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Microplastics pollution in sediments of the Thames and Medway estuaries, UK: Organic matter associations and predominance of polyethylene

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ABSTRACT

Microplastics at 10 sites along a 77 km transect of the river Thames estuary (UK) and 5 sites along 29 km of the Medway estuary were separated from sediment and analysed by ATR-FTIR spectroscopy. Microplastics were observed at all sites. Highest Thames concentrations were in urban London between Chelsea and West Thurrock (average 170.80 particles $kg^{-1} \pm 46.64$, 3.36 mg $kg^{-1} \pm 1.79$ by mass), mid-outer estuary sites were two to three times lower. Microplastics were slightly dominated by particles (54 %) over fibres (45 %), including polymer types ranked: polyethylene > PET > polypropylene > polyamide. Medway microplastics decreased seaward, with one urban-municipal site impacted by a combined-sewer-overflow containing a high proportion of fibres (Rochester, 484 particles kg^{-1}, 7.39 mg kg^{-1} by mass). Microplastic abundance was correlated to organic carbon (TOC %) (R^2 of 0.71 Thames and 0.96 Medway), but not sediment particle size. Sedimentary microplastics accumulation in the Thames was controlled by urbanisation-distance, and site hydrodynamics.

1. Introduction

Estuarine environments are considered key sources of plastic pollution, connecting terrestrial sources to marine sinks, but are relatively understudied in comparison to fully open marine ecosystems (Sadri and Thompson, 2014; Jambeck et al., 2015). Previous evaluations have reported high concentrations of microplastics both in estuarine sediments and the water column, with several factors influencing distribution and transport rates including surrounding land use, seasonal trends, and variations in hydrodynamic conditions (Klein et al., 2015; Mani et al., 2015; Nel et al., 2018; Rodrigues et al., 2018). Microplastics are an important component of anthropogenic pollution that spans chemical, biological, and physical forms, with frequent microplastic interaction found to have several consequences for aquatic organisms (Browne et al., 2008; Brennecke et al., 2015). These can range from mechanical injury to fibrosis (a disease recently termed 'plasticosis'), and translocation across cell membranes leading to further disease both directly, and indirectly, by acting as a vector for other pollutants (Browne et al., 2008; Teuten et al., 2009; Wright et al., 2013; Brennecke et al., 2015; Eerkes-Medrano et al., 2015; Andrady, 2017; Bucci et al., 2019; Mondal and Subramaniam, 2020; Santos et al., 2021; Charlton-Howard et al., 2023). Research so far has primarily focused on aquatic organisms, but initial studies have indicated possible microplastic presence in humans, with multiple internal pathways possible following ingestion (Wright and Kelly, 2017; Ragusa et al., 2021; Leslie et al., 2022). Identifying microplastic pathways in dynamic estuarine environments and generating sedimentary storage baselines will be an important component of understanding and monitoring microplastic behaviour in order to mitigate these impacts from urban municipal and industrial waste streams.

The Thames estuary (UK) forms a key shipping transport route for Greater London and the UK and is historically one of the most populous cities globally with an estimated population of 8.8 million (Office for National Statistics (ONS), 2021; Vane et al., 2022). As a result, a combination of industrial, domestic and municipal wastes are treated and discharged into the Thames. Under normal meteorological conditions, waste effluent is treated at outflows located each in Beckton (north) and Crossness (south), but there are also a number of combined sewer overflow (CSO) points along the estuary which discharge untreated effluent during periods of high rainfall (Vane et al., 2015). Thames estuary sediments have previously been assessed for a variety of chemical

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pollutants including trace metals, polycyclic aromatic hydrocarbons (PAH), organochlorines, brominated flame retardants, sewage compounds, and pharmaceuticals (Scrimshaw and Lester, 1997; Murray et al., 2011; Pope and Langston, 2011; Vane et al., 2015; Ganci et al., 2019; Vane et al., 2020a; Vane et al., 2022; Downham et al., 2024). In terms of plastic pollution, high concentrations of sub-surface plastic debris have been found in the upper estuary (Morritt et al., 2014), and microplastics have been found in abundance within the estuary water column (Rowley et al., 2020; Devereux et al., 2023), suggesting that the Thames is likely to be a significant source of plastic pollution into the marine environment. The Medway estuary is an area of mixed river side use including strategically important commercial port at Sheerness and histoic Naval (Military) dockyards at Chatham (1600–1984) as well as power station at Isle of Grain. Interest in the Medway estuary also stems from its extensive salt marshes (e.g. Bishop Hoo, Hamm Ooze, Sharfleet Saltings and Deadmans Island) that are designated Ramsar wetland and a site of special scientific interest (SSSI).

Although the presence of plastic pollution including microplastic pollution in the UK rivers and particularly the Thames estuary has received considerable interest from media and general public there is a lack of data from sub-tidal sediments. The purpose of this study is to bridge this knowledge gap by providing a baseline microplastics data-set against which future mitigation schemes and non-statutory legislation can be set.

Chemical pollution including trace metals and organo chlorine compounds (PCBs) and polycyclic aromatic hydrocabons (PAH) in the Thames are associated with organic carbon content (TOC %) due to sorption to organic coatings on fine grained particulates and also co-occurrence with sewage effluent (Vane et al., 2020a; Vane et al., 2015; Pope and Langston, 2011). A second motivation of this study was therefore to establish whether microplastics distribution was similarly influenced by sediment particle size, and or organic matter co-factors.

