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Microplastics in surficial sediments from some UK rivers and canals: seasonal and spatial variation and relationship with concentrations of organophosphate esters†

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The relationship between microplastics (MPs) and organic pollutants such as organophosphate esters (OPEs), which are widely used as plastic additives is poorly understood. Given the potential toxic implications for such chemical additives, this is a substantial research gap. To address this, we collected 12 sets of freshwater sediment samples from 3 rivers and an urban canal in the West Midlands of the UK between November 2019 and April 2021. Riverine sediment samples were collected both upstream and downstream of waste water treatment plants (WWTPs) discharge points. The mean number of MPs per kg (dw) for all four UK study locations ranged from 67–267 (Birmingham and Worcester Canal), 133–283 (River Tame), 66.67–317 (River Severn), and 67–233 (River Sowe) per month. The highest mean number of MPs per kg was recorded in the River Tame. Overall, 57% of the mean number of MPs identified across all three locations over the 12 months period were detected downstream of the WWTPs while 43% were upstream; however this difference was not significant. Using previously reported concentrations of OPEs in the same samples by our research group, we observed a significant negative correlation ($p < 0.05$) between mean MPs number and OPE concentrations in sediment at the River Tame over a 12 months sampling period. Additionally, a significant negative correlation was observed between concentrations of Tris(2-butoxyethyl) phosphate (TBOEP)-the most abundant OPE and mean particle number ($r = -0.309$, $p = 0.004$). A similar negative correlation was observed between Tri-*n*-butyl phosphate (TnBP) concentrations and mean MPs per kg at the River Severn. These results suggest that the sources of MPs and OPEs in these waterways may differ and imply that MPs could potentially adsorb OPEs from the sediment in the samples studied.

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Environmental significance

To enhance their properties, chemical additives like plasticisers, pigments, and flame retardants are commonly incorporated into plastic polymers. This study explores the relationships between microplastic (MP) concentrations and organophosphate esters (OPEs) in freshwater sediments from the West Midlands, England. A significant negative correlation ($p < 0.05$) was observed between MP counts and OPE concentrations at some locations. These findings suggest sources of MPs and OPEs in waterways are different and indicate the possibility that MPs may adsorb OPEs from sediment, with resultant impacts on OPE transport and bioavailability in waterbodies.

Introduction

Microplastic pollution has become a global environmental problem[1,2] and waste water treatment plants (WWTPs) have been suggested as potential sources of microplastics (MPs) to water bodies.[3] Twenty five percent of the MPs entering the marine environment are estimated to be from WWTP effluents,[4] most of which enter the marine environment through freshwater systems such as rivers.[5,6] It has been shown that a single use of everyday products such as exfoliants and toothpastes can release between 4000 to 95 500 microbeads into the wastewater system, while a washing machine with 5 to 6 kg load of synthetic fabrics can release up to 6 million fibres during a single wash cycle.[4,7,8] This is particularly disturbing because some of these MPs end up in the environment through the final effluent and sludge products of WWTPs.[9–11] To illustrate, it was reported that a WWTP in the UK discharges approximately 65 million MPs into the aquatic environment daily.[12] Another study in Italy

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† Electronic supplementary information (ESI) available: Details including laboratory procedure for analysis of sediment samples for OPEs, Quality assurance and Quality control (QA/QC) for analysis of microplastics, and MP abundance in all sampled rivers *etc.* are provided. See DOI: https://doi.org/10.1039/d5em00139k

reveals a daily discharge of approximately 160 million MPs from a WWTP that serves ~1 200 000 inhabitants.[13]

The risks associated with MPs in the aquatic environment include: disruption of the food chain due to the effect of MPs on algae photosynthesis and growth reduction in some aquatic organisms;[14–16] as well as toxicological impacts such as: intestinal damage and potential harm from weathered plastics,[17,18] accumulation in vital organs and tissues,[19] disruption of metabolism[16,20] and the capacity to serve as vectors for harmful pathogens.[21] However, accurate quantitative assessment of these risks is complex given the risks may be attributed not only to MPs themselves, but also to associated chemical additives. Therefore, differentiating the impacts of MPs themselves from those of associated additive chemicals; as well as those of additives leached from MPs and larger plastic waste into the environment, is an important research goal.[22]

Organophosphate esters (OPEs) are important chemical additives used in synthetic polymers as they are used as both flame retardants and plasticisers.[23,24] Unlike "reactive" flame retardants which are bound chemically to the polymer matrix, OPEs are incorporated physically by mixing with the polymer during manufacture, and are therefore more easily released into the environment.[25–29] This likely explains their ubiquity and reported abundance in various environmental matrices, including sediments.[30–34] Although there is very little known about this interaction between chemical additives and the polymers,[5,22] some studies have identified leaching from plastics as one major way these OPEs find their way into the environment.[35] In fact, Cho *et al.* traced the increase in OPE concentrations in a rural river (Kurose River, Higashi-Hiroshima) to the leaching of TCP from agricultural plastic films used for a greenhouse.[36]

Along with their reported abundance in a wide range of environmental matrices,[27,37–42] OPEs have been associated with adverse health effects, including infertility,[43,44] neurotoxicity[45,46] and cancer, among several other health concerns.[47,48] Indications of a potential connection between OPEs concentrations and microplastic loads have been previously reported in seabirds.[49]

Against this background, this study seeks to further understand potential association in sediment between MPs and OPEs as exemplar chemical plastics additives. To further understand the partitioning of chemical plastics additives in sediments between sediment particles and the microplastics themselves, the possibility of correlation between microplastic concentrations and the concentration of OPEs in the same sediment samples was investigated. Sediment samples were collected upstream and downstream of WWTPs effluent discharge points along four UK rivers. This further provided an opportunity to account for the possible impact of WWTPs on the concentration of MPs/OPEs in sediment.[9–11] The present study reports concentrations, polymer type, and morphology of MPs in these samples and examines relationships between MP concentration with previously reported concentrations of OPEs in the same samples.[50] Sediment samples were collected over 12 months; thereby allowing investigation of seasonal and spatial trends of MPs in UK freshwater sediments, as well as other potentially influential factors.

