's Honestly Significant Differences (HSD) post hoc tests were conducted to identify the specific pairwise differences between sites and seasons.

Pearson correlation analysis was first conducted to examine bivariate relationships between hydrological variables and contaminant adsorption. Multivariate analysis of variance (MANOVA) was applied to test the overall effects of hydrological conditions on the combined adsorption responses, with significance evaluated using Pillai's trace and Wilks' lambda. When compounds were analysed individually, ANOVA was used to assess factor effects on each adsorption response. Subsequently, regression models were fitted to evaluate the effects of land use, seasonality, and hydrological conditions on the adsorption of SMX, CIP, and E2 onto PET MPs. A linear model (LM) was used to explore the relationship between variables, and a generalised linear model (GLM) was used to extend the non-linear response distribution. When both LM and GLM failed to adequately capture the relationship due to violations of parametric assumptions such as linearity, normality of residues, and homogeneity of variance, a generalised additive model (GAM), and a generalised additive mixed model (GAMM) were fitted to accommodate potential effects of land use, seasonality, and hydrological conditions on the adsorption of SMX, CIP, and E2, while GAMM additionally accounted for random effects. Model comparison was tested using Akaike information criterion (AIC), Bayesian information criterion (BIC), and likelihood ratio tests, with selection based on the lowest AIC/BIC and explanatory power. Statistical significance was set at $\alpha = 0.05$.

3. RESULTS

3.1. Microplastics characterisation

SEM-EDX images of PET MPs after retrieval indicated several micropores with cracked surfaces, indicating some change in the surface morphology (Figure 2). The EDX micrographs of the retrieved PET MPs indicated several associated elements, including Fe, K, Al, Mg, P, S, and Si, an indicator of reactive sites on PET suitable for interaction with aqueous contaminants.

3.2. Spatial-temporal variability of the concentrations of sulfamethoxazole, ciprofloxacin, and 17 β -estradiol adsorbed to PET microplastics

The adsorption of SMX, CIP, and E2 onto retrieved PET microplastics varied significantly among sites, reflecting differences in land use (Figure 3). SMX concentrations were statistically significant between sites ($p = 0.0234$), with the highest concentration at B3, of nearly 900 ng L⁻¹, with a p -value of 0.018, compared to B4 (Table 2). Similarly, the comparison between B3 and B2 was significant ($p = 0.0040$).

Adsorbed concentrations of CIP revealed a significant effect of site ($p = 0.0231$), Table 2. A pairwise comparison showed that adsorbed concentrations at B4 were significantly lower than at B3 ($p = 0.0282$) (Table S13). No significant difference was observed between Sites B4 and B1 ($p = 0.0813$) and B4 and B2 ($p = 0.0556$). Adsorbed concentrations of E2 indicated no statistically significant differences between the sites ($p = 0.398$) (Table 2 and Table S13).

Seasonality influenced SMX adsorption but had limited effects on CIP and E2 (Table S10). For instance, the adsorbed concentrations of sulfamethoxazole were lower during the summer season relative to the autumn ($p = 0.0163$), indicating

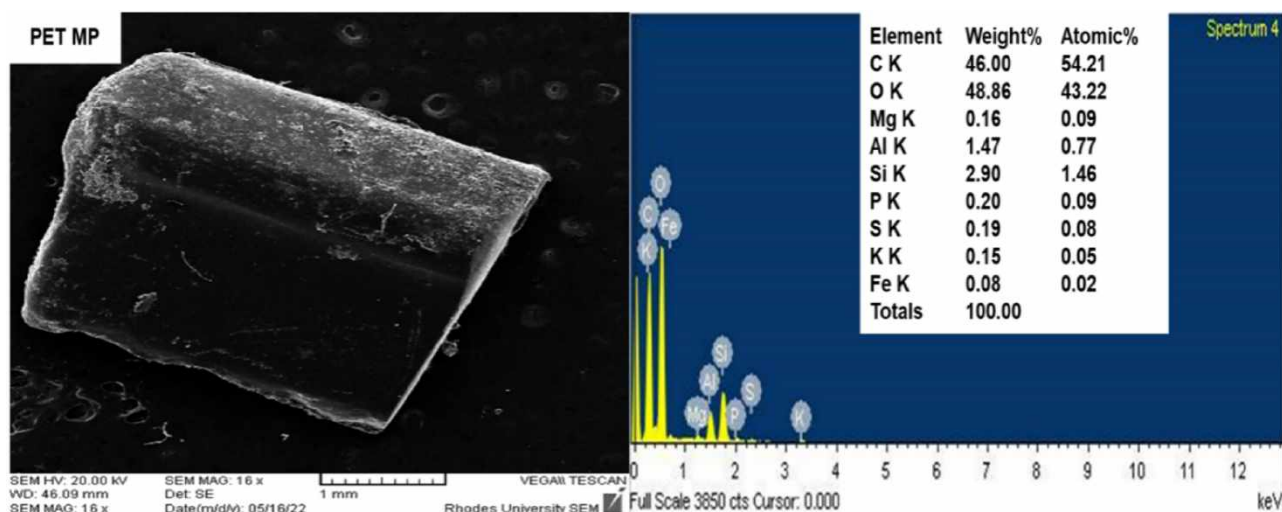


Figure 2 | SEM-EDX micrographs of a single retrieved PET microplastic showing the surface morphology and elemental composition.