2. Materials and methods

2.1. Study area

The Thames River (UK) has a catchment area of 14,000 km^2 and flows in an easterly direction from its source in Gloucestershire, bisecting central London before discharging into the southern North Sea (Vane et al., 2022). The tidal portion of the river is approximately 110 km long and predominantly urban, beginning at Teddington Weir in west London. The transect of the Thames used in this study was 77.14 km long, spanning from downstream of Teddington weir (T1) (near Chelsea, London) to Sheerness (T10) (Kent). Ten sample sites were divided into an urban transect (T1–T5) spanning Chelsea (London) to West Thurrock (Essex), and a seaward downstream estuary transect (T6–T10) spanning Gravesend (Kent) to Sheerness (Kent) (Fig. 1). Site T4 was next to the Beckton sewage treatment works (STW) outflow point, and many other sites were located close to CSO points.

The river Medway (UK) is a tributary of the Thames estuary, travelling in a north-easterly direction from its source in West Sussex to its confluence with the Thames near Sheerness, becoming tidal below Maidstone, Kent. It has a largely rural catchment with an area of 1843 km^2, although the river passes through some major towns including Rochester (Southern Water, 2022). The transect used in this study was tidal at 29.54 km long, spanning from just upstream of Rochester at Snodland (M1) to Sheerness (M5), with a total of 5 sample sites (Fig. 1). The river Blackwater rises as the river Pant south-east of Saffron Walden, Essex, UK. It generally flows in a south-easterly direction, becoming the Blackwater below Braintree, Essex. It is largely a rural river, but it does flow through some small urban towns including Braintree and Maldon, Essex. The Blackwater portion has a catchment area of 131.625 km^2, emptying first into the Blackwater estuary and onto the North Sea (Environment Agency (EA), 2023). The study site used in this study was in the Blackwater estuary, near Mersea Island, Essex (B5) (Fig. 1).

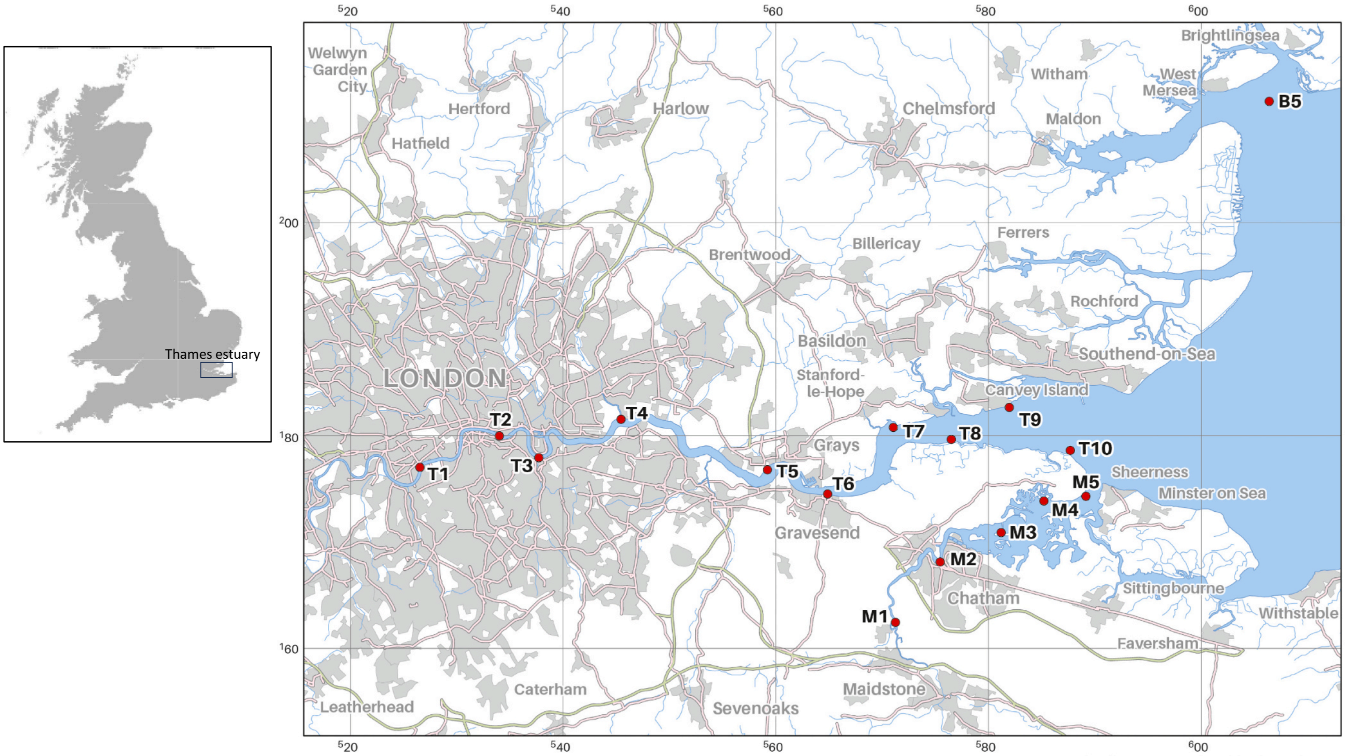

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Fig. 1. Site map showing location of Thames estuary sediments (T1–10), Medway estuary (M1–5) and Blackwater Estuary (B5), UK.

2.2. Sample collection

A total of ten surface sediments from the active channel of the tidal Thames (UK) were collected between 2nd and 3rd September 2020 using a Day grab (0.1 m^2) from the vessel 'Thames Guardian' (samples T1–10). The position of each site was recorded using a handheld Garmin GPSMAP, as well as the water depth (Table S1). Weather conditions were good, partly cloudy, with air temperature ~ 16 °C, wind 8–9 mph. At each site, sub-tidal surface (0–10 cm) grab deployments were combined to generate 400 g of sediment which was then sealed in 1 L amber glass jars (images of each sample are available in Fig. S1). After each deployment the grab sampler was washed with sea water and rinsed with deionised sterile water. No background control samples or replicate surface grab samples were taken. Upon return to the laboratory, the samples were refrigerated (~4 °C) until analysis. Using the same method, a further five surface samples were collected from the Medway (Essex, UK) and one from the Blackwater (Kent, UK) rivers between 3rd and 4th November 2020 (sixteen samples total). The five Medway samples (M1–5) and one Blackwater sample (B5) were analysed for comparison to the main estuary channel of the Thames (images of each Medway sample are available in Fig. S2).