Materials and methods

Study areas

All sampling points in this study are located within the West Midlands region of the UK (Fig. 1) and were chosen because of their accessibility to researchers and because they provided a range in values of parameters of interest (Proximity to WWTPs, urban and rural mix, *etc.*). Despite challenges like fluctuating water levels and accessibility, we aimed to maintain

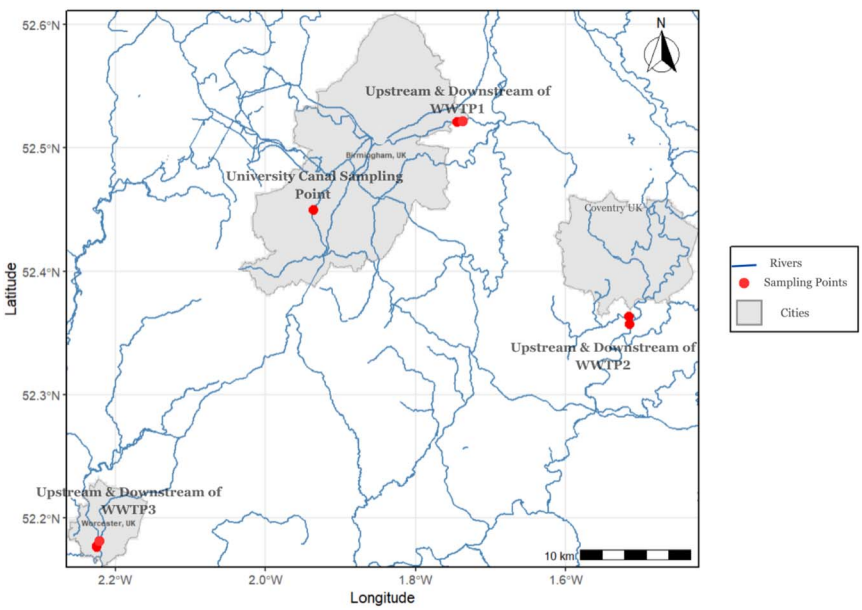

Fig. 1 Map of west midlands showing sampling locations.

a consistent sampling distance of approximately 50 m from the WWTP outfall at all locations. The sampling points along River Tame were located upstream and downstream of the effluent discharge point of a wastewater treatment plant that services ~2.5 million people.[50] This WWTP is located in an urban area and its operational processes include both primary and secondary treatments.

The sampling points along the River Sowe differed from those on the tame as the operational processes at the WWTP targeted on the Sowe are primary, secondary, P-removal and sand filtration. Also, the population serviced by the WWTP is approximately 430 000 people.[50] Samples were collected upstream and downstream of the effluent discharge point all of which were between 0.5 to 1 km away from residential areas.

For River Severn, the sampling points were in an urban area with a few areas of farmland approximately ten metres from the riverbanks (with conservation buffers in place). The targeted WWTP here services between 50 000 to 200 000 people and the operational processes are primary, secondary and P- removal.[50]

The sampling point along the Birmingham and Worcester Canal is located ~3 km southwest of Birmingham city centre. It is the only sampling station without a WWTP and is located in an urban location.

Sampling

Surface sediment samples were collected on 12 occasions (upstream and downstream of WWTP discharge points every month). These were: November 2019, December 2019, January 2020, February 2020, March 2020, as well as every month from July to November 2020. Samples were also collected in April, May, and June 2021, as collection during the equivalent months in 2020 were not possible due to the national UK COVID 19 lockdown. A stainless-steel extensible soil auger was used at each sampling point to collect sediment samples to an approximate depth of 6 cm. The collected sediment samples were then stored in pre-rinsed glass jars and covered with lids lined with aluminium foil before transportation to the laboratory at the University of Birmingham for analysis. Hydrological data on: precipitation, water level, and river flow rate, were obtained from the National River Flow Archive[51] and Water levels UK.[52] Monthly average water level and flow rate were calculated based on average readings per day.

Quality assurance and quality control

QA and QC measures employed for the analysis of MPs include a strict use of non-plastic sampling, storage, and processing tools.[53] Use of 100% cotton lab coats as well as nitrile gloves was also undertaken. All apparatus was rinsed 3 or 4 times with distilled water,[54–56] the workspace was cleaned with 70% alcohol[54] and all liquids and solutions were filtered through 0.45 μm filters before use.[56,57] All equipment and glass containers were covered with aluminium foil.[57] Procedural blanks, as well as field blanks (open containers filled with ultrapure or deionised water), were analysed alongside each sample batch to account for all sources of background contamination and interference. The microplastics detected in these blanks were then used to calculate the limits of detection (LOD) and quantification (LOQ). Also, prior to the commencement of extraction and analysis of the actual samples, the efficacy and recovery of the method, was extensively evaluated as part of the method validation for a separate project.[58]

In the case of OPEs, a detailed discussion of the QA/QC measures including five-point calibration, analysis of procedural blanks, and calculation of the limit of detection (LOD) and the limit of quantification (LOQ) was presented in a previous publication.[50]