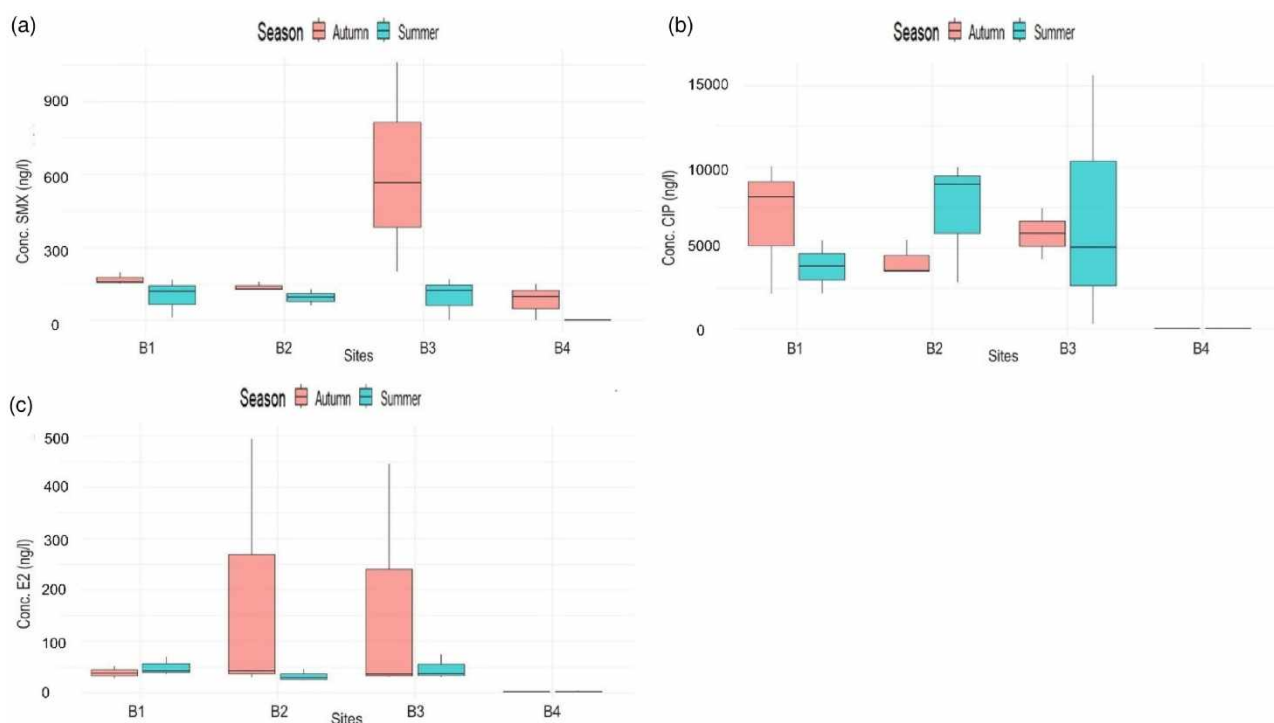


Figure 3 | Adsorbed concentrations of SMX (a), CIP (b), and E2 (c) on polyethylene terephthalate (PET) microplastics across sites (B1–B4) during autumn and summer seasons in the Bloukrans River. B1: municipal waste refuse impacted area, B2: downstream of the wastewater discharge point, B3: agriculture impacted site, and B4: Palmiet River (control site).

temporal variation (Table S12). A contrasting pattern was displayed for adsorbed concentrations of ciprofloxacin, with B2 and B3 showing higher summer adsorption (up to $\sim 10,000$ ng L⁻¹ at B3). Absorption during the autumn season was relatively low, indicating potential temperature or flow-mediated effects on adsorption. However, overall, no significant seasonal differences were observed for ciprofloxacin ($p = 0.8354$) (Table S13). For E2, no significant seasonal differences were observed ($p = 0.211$).

Table 2 | Summary of ANOVA for effects of site, season, and their interaction on adsorbed concentrations (ng L^{-1}) of SMX, CIP, and E2 onto PET MPs

	Sulfamethoxazole		Ciprofloxacin		17 β -estradiol	
	ANOVA F(df)	p - value	ANOVA F(df)	p - value	ANOVA F(df)	p - value
Site	F(3,16) = 4.16	0.0234*	F(3,16) = 4.18	0.0231*	F(3,16) = 1.05	0.398
Season	F(1,16) = 7.20	0.0163*	F(1,16) = 0.05	0.8354	F(1,16) = 1.70	0.211
Site $\times$ Season	F(3,16) = 2.91	0.0668	F(3,16) = 0.76	0.5356 ns	F(3,16) = 0.68	0.577

Sig. Code: $p < 0.05$ (*), and p is the probability value.

For interaction between site and season (Table 2), none of the analytes (SMX, CIP, and E2) showed a statistically significant effect. Although SMX had a lower p -value ($p = 0.0668$) compared to CIP and E2. Pairwise comparison showed autumn adsorption at B3 was significantly higher than at B4 ($p = 0.018$) and higher than all summer values ($p < 0.05$) (Table S13). CIP and E2 displayed no significant site-season interactions (Table 2).

3.3. Relationship between hydrological variables and adsorption of sulfamethoxazole, ciprofloxacin, and 17 β -estradiol adsorbed onto PET microplastics

Box plots of the measured water velocity (m/s) across the four sites (B1 – B4) and two seasons (autumn, summer) and the calculated water flow rates (m^3/s) indicated spatial-temporal variability (Figure 4). Measured water velocities were generally higher at B1 and B4, with autumn exhibiting peak values ($>1.5 \text{ m}^3/\text{s}$), while lower velocities ($<0.5 \text{ m}^3/\text{s}$) recorded at B2 across both seasons. B1 and B2 had elevated summer velocities, indicating that land use type interacts with seasonal hydrology in influencing flow dynamics. Water flow rate followed a similar spatial trend, with median flows generally higher in summer than in autumn. Median flows at B1 and B2 were higher during summer ($0.5\text{--}0.75 \text{ m}^3/\text{s}$), while reduced flows