2.3. Microplastics extraction

For each sample, sediment (400 g) was wetted with filtered deionised water and successively wet-sieved through a 5 mm and 0.3 mm (stainless steel sieve mesh) to give 0.3–5 mm size fraction. The sieved material was transferred to a 500 mL glass separating funnel, to which 300 mL of $ZnCl_2$ at a density of ~1.6 g cm^{-3} was added (Horton et al., 2017; Lloret et al., 2021; Tibbetts et al., 2018; Coppock et al., 2017). The apparatus was sealed then shaken (×3), before the contents was allowed to completely settle overnight (~14 h). The floated density separated material was then decanted and filtered through a membrane (0.3 mm) and rinsed with deionised water. Remaining natural organic matter within the density separated sample was digested by repeat addition of using 50 mL H_2O_2 (30 w/v) and heating at 60 °C for 24 to 72 h. The isolated sample was then filtered through a membrane filter and dried at 40 °C. Under a dissecting microscope (Olympus) set at 40× magnification, the identifiable microplastics were collected and added to a watch glass, according to the criteria set by Nor and Obbard (2014). Identified microplastics were counted and characterised as either fragments, fibres, or microbeads, and were weighed using a microbalance to obtain the mass of suspected microplastic particles. Cotton laboratory coats were worn during microplastics extraction with handling conducted in a HEPA-filtered ductless fume hood with upward unidirectional flow.

Quality control was achieved by spiking 100 g of sand with 20 fragments of microplastic (0.3–5 mm) as well as a laboratory control of unspiked baked sand (Fig. S3). Both samples were then subject to the same microplastic separation procedure (wet sieve, density separation, H_2O_2 digest, identification) which indicated a 99 % recovery rate. Samples of unspiked baked sand yielded no observable microplastics; suggesting no contamination occurred during processing. Abundance is reported by count (particles kg^{-1}), and as mass (mg kg^{-1}), with standard error of the mean (SEM) stated for calculated averages.

2.4. Fourier-Transform Infrared Spectroscopy (ATR-FTIR)

For each sample, an average of ten suspected microplastic particles considered most representative of the sample were selected for analysis using an Agilent Technologies Cary 600 Series Fourier-Transform Infrared spectrometer (FTIR) with an Attenuated Total Reflectance (ATR) module. Each particle on the slide was scanned between two and three times each, depending on the observed quality of the output spectra. Absorbance was measured across wavenumbers 4000–950 λ at a resolution of 4 cm^{-1} (64 scan repetitions per scan, and 128 for background scans). Spectra were processed to remove background noise and the CO_2 signal. Extended multiplicative signal correction (EMSC) was used for baseline correction, before using the Open Specy (Cowger et al., 2021) polymer matching software to identify the material typology of each particle scanned. A minimum Pearson's score of 0.7 for one of the scans of each particle was needed in order to be considered a positive match to a material. Particles not meeting this criterion were labelled as 'unknown' particles.

2.5. Sediment particle size analysis

In preparation for particle size analysis, organic matter was first removed from 1 g of each sediment by repeat addition of 25 mL H_2O_2 and heating at 20 °C, and then 70 °C in a water bath (Gray et al., 2010). Particle size was measured using a Beckman Coulter LS™ 13,320 MW, operated under identical conditions to that of Vane et al. (2015). The proportions of particles at each size class (117 groups, from 0.1 μm to 2000 μm) were calculated using the Fraunhofer model, based on refractive indices of 1.33 for H_2O and 1.55 for quartz. The 117 groups were then summed according to the following categorisation scheme: clay (< 4 μm); silt (4–64 μm); and sand (>64–2000 μm) (Folk and Ward, 1957; Vane et al., 2020b).

2.6. Rock-Eval(6) pyrolysis

Freeze-dried sediments were ground to a fine powder (<250 μm) using a Retsch 400 ball-mill, and 150 mg sub-sample was analysed using a Rock-Eval(6) (Vinci Technologies). The instrument was operated using standard bulk-rock programme: 300 °C for 3 min (S1 stage), 650 °C at a rate of 25 °C min^{-1} in an inert N_2 atmosphere (S2 stage). The residual carbon was then oxidised from 300 °C to 850 °C at a rate of 20 °C min^{-1} and held there for 5 min (S3 stage). Released hydrocarbons were measured with a flame ionisation detector, and CO and CO_2 with an IR cell (Newell et al., 2016; Brown et al., 2023; Williams-Clayson et al., 2023). Rock-Eval parameters were then derived from the integration of the amounts of thermally vaporised free hydrocarbons (S1), and hydrocarbons released from the cracking of bound organic matter (S2) (both expressed as mg HC g $rock^{-1}$). Total organic carbon (TOC) (wt%) was calculated by summing the carbon moieties (HC, CO and CO_2). Tmax (°C) related to the pyrolysis temperature where the greatest amount of bound hydrocarbons were released during the cycle. The hydrogen index (HI) (expressed as mg HC g TOC^{-1}) corresponded to the amount of bound hydrocarbons released relative to the TOC, while the oxygen index (OI) (expressed as mg CO_2 g TOC^{-1}) referred to the quantity of oxygen released as CO and CO_2 relative to the TOC (Sebag et al., 2016; Brown et al., 2023).