Laboratory analysis

For microplastic analysis (Fig. S1†), sediment samples were freeze dried until constant weight (typically between 48 to 72 hours). The dry sediment sample was then homogenised with a metal spatula before weighing out 30 g for microplastic extraction using a modification of the Sediment Microplastic Isolation (SMI) unit.[59,60]

The weighed sediment sample and a magnetic stirrer were placed in a pre-rinsed SMI unit before filling it with 700 mL of pre-filtered zinc chloride (1.5 g cm^{-3}) solution. The $ZnCl_2$ solution was filtered using a vacuum filtration system fitted with a Whatman GF/D glass microfibre filter (2.7 μm; 47 mm diameter). The SMI unit was covered with aluminium foil and the sample homogenised for 10 minutes using a magnetic stirrer running at 400 to 600 rpm. The sample was then left to settle for 24 hours before completing the extraction process.

Following the modification by Nel *et al.*, 2019, the supernatant was decanted over a 63 μm mesh size sieve while keeping the ball valve open and the upper part of the SMI unit was detached and rinsed thoroughly over the sieve using DI water. Once the water was properly drained from the sieve, hydrogen peroxide (35%) was then used to wash the remaining matter on the filter into a 200 mL glass beaker and left in the oven to digest for 48 hours at 50 °C.[60]

After digestion, the extract was rinsed over the 63 μm mesh size sieve ensuring that no particles are left sticking to the wall of the glass beaker and then from the filter into pre-rinsed Petri-dishes. This was then left to dry in the oven before staining with Nile Red (5 μg mL^{-1}) and left to incubate for 24 hours at 50 °C.[58] To account for variability at each sampling point, the procedure was performed in quintuplicate, and the mean value recorded for subsequent analysis.

With the extract still in the Petri dishes, a Nikon SMZ-1000 stereo microscope fitted with a mercury light source and GFP-B filter set was used to identify and quantify the MPs. Features such as pixel brightness (above 100 a.u.), presence or absence of cellular structure and colour were used to identify and group MPs into fragments, fibres and pellets (Fig. S2 and S3†).[58,61–64]

Following the identification of MPs using the Nikon SMZ-1000 stereo microscope fitted with a Nikon Intensilight C-HGF1 long-life mercury light source and a Nikon DS-Fi1 5-megapixel digital microscope camera head, the various MPs were grouped into fibres, fragments, and pellets as shown in Fig. S3†.[65] The identified MPs are then isolated using stainless

steel and stored in prewashed Petri dishes for characterization. To account for variability within the same sampling point, this process was repeated in quintuplicate and the average recorded.

Identification of polymer type

The isolated MPs were characterised by a PerkinElmer Spotlight 400 μ-FT-IR using the spectrum IMAGE and spectrum IR software (Fig. 2). Reflectance spectra were obtained at a spectral resolution of 16 cm^{-1} and a pixel resolution of 25 μm in the wave number range of 4000 cm^{-1} to 710 cm^{-1}. To determine the polymer type, infrared image data were analysed with the spectrum IR software and all spectra were compared with the standard spectral library (PerkinElmer Library). A minimum match of 70% between the standard spectra and the polymer type characteristic peaks was used as a criterion for confirmation.

Concentrations of OPEs in the same sediment samples analysed here for MPs are reported elsewhere.[50]

Statistical analysis

The main statistical tools used for data analysis are IBM SPSS statistics software version 28.0.0 and Microsoft Excel. Data were log10 transformed to allow parametric statistical tests and the distribution of data set assessed using a Kolmogorov–Smirnov test in SPSS. One-way analysis of variance (ANOVA) was used with a post hoc Tukey test to assess significant spatial differences among different waterways and potential correlation was tested using Pearson correlation. In all cases, a p value of < 0.05 was set as the statistical significance level.

Results and discussion

The recovery rates recorded for high-density polymer (PET) and low-density polymers (PE and PP) ranged from 92% to 98%. As shown on the Table S1,† the Limit of Detection (LOD) and Limit of Quantification (LOQ) were calculated based on the average number of particles (fibres only) isolated during blank analysis.[66] An LOQ value of 9 was established, and only samples with values higher than this, following blank correction, were included in the analysis.

Occurrence and concentrations of MPs in UK freshwater sediments

As shown on Table S2,† the mean number of particles per kg (dw) for all 4 study locations ranged from 66.67–266.67 (Birmingham and Worcester Canal), 99.74–366.68 (River Tame),