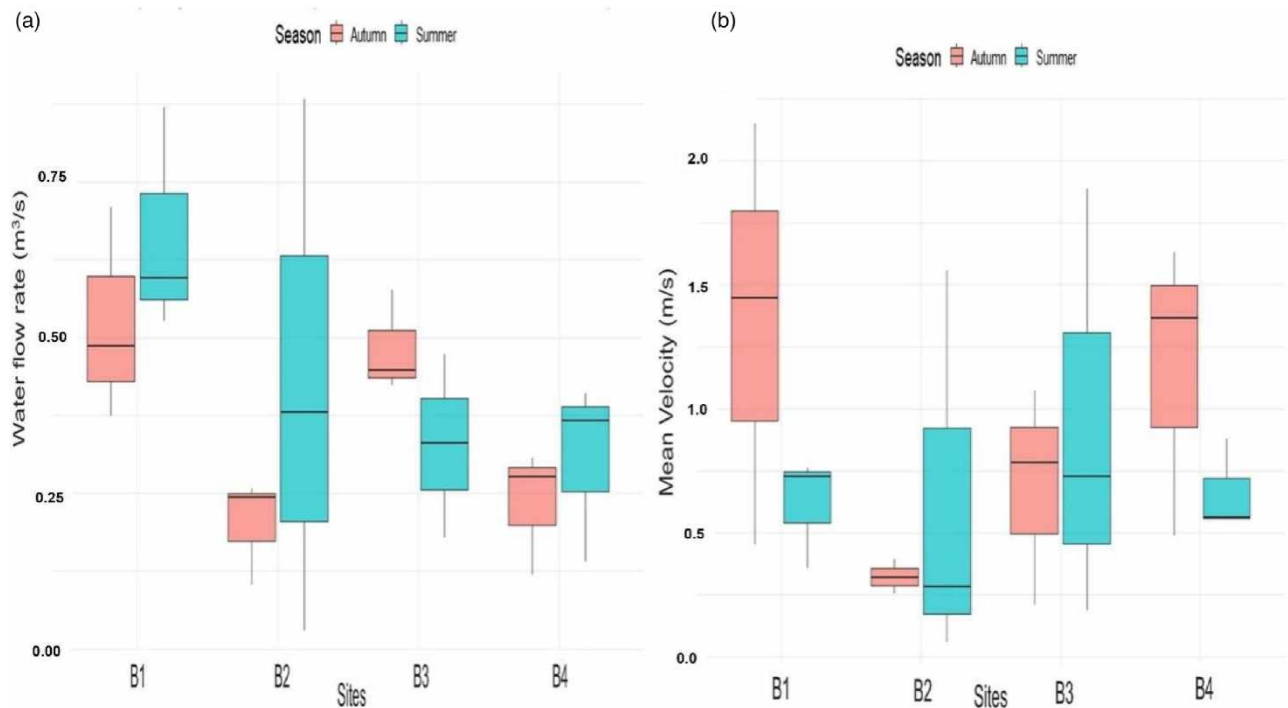


Figure 4 | Spatial-temporal variations in water flow rate (m^3/s) (A) and water velocity (m/s) (B) across land use sites (B1–B4) during autumn and summer seasons in the Bloukrans River system. Boxplots represent median values, interquartile ranges, and variability, showing the influence of land use type and seasonal hydrological changes on river dynamics.

characterised B3 and B4 in autumn ($<0.4 \text{ m}^3/\text{s}$). Site B2 showed the seasonal variation in flow, indicating a potential influence of seasonal rainfall patterns.

3.4. Pearson correlations and multivariate analysis

The Pearson correlation matrix (Figure 5) indicated varying degrees of association between the measured hydrological variables and the concentrations of SMX, CIP, and E2 adsorbed onto PET MPs in the Bloukrans River systems. The water flow rate showed a weak positive correlation with river width ($r = 0.35$) and mean velocity ($r = 0.330$) and a negligible correlation with water depth ($r = 0.03$). Among the measured hydrological variables, mean velocity exhibited a moderate negative correlation with water depth ($r = 0.46$), while width was negatively correlated with water depth ($r = -0.29$).

Regarding contaminant adsorption, river width demonstrated a moderate positive correlation with SMX concentration ($r = 0.51$), suggesting a potential influence of channel morphology on contaminant–microplastic interaction. SMX concentrations were also positively correlated with CIP ($r = 0.320$) and weakly with E2 ($r = 0.08$). However, ciprofloxacin and 17β -estradiol exhibited no meaningful association ($r = -0.02$). The measured hydrological drivers were generally weakly correlated with contaminant concentrations, with water depth showing a weak negative correlation with sulfamethoxazole ($r = 0.25$).

Results from Pillai trace and Wilk's lambda test from a multivariate analysis of variance (MANOVA) indicated that none of the selected hydrological variables had a statistically significant effect on the contaminant concentrations (Table S14). ANOVA was used to explore the impact of the measured hydrological drivers on each contaminant separately (Table S14), with SMX adsorption significantly differing by river width ($p = 0.017$).

3.5. Regression analysis and model comparison

Diagnostic plots (Fig. S2–S4) for both LM and GLM for SMX, CIP, and E2 adsorption data revealed systematic departure from model assumptions. Hence, GAMs and GAMMs were evaluated that allow flexible non-linear effects. SMX adsorption ($P < 0.05$), Table 3, LM, and GLM indicated a significant effect of season. Hydrological conditions were not individually significant (all $p > 0.120$). Model comparison for SMX adsorption showed that GAMM provided the best fit (ΔAIC and $\Delta\text{BIC} = 0$),