3. Results

3.1. Spatial variation in microplastics

Microplastic particles were found at all Thames, Medway, and Blackwater sites. Microplastic concentrations in the Thames estuary averaged 170.80 particles kg^{-1} ± 46.64 in the urban transect (T1–T5), and 67.00 particles kg^{-1} ± 16.47 in the seaward downstream transect (T6–T10). By mass, there was an average of 3.36 mg kg^{-1} ± 1.79 in the urban transect and 1.16 mg kg^{-1} ± 0.44 in the downstream transect (Fig. 2a). Sites T1 (Chelsea) and T3 (Deptford) contained the highest suspected microplastic concentrations by number (286 and 273 particles kg^{-1}, respectively) and mass (2.7 and 10.4 mg kg^{-1}, respectively). In contrast, site T8 (Cliffe) contained the least microplastics in terms of number and mass (9 particles kg^{-1}, and 0.06 mg kg^{-1}). A *t*-test assuming unequal variances to compare the urban and seaward downstream transects indicated a significance of 0.09 when using particle counts, and no significant difference between the transects when using mass ($p = 0.29$). When investigating microplastic abundance by number with distance downstream from T1, there was a weak correlation R^2 of 0.45,

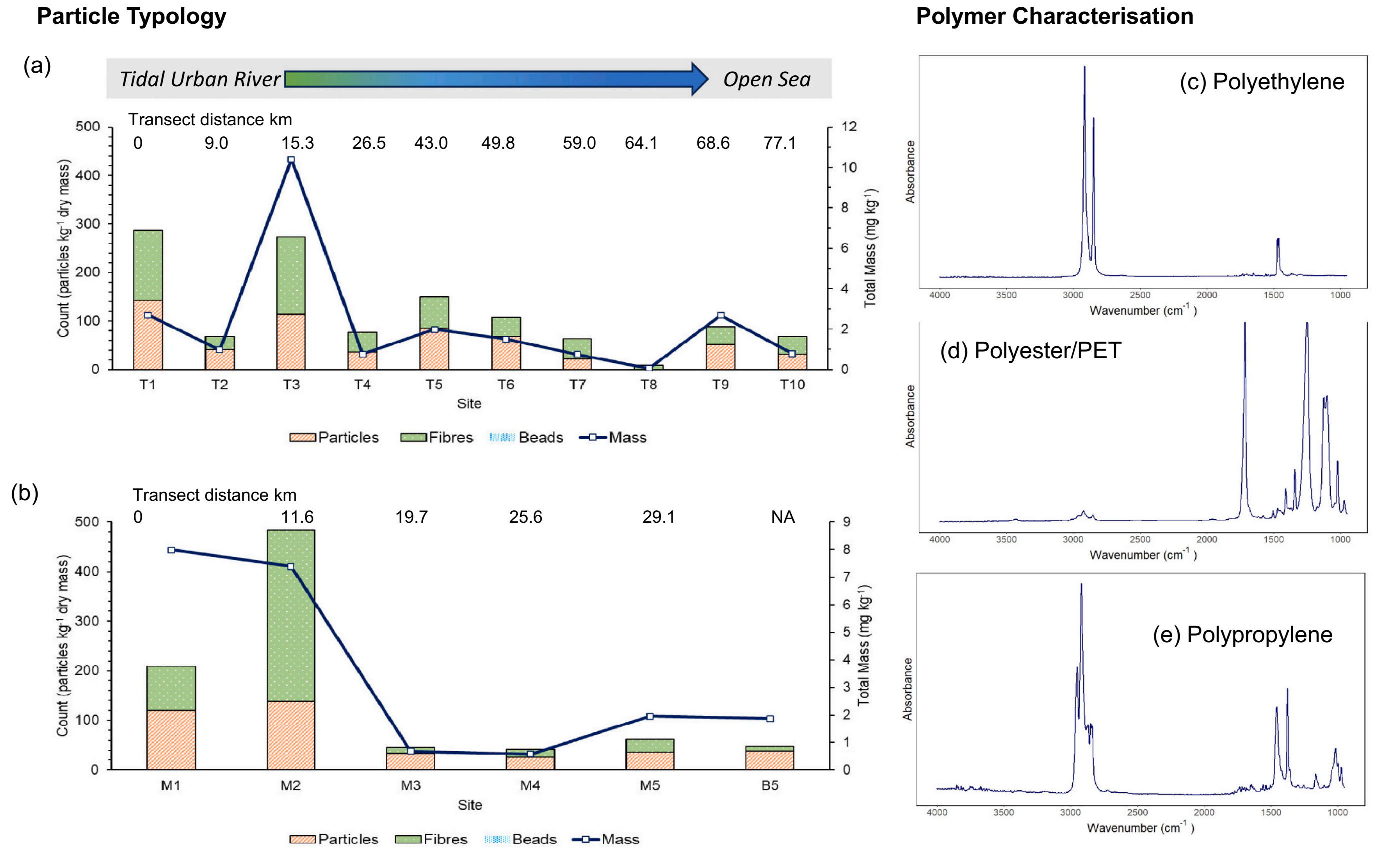

Fig. 2. Particle typology plots (a, b), illustrate concentrations of microplastics within the sediment at each site used in the study. (a) depicts sites on the Thames estuary, while (b) shows sites on the Medway and Blackwater. For each site, the abundance is shown in count by the bars and in mass by the line plot. Each bar is split into the respective typologies- note that no microbeads were found at any site used in this study. Polymer characterisation plots (c), (d), and (e) show Examples of the most common FTIR spectra obtained when scanning suspected microplastic particles within this study. Spectra were obtained using an attenuated total reflectance (ATR) module, and each particle was scanned at least twice to produce an average spectrum for the particle. Materials depicted are (c) polyethylene, (d) polyester/PET, (e) polypropylene.

indicating fluctuations in abundance within the dataset with some significant linear relationship. There was a strong correlation mid-transect between neighbouring sites T5–T8 (West Thurrock to Cliffe) with an R^2 of 0.98. By mass, there was no correlation between microplastic abundance and distance downstream (R^2 of 0.16).