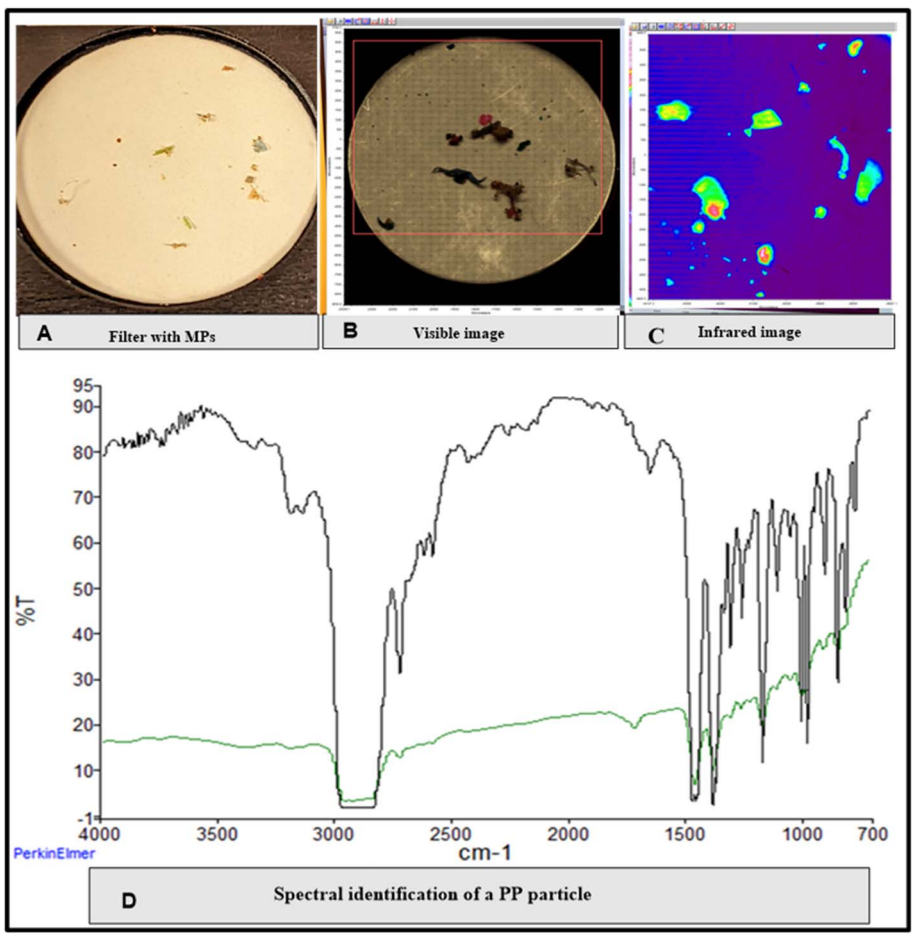

Fig. 2 Polymer type identification. (A) Filter with microplastics (B) visible image, (C) infrared image (D) spectral identification of a polypropylene (PP) particle.

Table 1 Comparison between MPs abundance, size, and shape in freshwater sediment this study and studies from other parts of the world

Study	Location	Mean MP abundance (MPs per kg)	Dominant shape	Dominant size range (μm)	Effect of WWTP	Seasonal variation	Most abundant type
This study	WWTP1	133 to 283	Fragments	200 to 399	Upstream < downstream	Highest in spring	
This study	WWTP2	67 to 233	Fragments	63 to 199	Upstream < downstream	Highest in winter	
This study	WWTP3	67 to 317	Fragments	200 to 399	Upstream < downstream	Highest in winter	
This study	Birmingham and Worcester Canal	67 to 267	Fragments	63 to 199	Upstream < downstream	Highest in winter	
91	Finland	100 ± 410	Fibres	100 to 500	Possible contributor of MP	NA	PE, PP, and PS
77	Maozhou River, China	25 to 560	Fragments	100 to 1000	Possible contributor of MP	More abundant in dry season	PE, PP, PS and PVC
87	Tallo River, Indonesia	16.67 ± 20.82 to 150 ± 36.06	Fragments	1000–5000	NA	More abundant in dry season	PE and PP
73	Cànoves stream, Spain	NA	Fragments	Higher number of small MPs[10–63, 68]	Possible contributor of MP	NA	PVC
92	Vistula River, Poland	190 to 580	Fibre	300 to 750	Possible contributor of MP	NA	PE, PP
79	Tanchon stream, Korea	340 to 500	Fragments	100 to 300	Unclear	More abundant in the rainy season	PE and PP
72	Lake Kallavesi, Finland	9 to 65 items per g	Fragment	28.2 to 828.6	NA	Highest in winter	PP
86	Liangfeng River, China	$(6.95–149.35) \times 10^3$	Fibres	50–500	NA	Higher in dry season	PE
93	Karnafully river, Bangladesh	143.33 ± 3.33 to 1240 ± 5.77	Fibres	<1000	NA	NA	PE, PET, PA/nylon, rayon, and PP
80	Lis River, Portugal	565	Fibres	<2000	Possible contributor of MP	Highest in winter and autumn	Polyethylene terephthalate and polyacrylate

66.67–432.67 (River Severn) and 33.37–233.33 (River Sowe) per month. The highest mean number of MPs per kg was recorded in the River Tame (199 MPs per kg) (Fig. S4†) which is the study location with effluent from the WWTP servicing the highest population of all three sampling locations (approximately 2.5 million people within the Birmingham area). This might be suggestive of a possible relationship between the population serviced by a WWTP and MP pollution, as suggested by some previous studies.[67] However, other factors such as proportion of industrial and domestic wastewater in the influence and wastewater treatment processes must be carefully considered before reaching such a conclusion.

One-way ANOVA and Tukey's *post hoc* test show that the mean number of MPs per kg recorded at the River Tame exceeds significantly concentrations recorded at the River Sowe ($p = 0.03$) which is the location with effluent from the WWTP servicing the second largest population (approximately 430 470 people within the Coventry area). The difference between MP concentration at River Tame and both Birmingham and Worcester Canal (the location without WWTP) and River Severn (location with effluent from the WWTP servicing the lowest population approximately 50 000 to 200 000 people within the Worcester area) was not statistically significant ($p > 0.05$).

Characterization of MPs

Polymer type. Across all four sampling locations, the relative abundance of the five polymer types identified was: polyvinyl chloride (PVC: 53%) > polypropylene (PP: 23%) > polyethylene terephthalate (PET: 11%) > polystyrene (PS: 9%) > polyethylene (PE: 4%) Fig. S5.† This result is similar to previous studies from other parts of the world with PVC and/or PP reported as the most abundant polymer type in freshwater sediment studied from other parts of the world (Table 1).