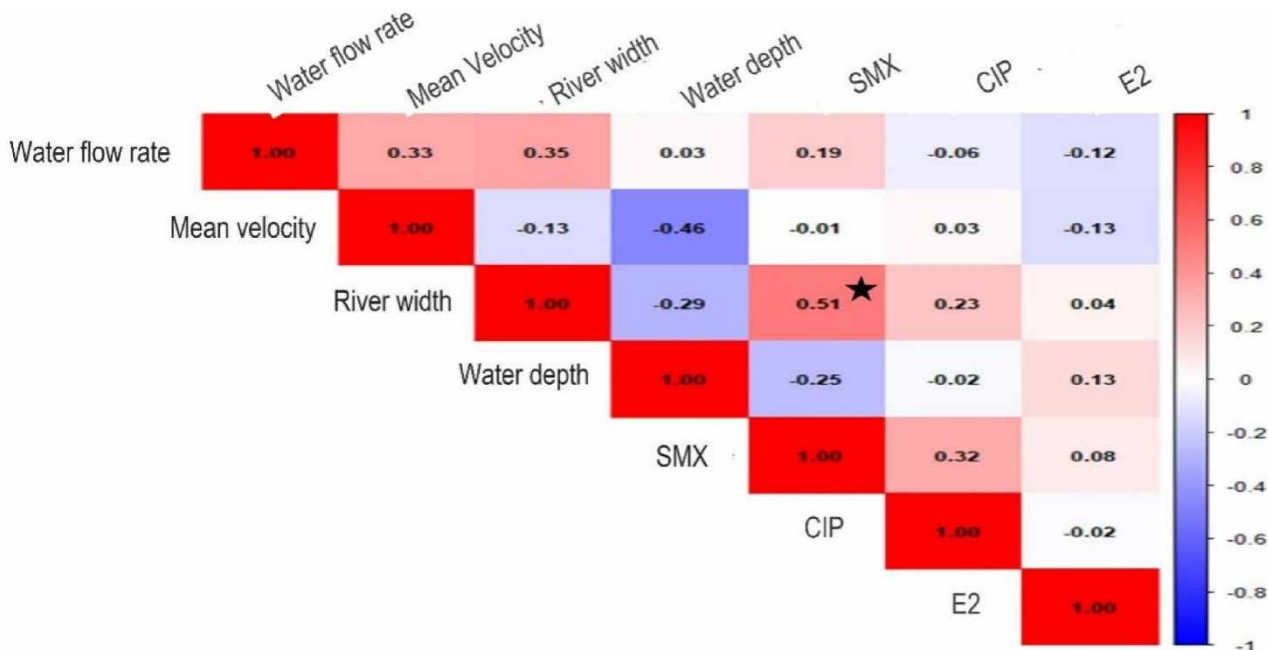


Figure 5 | Pearson correlation matrix showing relationships between hydrological drivers (water flow rate, mean velocity, river width, and water depth) and concentrations of SMX, CIP, and E2 adsorbed on PET microplastics in the Bloukrans River system. Positive correlations are shown in red and negative correlations in blue, with intensity proportional to correlation strength. The statistically significant correlation between SMX and river width (0.51) is marked with an asterisk.

Table 3 | Comparison of regression model performance (LM, GLM, GAM, GAMM) for predicting adsorption of SMX, CIP, and E2 onto PET microplastics, showing AIC, BIC, Δ AIC, and Δ BIC, with GAMM identified as the most robust approach accounting for site-level random effects

Compound	Model	AIC	BIC	Δ AIC	Δ BIC	Adj. R^2	p-values summary
SMX	LM	326.95	339.91	88.51	90.60	0.34	0.00095
	GLM	326.95	339.91	88.51	90.60	0.34	
	GAM	326.96	339.92	88.51	90.61	0.598	
	GAMM	238.44	249.31	0.00	0.00	0.598	
CIP	LM	462.4	475.4	145.0	147.1	0.432	0.427/0.584
	GLM	462.4	475.4	145.0	147.1	0.486	
	GAM	462.4	475.4	145.0	147.1	0.427/0.584	
	GAMM	317.5	328.3	0.0	0.0	0.327	
E2	LM	411.1	424.0	123.6	125.7	-0.325	all >0.36
	GLM	411.1	424.0	123.6	125.7	-0.325	all >0.35
	GAM	411.1	424.0	123.6	125.7	0.193	all >0.69
	GAMM	287.5	298.4	0	0	19.3%	all >0.42

explaining 59.8% of the variance (adjusted $R^2 = 0.34$). For CIP, LM, site ($p = 0.001$), and river width ($p = 0.0075$) were significant, while season and other hydrological factors were not. GLM and GAM models corroborated these findings, showing no evidence of non-linear effects from smooth terms. The GAMM substantially improved model fit (Δ AIC > 140) relative to LM/GLM/GAM. All models failed to detect significant effects of season, site, or hydrological conditions on E2 adsorption (all $p > 0.35$). However, the GAMM improved model fit substantially (Δ AIC = 123.6), suggesting that unmeasured site-specific factors rather than measured hydrological variables likely influenced adsorption dynamics.

4. DISCUSSION

SEM-EDX characterisation of the retrieved PET MPs revealed surface cracks, micropores, and mineral-associated elements such as Iron (Fe), aluminium (Al), magnesium (Mg), silicon (Si), phosphorus (P), and sulphur (S). These features are consistent with environmental weathering processes, including UV radiation, abrasion, and biofouling, that enhance surface roughness and functional group availability (Furfaro *et al.* 2022; Rostampour *et al.* 2025). The presence of mineral elements suggests interactions with suspended sediments and biofilms, which can increase the density of sorption sites for organic contaminants (Tourinho *et al.* 2019). Such surface alterations are well documented to increase contaminant affinity for deployed microplastics and likely played a central role in facilitating the adsorption of SMX, CIP, and E2 in the system (Li *et al.* 2018).

Seasonally, adsorbed concentrations of SMX were consistently higher in autumn, particularly at B3 (~ 900 ng L⁻¹), a site downstream of WWTWs and the municipal refuse-impacted site. This seasonal pattern may be explained by reduced dilution during lower-flow autumn conditions, which prolongs contaminant-MP interaction. Similar findings have been reported elsewhere, where cooler conditions and slower flows enhanced pharmaceutical adsorption onto MP by limiting photodegradation and increasing physicochemical interactions (Ji *et al.* 2024). In contrast, CIP adsorption peaked during summer (reaching $\sim 10,000$ ng L⁻¹), suggesting that higher temperatures and altered hydrological conditions may have enhanced its hydrophobic interactions with PET surfaces, aligning with some observations made by Karapanagioti & Werner (2019). By comparison, E2 showed no substantial seasonal variation, possibly reflecting its lower concentrations in the river system and weaker affinity for synthetic polymers relative to organic matter. These results indicate that seasonal effects are compound-specific: SMX adsorption appears controlled by flow-related dilution, ciprofloxacin by temperature-driven interactions, and E2 more by its inherent chemical properties than seasonality. Therefore, the null (H_0) was rejected for the seasonal hypothesis, and the alternative (H_1) was accepted for SMX, where autumn adsorption was significantly higher than summer.