For the Medway, suspected microplastic concentrations averaged 168.4 particles kg^{-1} ± 84.79 by number, and 3.72 mg kg^{-1} ± 1.64 by mass (Fig. 2b). The Blackwater sample contained 48 particles kg^{-1} of microplastics, or 1.87 mg kg^{-1} (Fig. 2b). Samples M1 (Snodland) and M2 (Rochester) had the greatest abundance both in terms of number (209 and 484 particles kg^{-1}, respectively) and mass (7.99 and 7.39 mg kg^{-1}, respectively) while M4 (Wallend) had the least (42 particles kg^{-1}, and 0.58 mg kg^{-1}). There was weak correlation between microplastic abundance and distance downstream from M1 for the Medway sites when using count (R^2 of 0.36). When using mass, there was a higher correlation R^2 of 0.77. Due to low sampling size (n = 5 total), a *t*-test was not used to compare urban and seaward downstream sites.

3.2. Microplastics shape and composition

Fragments and fibres were in equal abundance at most sites on the Thames, with an average of 54 % fibres, and 46 % fragments, in contrast no microbeads were observed in any of the samples. A *t*-test assuming unequal variances found there to be no statistically significant difference between the number of fragments and fibres in the Thames samples (p = 0.99). In contrast, fragments dominated at all Medway sites (average 55 % fragments) and the Blackwater site (79 % fragments), except for site M2, where fibres were more dominant (71 % fibres at this site). There was no statistically significant difference between the number of fragments and fibres at all sites along the Medway (p = 0.71). There were also no microbeads retrieved in any samples on the Medway or Blackwater. It should be noted that the data presented herein is extrapolated from smaller sample than 1 kg which can introduce error; potentially exaggerating and or omitting features that might otherwise be present in a full sample (1 kg) (Table S2). Notwithstanding, differences in microplastics separation methodology this extrapolation does however facilitate comparison between studies.

A total of 163 suspected microplastic particles were scanned across all sites using FTIR (typically 10 of the most representative particles per site) (see Fig. 2c, d, e for example spectra). For the Thames samples, 83 of 103 (80.6 %) total particles scanned could be confirmed to be of plastic origin, 6.8 % could not be identified, and 12.6 % were confirmed to be of natural origin. Of those confirmed as plastic, 45.8 % were polyethylene (which was also the most common fragment material), and 15.7 % were polyester/PET (also the most common fibre material) (Fig. 3a). The types of plastic found were very similar between the urban and downstream transects (Fig. 4b, c). For the Medway sites, 41 of 50 particles scanned (82 %) were confirmed as plastic, 3 (6 %) could not be identified, and 5 (10 %) were of natural origin. As with the Thames, polyethylene was the most identified both overall and of the fragments (39 % of those identified as plastic) (Fig. 3d). The most common fibres were equally polyester/PET and nylon/polyamide. All ten of the particles scanned for the Blackwater sample B5 were of plastic origin (100 %), 30 % of which were polystyrene. 40 % were classified as ‘other’ plastics, comprising plastics such as polyurethane and PDMS (Fig. 3e).