Shape and size. The dominant morphological groups in all the isolated MPs across all 4 study locations over the 12 monthly samples are: fragments (71%), pellets (20%), and fibres (9%) (Fig. S6a and b†). This low percentage of fibres can be attributed to a number of factors, of which one is their shape and low density which can reduce their settlement.[69] Also, previous studies have reported that the Nile Red method is not very effective at identifying MPs that are fibres and microfibres, especially polyamide or polyester fibres.[58,70,71] The abundance of fragments suggest that MPs in these locations may originate from secondary sources.[72]

The relative abundance of fragments, pellets, and fibres at individual study locations (Fig. S6a†) resembled closely their average morphology abundance in all samples (Fig. S6b†), with fragments being the most abundant shape. In sediment from the Birmingham and Worcester Canal, the dominant MP type was fragments (84%) and the least abundant fibres (5%). Fragments were also dominant at the River Tame (85%), River Severn (85%), and River Sowe (80%). Similar to the present study, the dominant MP shape reported in most previous studies ($N = 10$; Table 1) are fragments, with fibres as the second most common. A study by Margenat *et al.*, 2021 reported 95% of identified MPs were fragments.[73] Similarly, in a study by Ramírez-Álvarez *et al.*, (2020b), fragments and fibres accounted for 70% and 28% respectively of the MPs identified.[74] This abundance of fragments in sediments reported in several studies can be attributed to the fact that fragments often sink to riverbeds because of their lower surface to volume ratio.[75]

In terms of size variation, there was an increasing trend from larger (5000 μm) to smaller size (63 μm) MPs across all study locations (Fig. S7†). In common with many other studies on the presence of organic contaminants in sediments, the cut off point for the lower size range in this study is 63 μm.[22] At the Birmingham and Worcester Canal, the most abundant size range (52%) is 63–199 μm. This is followed by the 200–399 μm size range which accounts for 24% of the MPs isolated at this location (Fig. S7A†). The most abundant size range in samples from the River Severn (29%) is 200–399 μm and the second most abundant the 63–199 μm (25%) size range. The larger size ranges in this study (1000–5000 μm) account for only 7% of the isolated MPs in this location which agrees with most previous studies (Table 1). In the River Sowe, 63–199 μm was the most abundant size range (41%) (Fig. S7C†), as was the case in the River Tame (39%) (Fig. S7D†). In contrast, in samples from the Birmingham and Worcester Canal (the only location without WWTP input), more than 50% of isolated MPs fall within the 63–199 μm size range (Fig. S7A†). Overall, the size distribution of MPs is more even at the locations receiving WWTP input (River Severn, River Sowe, and River Tame) than observed in the Birmingham and Worcester Canal. The different size distribution of MPs at the 3 locations receiving WWTP effluent compared to the site not impacted by a WWTP, may indicate some impact of WWTPs.

The variation of size range in the present study is similar to previous studies in other parts of the world. The smaller size range (<1 mm) was the most dominant in studies from India,[76] China,[77] Thailand,[78] and Korea.[79]

MP concentrations and profiles upstream and downstream of WWTPs

The abundance, as well as distribution of MPs in samples taken upstream and downstream of the WWTP discharge points at the Rivers Tame, Sowe, and Severn was examined (Table S2†). Overall, 57% of the mean number of MPs identified across all three locations over the 12 months of sampling were detected downstream of the WWTP effluent discharge points (Fig. S8†). Moreover, Fig. S9† shows there were more MPs downstream of WWTPs than upstream for all three locations (River Tame, River Sowe, and River Severn). However, while MP concentrations are higher downstream than upstream, the difference is not statistically significant ($p > 0.05$; paired *t*-test). For the River Severn (WWTP3), the mean number of MPs upstream and downstream of WWTPs ranged from 67 to 267 and 67 to 433 MPs per kg dw respectively. In the River Sowe (WWTP2), the monthly mean number of MPs upstream and downstream of WWTP2 ranging from 67 to 167 and 33 to 300 MPs per kg dw respectively. Finally, the monthly mean number of MPs upstream and downstream of the WWTP 1 on the River Tame ranged from 100 to 267 and 100 to 367 MPs per kg dw respectively.

Previous studies have identified WWTPs as potential contributors to MP pollution in the freshwater environment.[73,74,80] Moreover, in 5 out of 10 reviewed studies from other parts of the world (Table 1), WWTPs were identified as a possible contributor of MP pollution in freshwater systems. The situation at our three WWTP-impacted watercourses contrasts to some degree with this, suggesting that the WWTPs in this study do not exert a significant influence on the concentration of MPs in receiving rivers.

In terms of polymer types, although not statistically significant ($p > 0.05$), PVC, PS, PE, and PET showed higher concentrations downstream than upstream while PP showed higher concentrations upstream (Fig. S10†). One possible explanation is density-driven removal in the WWTPs removing more of the buoyant PP (0.89–0.91 cm^{-3}) by surface skimming than the denser polymers such as PVC (1.20–1.55 g cm^{-3}), PET (1.38–1.40 g cm^{-3}), PS (1.04–1.11 g cm^{-3}) and PE (0.94–0.97 g cm^{-3}).[81] It is also possible that additional urban or industrial inputs downstream of the WWTPs contain higher amounts of PVC, PET, PS and PE.

Regarding morphological distribution, our analysis revealed a greater abundance of fragments downstream compared to upstream of WWTPs across all three study locations, as depicted in Fig. 3. However, the distribution of fibres and pellets exhibited less distinct patterns. Specifically, while the number of fibres downstream was higher for both Rivers Severn and Tame, it remained broadly constant upstream and downstream for River Sowe. Likewise, a higher number of pellets were observed downstream for Rivers Sowe and Tame, yet for River Severn, the higher number of pellets was recorded upstream as opposed to downstream.