Land use further influenced adsorption dynamics. Sites downstream of the wastewater effluent inputs (B2 and B3) consistently exhibited higher concentrations of adsorbed contaminants than the less impacted control site (B4). This emphasises the role of local contaminant inputs in creating hotspots of contaminant-microplastic interactions. Enhanced adsorption in the urban-impacted reaches is consistent with previous studies showing that intensification of anthropogenic

activity increases both contaminant loading and microplastic abundance, thereby magnifying sorption of contaminants onto microplastics (Stovall & Bratton 2022; Zhang *et al.* 2024). The markedly lower adsorption at B4 indicated that land use is a fundamental determinant of contaminant-plastic dynamics, reinforcing that point-source discharges such as WWTWs are pivotal in driving pharmaceutical-plastic interactions. This provides evidence that rejects the null hypothesis (H_0) for SMX and CIP, as adsorption differed significantly by site, particularly in impacted sites (B1, B2, and B3), but accepts the alternative hypothesis (H_1) for 17 β -estradiol, where no significant site variation was observed.

Hydrological conditions, including reduced flows and narrower cross sections in autumn, coincided with higher SMX adsorption, significantly influencing contaminant adsorption, indicating that hydrodynamic variability likely influenced the physical retention, and longer residence time enhanced contaminants' adsorption. Statistical analyses confirmed a moderately significant relationship between river width and sulfamethoxazole adsorption, suggesting that depositional environments created by broader channels may favour contaminant retention. This aligns with previous research studies that showed wider sections of rivers often accumulate more suspended matter (Cao *et al.* 2023). CIP and E2, however, showed no significant hydrological correlations, indicating that their adsorption may be governed more by intrinsic chemical characteristics such as hydrophobicity, polarity, and molecular structure, rather than flow-related hydraulics. Thus, the hydrological variables hypothesis (H_0) was rejected for river width, which significantly influenced ciprofloxacin adsorption, but accepted for most other hydrological variables, as they did not significantly affect the adsorption of ciprofloxacin and 17 β -estradiol.

SMX and CIP adsorption were moderately correlated, suggesting possible co-occurrence and co-adsorption mechanisms, possibly due to structural similarities as polar pharmaceuticals with partial hydrophobicity. This could reflect similar input pathways from wastewater discharges or overlapping adsorption domains on PET surfaces. Nonetheless, the negligible correlation between E2 and the two pharmaceuticals could suggest that endocrine disruptors may partition differently, often preferentially binding to natural organic matter rather than synthetic polymers (Vethaak & Leslie 2016). This reinforces the view that MPs act as selective, rather than universal, vectors for contaminants (Zhang *et al.* 2018).

These findings suggest that adsorption dynamics in this river system are shaped by a complex interplay of environmental conditions and compound-specific properties, with seasonality exerting its influence primarily through hydrological modulation of residence time and temperature effects. At the same time, land use determines contaminant supply and exposure hotspots, with hydrological conditions amplifying or suppressing the interactions, particularly for SMX. Notably, the distinct behaviours of CIP and E2 illustrated that the chemical properties of individual compounds can sometimes outweigh external environmental controls. Thus, the overarching null hypothesis is partially rejected, and the alternative (H_1) is accepted, with contaminant-specific differences highlighting the complexity of MPs-contaminant interactions.

While these results provide novel insights into pharmaceutical and endocrine disruptor adsorption onto PET MPs in a South African urban river, some limitations remain. High within-group variability suggests that longer-term sampling, spanning multiple years and additional seasons, would be necessary to fully capture temporal trends (winter, spring, and, if possible, multiple years). Moreover, extending the analysis to multiple plastic polymers and linking contaminants to ecological endpoints such as microbial resistance or endocrine disruption would provide a more holistic risk assessment. Nevertheless, this study demonstrates that a single driver cannot explain the adsorption of pharmaceuticals and endocrine disruptors onto PET MPs in urban rivers; instead, it emerges from the intersection of seasonality, land use, hydrology, and the intrinsic properties of each compound.

5. CONCLUSION

The study demonstrates that the adsorption of pharmaceuticals and hormones onto PET MPs is shaped by the combined influence of land use, seasonality, and hydrological conditions, but with contaminant-specific patterns. For SMX, both season and site effects were significant. At the same time, CIP adsorption was influenced by spatial variations across sites. Hydraulic variables, especially river width, played a significant role in shaping adsorption dynamics for SMX.

These findings, therefore, have important implications for water quality and public health in small-urban rivers. MPs act as transient reservoirs of antibiotics, particularly under autumnal low-flow conditions, potentially prolonging their environmental persistence and facilitating microbial resistance development. The negligible adsorption of E2 could indicate a lower risk of MP-mediated transport for endocrine-disrupting compounds in these systems, although sporadic adsorption events cannot be ruled out. Additionally, the relatively weak role of seasonal variability suggests that management

interventions targeting site-specific drivers (e.g., wastewater treatment upgrades, stormwater management) may yield more consistent reductions in pharmaceutical–MP interactions. Finally, the observed polymer-specific adsorption of CIP onto PET underscores the need to integrate MPs into contaminant fate models, particularly in urban river systems where both pollutants co-occur.

ACKNOWLEDGEMENTS

This research manuscript has been supported by the African Water Resources Mobility Network (AWaRMN), which received funding from the Intra-African Academic Mobility Scheme of the European Union, Grant No. 2019-1973/004-001. We credit Rhodes University for granting access to the Electron Microscope facilities. We also thank Dr D. van Niekerk and Mr M. Randall for technical support.