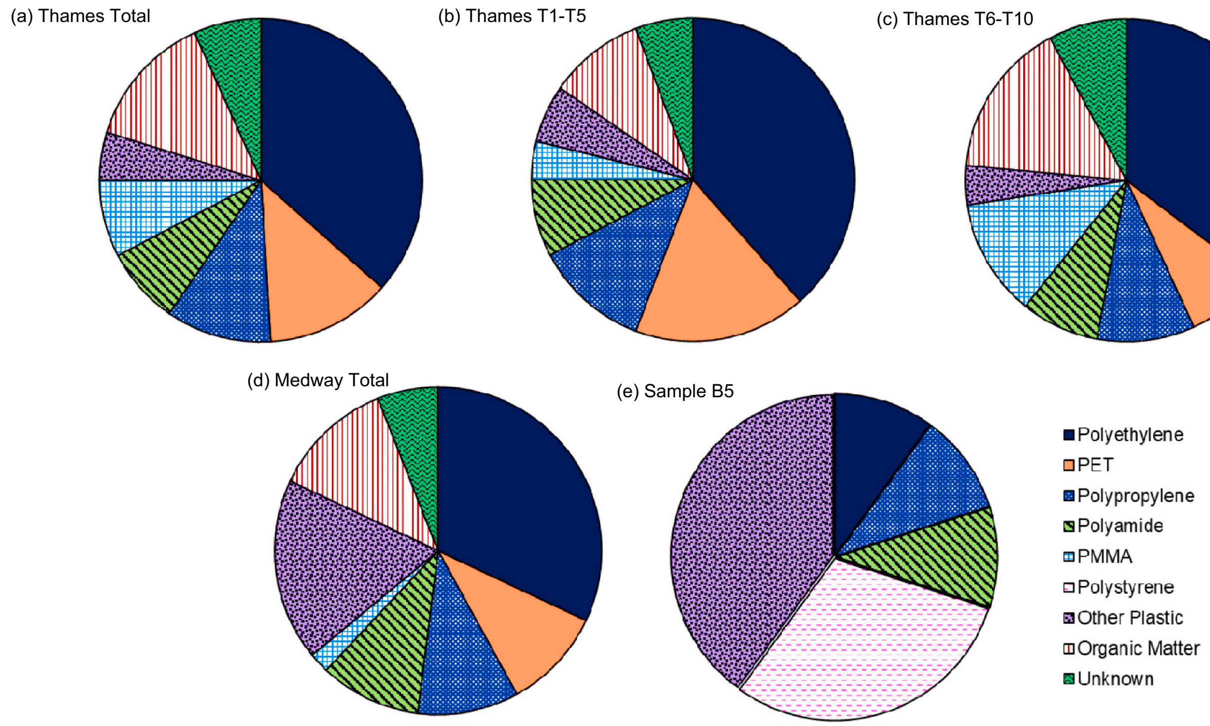

Fig. 3. Pie charts showing the material composition of suspected microplastics scanned using FTIR. Chart (a) contains the combined materials identified from all sites on the Thames estuary, (b) depicts those found on the urban upstream transect only (T1–T5), (c) the downstream transect only (T6–T10), (d) all sites on the Medway, and (e) the Blackwater sample.

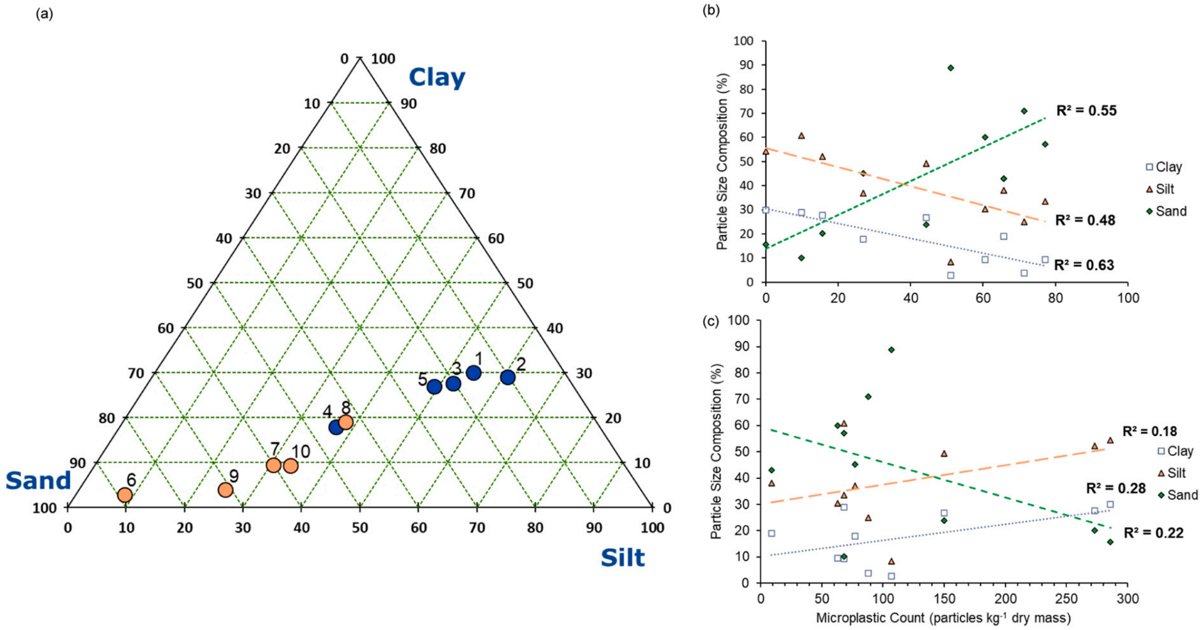

Fig. 4. Sediment particle size analysis of Thames estuary sub-tidal samples. Plot (a) is a triangular plot showing the particle size composition of each site on the Thames estuary in terms of percentage sand, silt and clays (%). Numbers 1–10 refer to the site number within the transect. Plot (b) depicts the relationship between each particle size class for each site and the distance downstream from T1, and (c) the correlation between each particle size class at each site and microplastic abundance in terms of count. Dotted lines on (b) and (c) represent the linear trendline for each size class.

3.3. Sediment particle size and microplastics

Thames sediment samples were a mix between sand (site T6-Gravesend), silty sand (majority seaward downstream transect samples), and clayey silt (majority urban transect samples) compositions (Fig. 4a). There was a correlation between the particle size class and distance downstream, with the proportion of silt and clay decreasing downstream (R^2 of 0.48 and 0.63, respectively) and the proportion of sand increasing (R^2 of 0.55) (Fig. 4b). The correlation improved for all classes when site T6 was excluded from the dataset (R^2 values of 0.72, 0.72 and 0.73, respectively). There was, however, minimal correlation between the particle size classes and the abundance of microplastics, generating an R^2 of 0.28 for clay, 0.18 for silt and 0.22 for sand classes (Fig. 4c).

For the Medway and Blackwater, samples were a mix between silty sand and clayey silt (Fig. S4a). The Medway showed some correlation between the particle size class and distance downstream (R^2 of 0.57 for silt, 0.56 for clay, and 0.58 for sand classes) (Fig. S4b). There was varying correlation between the size classes and the abundance of microplastics for the Medway, with R^2 values of 0.21 for clay, 0.42 for silt, and 0.35 for sand classes (Fig. S4c).

3.4. Organic matter and microplastic

Rock-Eval(6) pyrolysis provides a bulk-level characterisation of organic matter to identify carbon source and decay state in wetland peats, coastal sediments, urban rivers, industrial brownfield soils, alongside traditional applications in hydrocarbon bearing shale-rock (Brown et al., 2023; Kemp et al., 2019; Vane et al., 2022; Williams-Clayson et al., 2023; Waters et al., 2019).