The size distributions of fragments, fibres and pellets at all three study sites (upstream and downstream) are shown in Fig. S11.† On average, fragments and fibres were marginally longer upstream than downstream, suggesting breakage or selective loss during downstream transport. As particles travel downstream, abrasion against other particles, hydrodynamic shear stresses or other mechanisms can reduce their length, while selective loss may occur due to biofouling or physical trapping.[82–84] Specifically, fragment lengths upstream ranged from 40 μm to 935 μm (median 376 μm), whereas downstream they ranged from 40 μm to 639 μm (median 345 μm). For fibres, the average length upstream ranged from 290 to 6189 μm (median 2495 μm), while downstream, lengths ranged from 285 to 6140 μm (median 1560 μm). In contrast, for pellets, there was no notable difference between upstream and downstream data. The average pellet length upstream ranged between 35 and 1110 μm (median 268 μm), whereas downstream, lengths ranged between 33 and 817 μm (median of 351 μm).

Although the distribution of fragments and fibres as shown in Fig. S11† shows higher length upstream than downstream, a paired *t*-test showed that the overall difference in MP length up and downstream of the WWTPs was not statistically significant ($p > 0.05$). The trend towards shorter particles downstream if traced to the impact of the WWTPs could suggest increased ecotoxicological effect as smaller plastics and fibres are more readily ingested by filter feeders and benthic invertebrates, potentially amplifying trophic transfer of chemical additives or sorbed contaminants.[85]

Seasonal variations

Seasonal variations in MP abundance/distribution have been reported with varying findings by different researchers. Some previous studies have reported increased abundance of MPs in surficial sediment in dry seasons compared to rainy seasons.[78,86,87] Such observations have been attributed to increased river flow rate in the rainy season mobilising previously settled MPs from surficial sediment into the water column.[88,89] However, other studies have reported contrasting results whereby higher MP concentrations in surficial sediments are seen in the rainy season.[76,79,90] These observations were attributed to increased run-off of terrestrial MPs into the water system during heavy rainfall.

In the current study, the highest mean number of MPs per kg was recorded in the winter months (December, January, and February) for all four study locations (Birmingham and Worcester Canal, River Tame, River Sowe, and the River Severn)

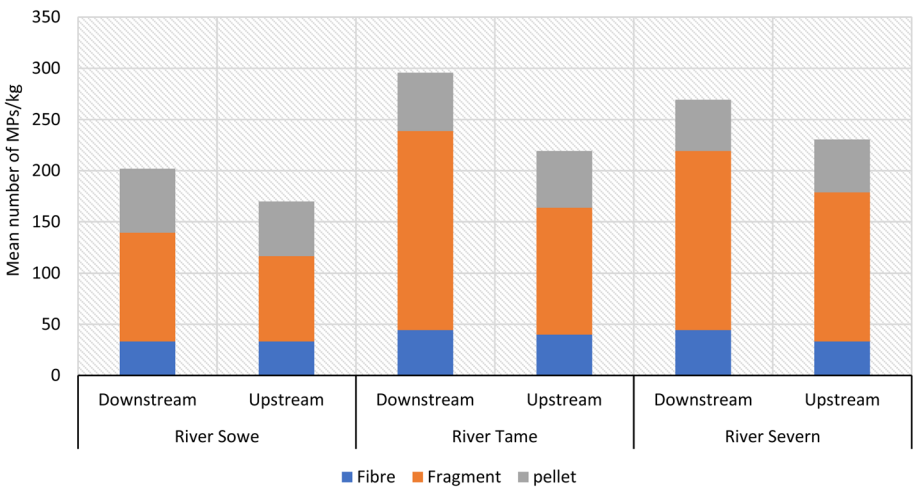

Fig. 3 Mean morphological distribution profiles of MPs upstream and downstream of the studied WWTPs.

as shown in Table S2 and Fig. S12.† This result which shows a significant difference between winter and all the other seasons (Spring–Winter: $p = 0.027$, Summer–Winter: $p = 0.018$ and Autumn–Winter: $p = 0.015$) is interesting as it contrasts with the seasonal variation, we reported previously for OPE concentrations in the same samples *i.e.*, $\sum_8$OPEs (tris(chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TClPP), tris(1,3-dichloro-2 propyl) phosphate (TDClPP), tri-*n*-butyl phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(phenyl) phosphate (TPHP), and tri-*m*-tolyl phosphate (TmTP)) concentrations were highest in Autumn.[50] A possible explanation for this observation is that more terrestrial MPs are washed off into the rivers because of the higher rainfall in winter, while for OPEs, the "dilution" effect of higher winter river flowrates is the dominant influence on surficial sediment concentrations.

In comparison with results from other parts of the world (Table 1), of the two studies that considered the seasonal variation of MPs over a similar seasonal classification as used in this study (summer, winter, spring, and autumn); both agreed with our study, *i.e.*, reporting the highest concentration of MPs to occur in winter.[72,80] Four studies did not report any seasonal variation while the four other studies reported variation in MPs between rainy and dry seasons. Of these, one study reported maximum concentrations of MPs in the rainy season while the other three observed highest concentrations in the dry season. The higher concentrations reported in the rainy season is consistent with our study as we recorded higher rainfall in winter months.