AUTHOR CREDIT

ONO and ET – conceptualisation; ET, ONO, CFN, XSN, FCA, GWN writing – draft, review and synthesis; ONO, CFN – funding acquisition; ONO, CFN, XSN, GWN – supervision.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Amelia, T. S. M., Khalik, W. M. A. W. M., Ong, M. C., Shao, Y. T., Pan, H. J. & Bhupalan, K. (2021) *Marine microplastics as vectors of major ocean pollutants and its hazards to the marine ecosystem and humans*, *Progress in Earth and Planetary Science*, **8** (1), 12. <https://doi.org/10.1186/s40645-020-00405-4>.
- Ashley, R. M., Balmfort, D. J., Saul, A. J. & Blanksby, J. D. (2005) *Flooding in the future -Predicting climate change, risks, and responses in urban areas*, *Water Science and Technology*, **52** (5), 265–273. <https://doi.org/10.2166/wst.2005.0142>.
- Atugoda, T., Vithanage, M., Wijesekara, H., Bolan, N., Sarmah, A. K., Bank, M. S., You, S. & Ok, Y. S. (2021) *Interactions between microplastics, pharmaceuticals, and personal care Products: implications for vector transport*, *Environment International*, **149**, 106367. <https://doi.org/10.1016/j.envint.2020.106367>.
- Boxall, A. B. A., Rudd, M. A., Brooks, B. W., Caldwell, D. J., Choi, K., Hickmann, S., Innes, E., Ostapyk, K., Staveley, J. P., Verslycke, T., Ankley, G. T., Beazley, K. F., Belanger, S. E., Berninger, J. P., Carriquiriborde, P., Coors, A., DeLeo, P. C., Dyer, S. D., Ericson, J. F. & Van Der Kraak, G. (2012) *Pharmaceuticals and personal care products in the environment: what are the big questions?*, *Environmental Health Perspectives*, **120** (9), 1221–1229. <https://doi.org/10.1289/ehp.1104477>.
- Brindha, K. & Schneider, M. (2019) *Impact of urbanization on groundwater quality*, *GIS and Geostatistical Techniques for Groundwater Science*, **2019**, 179–196. <https://doi.org/10.1016/B978-0-12-815413-7.00013-4>.
- Cao, S., Liang, S. & Li, Y. (2023) *Adsorption and environmental behavior of mercury on Suspended particulate matter from the Yellow River and Xiaoqing River estuaries*, *Science of the Total Environment*, **893** (June), 164860. <https://doi.org/10.1016/j.scitotenv.2023.164860>.
- Dalu, T., Wasserman, R. J., Magoro, M. L., Froneman, P. W. & Weyl, O. L. F. (2019) *River Nutrient water and sediment measurements provide information on nutrients. Retention, with implications for eutrophication*, *Science of the Total Environment*, **684**, 296–302. <https://doi.org/10.1016/j.scitotenv.2019.05.167>.
- Farounbi, A. I. & Ngqwala, N. P. (2020) *Occurrence of selected endocrine disrupting compounds in the Eastern Cape Province of South Africa*, *Environmental Science and Pollution Research*, **27** (14), 17268–17279. <https://doi.org/10.1007/s11356-020-08082-y>.
- Filella, M. & Turner, A. (2018) *Observational study unveils the extensive presence of Hazardous elements in beached plastics from Lake Geneva*, *Frontiers in Environmental Science*, **6**, 1–8. <https://doi.org/10.3389/fenvs.2018.00001>.
- Fu, L., Li, J., Wang, G., Luan, Y. & Dai, W. (2021) *Adsorption behavior of organic pollutants on microplastics*, *Ecotoxicology and Environmental Safety*, **217**, 112207. <https://doi.org/10.1016/j.ecoenv.2021.112207>.
- Furfaro, G., D'Elia, M., Mariano, S., Trainito, E., Solca, M., Piraino, S. & Belmonte, G. (2022) *SEM/EDX analysis of the stomach contents of a sea slug snacking on a polluted seafloor reveals microplastics as a component of its diet*, *Scientific Reports*, **12** (1), 1–14. <https://doi.org/10.1038/s41598-022-14299-3>.
- Gola, D., Kumar Tyagi, P., Arya, A., Chauhan, N., Agarwal, M., Singh, S. K. & Gola, S. (2021) *The impact of microplastics on the marine environment: a review*, *Environmental Nanotechnology, Monitoring and Management*, **16**, 100552. <https://doi.org/10.1016/j.enmm.2021.100552>.