For the Thames samples, the Rock-Eval data found an average TOC in the sediment samples of 1.63 % ±0.37 (SEM). It was at its highest at site T2 (Tower Bridge) (3.47 %), and its lowest at T10 (Sheerness) (0.42 %). There was a negative correlation between TOC % and distance downstream from T1 (R^2 of 0.82), likely due to the increasing presence of marine influence in the sediment (Fig. 5a). There was also a strong positive correlation between TOC and the number of microplastics (R^2 of 0.71) (Fig. 5b).

A Tmax vs HI plot was indicative of primarily fresh organic carbon components in all Thames samples (Fig. S5a). A consistent Tmax (average 413.2 °C) indicated a homogenous organic material composition, and the relatively low HI values (average 156.5 mg HC g TOC^{-1}) also reflected a persistence of primarily woody materials (which contain higher lignin concentrations) within the sediments (Disnar et al., 2003; Marchand et al., 2008). There was, however, some variation within the HI, and this was further investigated by comparing the HI and OI in a pseudo Van Krevelen diagram (Fig. S5b). This showed overall that the organic carbon was humic and of a terrestrial catchment origin (Type III kerogen), but the negative correlation between the two indices suggested some sites had more degraded carbon than others (R^2 of 0.74). Plotting both the HI and OI against distance downstream from T1 highlighted a negative correlation trend for HI ($R^2 = 0.80$), and a positive trend for OI ($R^2 = 0.61$) (Fig. S5c). This is indicative of organic material becoming increasingly degraded as it is transported downstream.

For the Medway, the average TOC in the sediment was 1.36 % ± 0.54 (SEM), with a range of 0.33 % (M5) to 3.04 % (M1). Like on the Thames, there was a correlation between TOC and distance downstream from M1 (R^2 of 0.96) (Fig. S6a). There was a weak correlation between the TOC and microplastics count (R^2 of 0.48) (Fig. S6b). The Blackwater sample (B5) contained a TOC of 0.65 %. A comparison for the Medway samples of the Rock-Eval Tmax (average 416.6 °C) and the HI (average 155.0 mg HC g TOC^{-1}) revealed a similar carbon composition to the Thames sediments; primarily fresh carbon components with a relatively low HI indicating the presence of mainly woody materials (Fig. S7a). A Van Krevelen pseudo diagram indicated the presence of humic non-marine carbon (Type III kerogen) but there was also a spread of values within this, particularly for the OI (R^2 correlation of 0.60 between the two variables) (Fig. S7b). As with the Thames samples, HI and OI were found to vary with distance downstream of M1, with a negative correlation trend for HI ($R^2 = 0.91$) and a positive trend for OI ($R^2 = 0.77$) (Fig. S7c). This is indicative of the organic material also becoming increasingly degraded as it is transported downstream.

4. Discussion

4.1. Spatial variation in microplastics

The average abundance of microplastics in the tidal Thames was lower than in the Medway, although the latter exhibited a wider range in abundance between sites, with a very high abundance at M2 (three times the total average) possibly skewing the average (average abundance of 118.9 particles kg^{-1} and 168.4 kg^{-1}, respectively). A second possibility is that there is a dilution effect whereby the microplastic input into the sediment is spread over a larger area within the larger Thames estuary as compared to the smaller magnitude catchment of the Medway. It should however be borne in mind that the variations in microplastics concentrations presented herein could be due to methodological error as no replicate evaluations of the same sediment were undertaken. Nevertheless, similar concentrations were also found in other urban river studies such as the river Tame (UK) (average abundance of 165 particles kg^{-1}) and internationally the tidal Changjiang Estuary (China) (average of 121 particles kg^{-1}) (Peng et al., 2017; Tibbetts et al., 2018). Concentrations were also similar, albeit slightly lower than, a study of large microplastics (1–4 mm) in four freshwater Thames tributaries situated further upstream than the current study (Horton et al., 2017). A significant presence of microplastics in these tributaries is indicative of upstream sources of microplastic pollution into the Thames, although it is also possible that discharge density changes and/or a dilution effect affects the behaviour and transportation of microplastics between these catchments, ultimately causing slightly lower abundance within Thames sediments.

Concentrations reported herein were, however, significantly lower than other studies of river sediments. In some cases, this may be due to differences in the hydrodynamic conditions of individual rivers — for example, the Salford Quays basin (Manchester, UK) was found to contain significantly higher average concentrations than the current study (average 914 ± 844 particles kg^{-1}) (Hurley et al., 2017). This is likely because the Salford Quays system is an urban, low energy freshwater system which would be more conducive to microplastic deposition than the Thames estuary, where higher energy flows and turbulence may cause microplastics to be transported more readily. In other cases, it

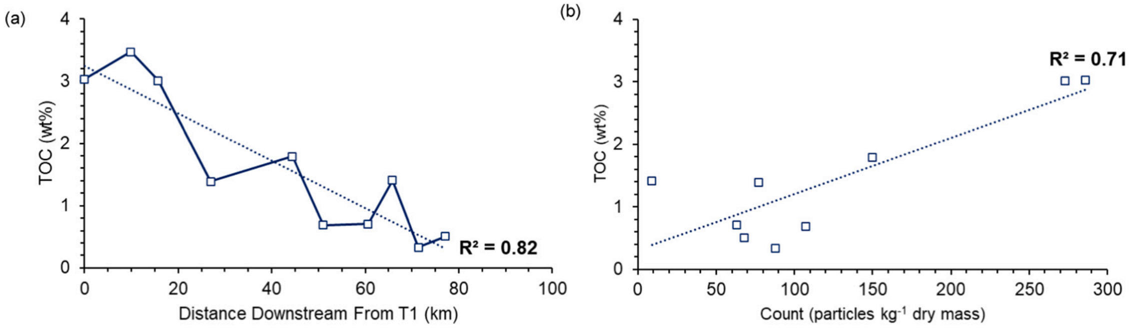

Fig. 5. Total organic carbon (TOC %) of sediment in the Thames estuary. Plot (a) depicts the relationship between the TOC for each site and the distance downstream from T1, and (b) the correlation between TOC at each site and microplastic abundance in terms of count. Dotted lines on both depict the linear trendline.

may be due to methodological differences, individual anthropogenic conditions, or other less understood conditions (see Table 1 for examples of other studies).