To understand the impact of weather conditions, MP abundance was compared to the flow rate and water level data for each river as shown in Fig. S14.† For the River Sowe (WWTP2), the highest flow rate and water level data were recorded in the winter months of January and February in line with MP abundance where the highest concentration was recorded in winter. The highest MP abundance observed for the River Severn (WWTP3) and River Tame were also recorded in winter and this falls within the same period of highest flow rate and water level data at the Rivers Severn and Tame (January to February). This period also falls within the severe flood of mid – late February 2020 at our River Severn location. Flow rate and water level data were not available for the Birmingham and Worcester Canal.

A Pearson correlation test was used to check the statistical significance of these observed trends and the results are presented in Tables S3–S5.† The results of the correlation tests at the River Severn show significant positive correlations between total number of MPs per kg and both water level ($r = 0.584$, $p = 0.046$) and river flow rate ($r = 0.694$, $p = 0.026$). For the River Tame and River Sowe; however, there was no statistically significant correlation as p-values exceeded 0.05.

Relationship between MPs abundance and OPEs concentrations in monthly sediment samples collected from each location

Few studies have looked at the role of MPs in transporting toxic organic pollutants within the environment.[94–96] However, questions remain on the relationship between MPs and these chemical pollutants under natural environmental conditions. This is partly due to the difficulty in reproducing the real life environmental conditions, such as variations in climate under which these interactions take place.[97] Nonetheless, understanding the relationship between MPs in sediments and associated additive chemicals, remains an important research goal.

A recent study by our research group reported the concentrations of OPEs in the same sediment samples analysed here.[50] Fig. 4 plots these OPE concentrations against those of MPs in the same samples.

These scatter plots reveal negative correlation between concentrations of MPs and $\sum_8$OPEs across all four sampling locations over the 12 months period with only River Tame reaching statistical significance ($p < 0.05$). The observed correlation is however only driven by one or two OPEs.

A Pearson correlation test showed significant negative correlations between total individual target OPE concentrations and mean MPs number across all four sites, specifically for TCIPP, TBOEP, and TPhP. Additionally, a significant negative correlation was observed between the sum of eight OPEs ($\sum_8$OPEs) and mean MPs number across all sampling locations (Table S6†).

To further understand this relationship between OPEs and MPs (especially for the three OPEs, with negative correlation), the organic matter content of the sediment samples were determined (Fig. S15†) and the potential influence of each OPE's organic carbon-water partition coefficient (K_{oc}) (Table S7†) on the observed patterns was considered. A correlation test between the three OPEs and sediment organic matter produced varied results across sites (Fig. S16–S19†) rather than the typical positive correlation.[98] At the River Tame, none of the relationships was statistically significant ($p > 0.05$), suggesting that factors other than organic carbon such as MPs sorption or variable input sources may be driving OPE concentrations in the sediment samples. At the River Sowe, however, TPhP showed a fairly strong ($r = 0.59$), significant ($p < 0.01$) positive correlation with organic matter content, consistent with its high K_{oc} (3.72) and low water solubility.[99,100] In contrast, TCIPP and TBOEP showed weak, non-significant negative correlations, indicating possible partitioning onto MPs.

The observed correlation at River Severn includes a moderate ($r = -0.56$), significant ($p < 0.01$) negative correlation with percentage organic matter for TCIPP, which may reflect its moderate water solubility and lower K_{oc} (2.59),[100] favouring its persistence in porewater or sorption onto MPs rather than association with organic matter. TPhP and TBOEP, by contrast, again showed only weak, non-significant correlations.

Along the Birmingham and Worcester Canal, none of the three OPEs correlated significantly with organic matter content (all $p > 0.05$), reinforcing that organic matter may not be the principal determinant of OPE distribution; instead, seasonal variation, MPs and other physico-chemical parameters also likely play important roles.

We also examined relationships between concentrations of individual target OPEs and the mean MPs particle number,