- Gonsioroski, A., Mourikes, V. E. & Flaws, J. A. (2020) Disruptores endocrinos en el agua y sus Effects on the reproductive system/
Endocrine disruptors in water and their effects on the reproductive system, *International Journal of Molecular Sciences*, **21** (6), 1929.
- Gqomfa, B., Maphanga, T. & Madonsela, B. S. (2023) An analysis of the effects that South Africa's informal settlements have impacted the Country's
River Systems, *Natural Environment, and Pollution Technology*, **22** (4), 1833–1843. <https://doi.org/10.46488/NEPT.2023.v22i04.011>.
- Guo, X. & Wang, J. (2019) The chemical behaviors of microplastics in the marine environment: a review, *Marine Pollution Bulletin*, **142**, 1–14. <https://doi.org/10.1016/j.marpolbul.2019.03.019>.
- Guo, X., Yan, Z., Zhang, Y., Xu, W., Kong, D., Shan, Z. & Wang, N. (2018) Behavior of antibiotic resistance genes under extremely high-
level antibiotics Selection pressures in pharmaceutical wastewater treatment plants, *Science of the Total Environment*, **612**, 119–128.
<https://doi.org/10.1016/j.scitotenv.2017.08.229>.
- Guo, X., Chen, C. & Wang, J. (2019) Sorption of sulfamethoxazole onto six types of Microplastics, *Chemosphere*, **228**, 300–308. <https://doi.org/10.1016/j.chemosphere.2019.04.155>.
- Hale, R. C., Seeley, M. E., La Guardia, M. J., Mai, L. & Zeng, E. Y. (2020) A global perspective on microplastics, *Journal of Geophysical
Research: Oceans*, **125** (1), 1–40. <https://doi.org/10.1029/2018JC014719>.
- Ji, H., Wan, S., Liu, Z., Xie, X., Xiang, X., Liao, L., Zheng, W., Fu, Z., Liao, P. & Chen, R. (2024) Adsorption of antibiotics on microplastics
(MPs) in aqueous environments: the impacts of aging and biofilms, *Journal of Environmental Chemical Engineering*, **12** (2), 111992.
<https://doi.org/10.1016/j.jece.2024.111992>.
- Karapanagioti, H. K. & Werner, D. (2019) Sorption of Hydrophobic Organic Compounds to Plastics in the Marine Environment: Sorption
and Desorption Kinetics. In: Karapanagioti, H. K. & Werner, D. (eds.) *Handbook of Environmental Chemistry*, Vol. 78. Cham,
Switzerland: Springer, pp. 205–219. https://doi.org/10.1007/698_2018_256.
- Li, J., Liu, H. & Paul Chen, J. (2018) Microplastics in freshwater systems: a review on Occurrence, environmental effects, and methods for
microplastics detection, *Water Research*, **137**, 362–374. <https://doi.org/10.1016/j.watres.2017.12.056>.
- Li, Y., Li, Y., Zhang, S., Gao, T., Gao, Z., Lai, C. W. & Xiang, P. (2025) Global distribution, ecotoxicity, and treatment technologies of
emerging contaminants in aquatic environments: a recent five-year review, *Toxics*, **4**, 1–41.
- Lo, H. S., Wong, C. Y., Tam, N. F. Y. & Cheung, S. G. (2019) Spatial distribution and source identification of hydrophobic organic
compounds (HOCs) on sedimentary microplastic in Hong Kong, *Chemosphere*, **219**, 418–426. <https://doi.org/10.1016/j.chemosphere.2018.12.032>.
- Magadini, D. L., Goes, J. I., Ortiz, S., Lipscomb, J., Pitiranggon, M. & Yan, B. (2020) Assessing the sorption of pharmaceuticals to
microplastics through in-situ experiments in New York City waterways, *Science of the Total Environment*, **729**, 138766. <https://doi.org/10.1016/j.scitotenv.2020.138766>.
- Munzhelele, E. P., Mudzielwana, R., Ayinde, W. B. & Gitari, W. M. (2024) Pharmaceutical contaminants in wastewater and receiving water
bodies of South Africa: a review of sources, pathways, occurrence, effects, and geographical distribution, *Water (Switzerland)*, **16** (6),
796. <https://doi.org/10.3390/w16060796>.
- Nantaba, F., Wasswa, J., Kylin, H., Palm, W. U., Bouwman, H. & Kümmerer, K. (2020) Occurrence, distribution, and ecotoxicological risk
assessment of selected pharmaceutical compounds in water from Lake Victoria, Uganda, *Chemosphere*, **239**, 124642. <https://doi.org/10.1016/j.chemosphere.2019.124642>.
- Ncube, S., Nuapia, Y. B., Chimuka, L. & Madikizela, L. M. (2021) Trace detection and quantitation of antibiotics in a South African stream
receiving wastewater effluents and municipal dumpsite leachates, *Frontiers in Environmental Science*, **9**, 1–9. <https://doi.org/10.3389/fenvs.2021.733065>.
- Ngqwala, N. P. & Muchesa, P. (2020) Occurrence of pharmaceuticals in aquatic environments: a review and potential impacts in South
Africa, *South African Journal of Science*, **116** (7–8), 1–7. <https://doi.org/10.17159/sajs.2020/5730>.
- Odume, O. N., Onyima, B. N., Nnadozie, C. F., Omovoh, G. O., Mmachaka, T., Omovoh, B. O., Uku, J. E., Akamagwuna, F. C. & Arimoro,
F. O. (2022) Governance and institutional drivers of ecological degradation in urban river ecosystems: insights from Case Studies in
African Cities, *Sustainability (Switzerland)*, **14** (21), 14147. <https://doi.org/10.3390/su142114147>.
- Owowenu, E. K., Nnadozie, C. F., Akamagwuna, F., Noundou, X. S., Uku, J. E. & Odume, O. N. (2023) A critical review of environmental
factors influencing the transport dynamics of microplastics in riverine systems: implications for ecological studies, *Aquatic Ecology*,
57 (2), 557–570. <https://doi.org/10.1007/s10452-023-10029-7>.
- Parolini, M., Ferrario, C., De Felice, B., Gazzotti, S., Bonasoro, F., Candia Carnevali, M. D., Ortenzi, M. A. & Sugni, M. (2020) Interactive
effects between sinking polyethylene terephthalate (PET) microplastics deriving from water bottles and a benthic grazer, *Journal of
Hazardous Materials*, **398**, 122848. <https://doi.org/10.1016/j.jhazmat.2020.122848>.
- Piccardo, M., Provenza, F., Grazioli, E., Cavallo, A., Terlizzi, A. & Renzi, M. (2020) PET microplastics toxicity on marine key species is
influenced by pH, Particle size, and food variations, *Science of the Total Environment*, **715**, 136947. <https://doi.org/10.1016/j.scitotenv.2020.136947>.
- Pluskal, T., Castillo, S., Villar-Briones, A. & Orešič, M. (2010) MZmine 2: modular framework for processing, visualizing, and analyzing
mass spectrometry-based molecular profile data, *BMC Bioinformatics*, **11**, 395. <https://doi.org/10.1186/1471-2105-11-395>.
- Puckowski, A., Cwiąg, W., Mioduszevska, K., Stepnowski, P. & Białk-Bielińska, A. (2021) Sorption of pharmaceuticals on the surface of
microplastics, *Chemosphere*, **263**, 127976. <https://doi.org/10.1016/j.chemosphere.2020.127976>.
- R Core Team (2025) R: A language and environment for statistical computing (Version 4.4.3) [Computer software]. R Foundation for
Statistical Computing. <https://www.r-project.org/>.

- Rochman, C. M., Hoh, E., Hentschel, B. T. & Kaye, S. (2013) Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris, *Environmental Science and Technology*, **47** (3), 1646–1654. <https://doi.org/10.1021/es303700s>.
- Rostampour, S., Jhang, S. S., Hsu, J. K., Cook, R., Li, Y., Fan, C. & Sung, L. P. (2025) Evaluating the environmental factors on microplastic generation: an accelerated weathering study, *Microplastics*, **4** (1), 1–15. <https://doi.org/10.3390/microplastics4010013>.
- Santos, L. H. M. L. M., Rodríguez-Mozaz, S. & Barceló, D. (2021) Microplastics as vectors of Pharmaceuticals in aquatic organisms – An overview of their environmental implications, *Case Studies in Chemical and Environmental Engineering*, **3**, 100079. <https://doi.org/10.1016/j.cscee.2021.100079>.
- Selwe, K. P., Thorn, J. P. R., Desrousseaux, A. O. S., Dessent, C. E. H. & Sallach, J. B. (2022) Emerging contaminant exposure to aquatic systems in the Southern African Development Community, *Environmental Toxicology and Chemistry*, **41** (2), 382–395. <https://doi.org/10.1002/etc.5284>.
- Stovall, J. K. & Bratton, S. P. (2022) Microplastic pollution in surface waters of urban watersheds in Central Texas, United States: a comparison of sites with and without treated wastewater effluent, *Frontiers in Analytical Science*, **2**, 1–10. <https://doi.org/10.3389/frans.2022.857694>.
- Sun, Y., Yuan, J., Zhou, T., Zhao, Y., Yu, F. & Ma, J. (2020) Laboratory simulation of Microplastics weathering and their adsorption behaviors in an aqueous environment: a systematic review, *Environmental Pollution*, **265**, 114864. <https://doi.org/10.1016/j.envpol.2020.114864>.
- Tourinho, P. S., Kočí, V., Loureiro, S. & van Gestel, C. A. M. (2019) Partitioning of chemical contaminants to microplastics: sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation, *Environmental Pollution*, **252**, 1246–1256. <https://doi.org/10.1016/j.envpol.2019.06.030>.
- Turner, A. & Holmes, L. A. (2015) Adsorption of trace metals by microplastic pellets in fresh water, *Environmental Chemistry*, **12** (5), 600–610. <https://doi.org/10.1071/EN14143>.
- Van, A., Rochman, C. M., Flores, E. M., Hill, K. L., Vargas, E., Vargas, S. A. & Hoh, E. (2012) Persistent organic pollutants in plastic marine debris found on beaches in San Diego, California, *Chemosphere*, **86** (3), 258–263. <https://doi.org/10.1016/j.chemosphere.2011.09.039>.
- Vethaak, A. D. & Leslie, H. A. (2016) Plastic debris is a human health issue, *Environmental Science and Technology*, **50** (13), 6825–6826. <https://doi.org/10.1021/acs.est.6b02569>.
- Vumazonke, S., Khamanga, S. M. & Ngqwala, N. P. (2020) Detection of pharmaceutical residues in surface waters of the eastern cape province, *International Journal of Environmental Research and Public Health*, **17** (11), 4067. <https://doi.org/10.3390/ijerph17114067>.
- Wang, T., Wang, L., Chen, Q., Kalogerakis, N., Ji, R. & Ma, Y. (2020) Interactions between microplastics and organic pollutants: effects on Toxicity, bioaccumulation, degradation, and transport, *Science of the Total Environment*, **748**, 142427. <https://doi.org/10.1016/j.scitotenv.2020.142427>.
- Wang, X., Bolan, N., Tsang, D. C. W., Sarkar, B., Bradney, L. & Li, Y. (2021) A review of Microplastics aggregation in the aquatic environment: influence factors, analytical methods, and environmental implications, *Journal of Hazardous Materials*, **402**, 123496. <https://doi.org/10.1016/j.jhazmat.2020.123496>.
- Wen, Y., Schoups, G. & Van De Giesen, N. (2017) Organic pollution of rivers: combined Threats of urbanization, livestock farming, and global climate change, *Scientific Reports*, **7**, 1–9. <https://doi.org/10.1038/srep43289>.
- Zhang, H., Wang, J., Zhou, B., Zhou, Y., Dai, Z., Zhou, Q., Christie, P. & Luo, Y. (2018) Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: kinetics, isotherms and influencing factors, *Environmental Pollution*, **243**, 1550–1557. <https://doi.org/10.1016/j.envpol.2018.09.122>.
- Zhang, Y., Ni, F., He, J., Shen, F., Deng, S., Tian, D., Zhang, Y., Liu, Y., Chen, C. & Zou, J. (2021) Mechanistic insight into the different adsorption of norfloxacin on Microplastics in simulated natural and real surface water, *Environmental Pollution*, **284** (May), 117537. <https://doi.org/10.1016/j.envpol.2021.117537>.
- Zhang, L., Li, X., Li, Q., Xia, X. & Zhang, H. (2024) The effects of land use types on microplastics in river water: a case study on the mainstream of the Wei River, China, *Environmental Monitoring and Assessment*, **196** (4), 1–13. <https://doi.org/10.1007/s10661-024-12430-7>.
- Ziani, K., Ioniță-Mîndrican, C. B., Mititelu, M., Neacșu, S. M., Negrei, C., Moroșan, E., Drăgănescu, D. & Preda, O. T. (2023) Microplastics: a real global threat for the environment and food safety: a state of the art review, *Nutrients*, **15** (3), 617. <https://doi.org/10.3390/nu15030617>.

First received 6 October 2025; accepted in revised form 17 April 2026. Available online 26 May 2026