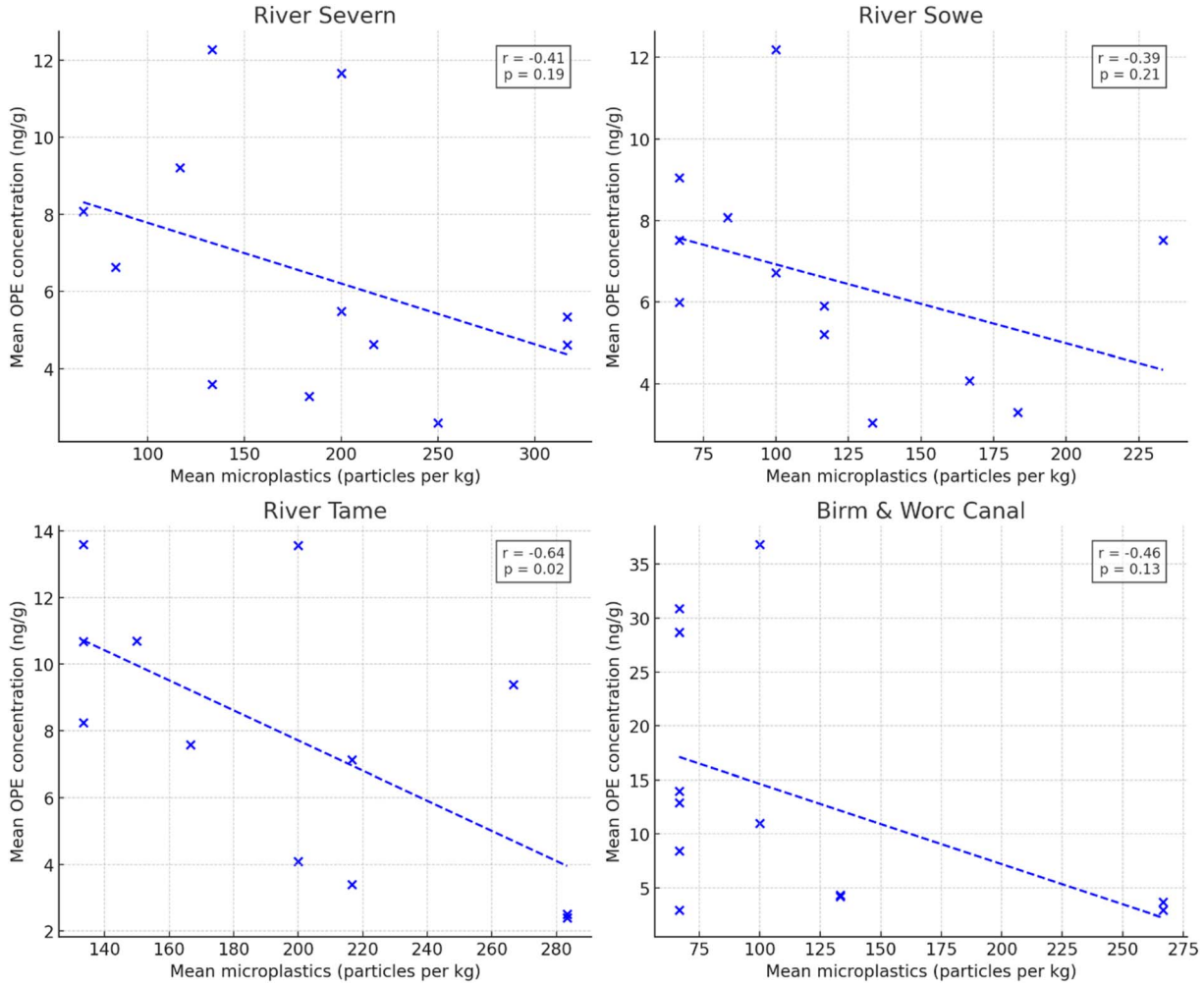

Fig. 4 Scattergram plots of mean MPs per kg and mean S_8OPE concentrations over 12 months at each individual study location.

median MPs particle number, mean MPs particle area, as well as median MPs particle area (Table S6†). This revealed significant negative correlation between TBOEP concentration (the most abundant OPE across all sampling points) and mean particle number ($r = -0.309$, $p = 0.004$). Moreover, we observed a significant negative correlation between TnBP concentration and mean MPs per kg at the River Severn (Table S15†), as well as between TMTP and mean MPs per kg at river Sowe (Table S11†).

These negative correlations between concentrations of MPs and some OPEs can potentially be attributed to several reasons; one of which is the sorption of organic pollutants by microplastics *i.e.*, increased abundance of MPs sorbs OPEs; thereby reducing OPE concentrations in sediments. Although no previous study has specifically investigated OPEs, to the best of our knowledge, extensive research has been conducted on the sorption of other pollutants, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlorobenzenes, and pesticides, onto microplastics.[101,102] The adsorption process typically involves a combination of mechanisms, including hydrophobic interactions, partition effects, electrostatic attraction/repulsion, halogen bonding, hydrogen bonding, π–π interactions, and van der Waals forces.[101] Physical interaction between OPEs and MPs is facilitated through factors such as crystallinity and surface area of MPs making them a suitable surface for organic pollutants to adhere to, thereby reducing the concentration of free pollutants in the sediment.[103]

However, the respective source(s) of both contaminants could also play a role in this observed relationship between OPEs and MPs. If both MPs and OPEs were from the same source(s), then the expectation would be a positive correlation. Therefore, our observed negative correlations might simply indicate that MPs and OPEs are from different sources. It could also be related to the different seasonality of MPs and OPEs with the dominant effect of higher winter rainfall diluting contaminants sorbed to sediments like OPEs, while for MPs the dominant effect of high winter rainfall can increase soil run-off and associated MPs.

Overall, though, we emphasise the need for further research that focuses on elucidating the relationships between MPs and organic chemical contaminants like OPEs in freshwater sediments. Our study shows concentrations of MPs, and some OPEs to be negatively correlated, implying a number of possibilities

as outlined previously but further study is required to see if this relationship is replicated at other sites and for other organic chemical contaminants.

Conclusion

This study investigated the presence and distribution of MPs in sediment samples from four different locations and evaluated the potential correlation with OPE concentrations. The results demonstrated significant spatial, temporal, and morphological disparities in MP concentrations, with the results suggesting a possible relationship between the size of the population serviced by a given WWTP and the levels of MP pollution. The majority of MPs identified were fragments, indicative of secondary sources such as plastic degradation processes. A seasonal trend was noted with the highest MP concentrations observed in the winter, possibly due to increased terrestrial runoff.

No significant difference in MP abundance upstream and downstream of WWTPs was observed, suggesting additional MP sources such as atmospheric deposition, sewage sludge used for agriculture, and breakdown of larger plastic pieces. Additionally, the study revealed a strong positive correlation between microplastic concentrations and both water level and river flow rate, emphasizing the role of hydrology in the distribution and transport of MPs.

Our observed negative correlations between the concentrations of MPs and some OPEs calls for further research aimed at further understanding the complex interactions between MPs, their chemical additives, and organic pollutants within freshwater environments. Such studies should also look at further experimental evidence of the possibility of sediment MPs adsorbing OPEs as well as examine factors impacting the release of hazardous additive chemicals from MPs into freshwater environments. These factors might include plastic polymer type, additive concentration and physicochemical properties, sediment organic content, and temperature. It would also be interesting to test the hypothesis in different water bodies for broader applicability.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare that they have no known competing interests.

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