Both the Thames and Medway exhibited at least some downstream trend in microplastic abundance in terms of both mass and count (albeit to different degrees), likely tied to changing degrees of urbanisation. As part of this, there was a statistically significant difference between the urban London transect and the downstream estuary transect on the Thames when using count. Similar trends in abundance in relation to urban land uses have been found in other river environments, both for sediments and the water column (Yonkos et al., 2014; Mani et al., 2015; Rodrigues et al., 2018; Fan et al., 2019; Chen et al., 2021). This is likely due to urban areas having higher population densities, intensive anthropogenic activity, and also a greater potential for runoff, ultimately leading to a higher input of microplastics both through diffuse pathways and via CSOs (Yonkos et al., 2014; Mani et al., 2015; Rodrigues et al., 2018; Fan et al., 2019; Chen et al., 2021).

Despite this, Site T2 had one of the lowest concentrations of microplastics within the Thames transect. This was unexpected as it was located in the most central part of London (Tower Bridge), taken from a similar water depth to adjacent sites, and located near to CSOs like many others in the urban transect. The site was unique in that it was immediately downstream of London's congestion charge zone (CCZ), an area of the city whose land use is defined primarily by tourism and commercial activities. It may be possible that dominance of these types of activity and sediment disturbance associated boat traffic influenced the microplastic input in this area, or it may be that a recent unknown discharge event or dredging led to the dilution of microplastics within the sediment. While the abundance of microplastics on a large-scale transect therefore can demonstrate the influence of large-scale processes and contexts such as urbanisation, differences between individual sites indicate that it is also important to consider small-scale influences that can affect microplastic abundance.

In this manner, T4 had a surprisingly low concentration of microplastics, given that it was located closest to the Beckton STW outflow. STW outflows have previously been found to be major point sources of microplastics to sediments, particularly where sewage has been discharged during periods of river flow which are too low to dilute and disperse microplastics further downstream (Horton et al., 2017; Kay et al., 2018; Woodward et al., 2021). Even where microplastic removal is efficient within an STW, the large volumes of sewage processed by STWs have still been found to result in large numbers of microplastics released into the environment (Murphy et al., 2016). A study of microplastics in surface waters of the Thames found high concentrations at sites close to Beckton STW, despite low concentrations found in the sediment within this study (Devereux et al., 2023). It may therefore be plausible that turbulence associated with the tidal flow on the Thames estuary encourages the dispersion of microplastics from this source so that microplastics within the outflow are not concentrated in local sediments, rather diluted and transported further downstream within surface waters. As a consequence, the effect of the STW on sedimentary microplastic concentration may have been weakened in comparison to the wider-scale sources relating to urbanisation.

On the Medway, M2 in the centre of Rochester had the highest concentration of microplastics, with nearly three times the average count for the Medway. The high abundance at M2 is supportive of an urban elevation in microplastic abundance, but it was also located near the outflow course of a CSO point and had a significant dominance of fibres, giving credence to the notion of a microplastic source from the CSO. Incorporation of microplastics into sediment at M2 but not T4 despite proximity of both to sewage outflows is likely to be related to the individual site hydrodynamics as well as the level of sewage treatment for each outflow. The Medway is a smaller catchment than the Thames, and M2 was located between a small dock and pier resulting in a low energy environment that likely leaves less opportunity for microplastics dilution and is more conducive to deposition instead. In addition, M2 was also located on the outside bend of a meander (on the thalweg) where helical secondary flow patterns may have affected the microplastics deposition, similarly to site T3 in Deptford on the Thames, which also had one of the highest microplastic concentrations. This meander process is known to sort sediments by particle size but is yet to be shown to specifically influence microplastic distribution (Enders et al., 2019; Hoellein et al., 2019; Thompson and MacVicar, 2022). However, in this current study the high % fibres encountered at M2 suggests that helical secondary flow patterns may possibly alter microplastic distribution, increasing the proportion of fibres to particles.

Changes in channel morphology and hydrodynamic conditions may also have influenced the abundance of microplastics at the mouths of the Thames and Medway rivers. Sites T10 and M5 near Sheerness were close to one another as the furthest downstream of their respective transects, and contained very similar concentrations of microplastics. Moreover, the sediments at the two sites further upstream of M5 contained a lower concentration of microplastics than M5, and similarly the two sites upstream of T9 and T10 contained lower concentrations than T9 and T10 did. Estuary mouths and river confluences have complex flow patterns which can cause the deposition and mixing of sediments, so it may be

Table 1
Comparison of studies of microplastic abundance in river sediments. Studies marked with * were originally reported in particles 100 g^{-1} and have been adjusted to particles kg^{-1} for comparison purposes.

Study	River	Microplastic size range (μm)	Average abundance (particles kg^{-1})	Abundance range (particles kg^{-1})	Abundance range (mg kg^{-1})
This study	Thames, UK	300–5000	118.9	9–286	0.059–10.4
This study	Medway, UK	300–5000	168.4	42–484	1.1–34.6
This study	Blackwater, UK	300–5000	48	–	–
Corcoran et al. (2020)	Thames river, Canada	63–5600	612	6–2444	–
Enders et al. (2019)	Warnow Estuary, Germany	500–5000	–	2–379 ± 28	–
Horton et al. (2017)	Thames Fresh water Tributaries, UK	1000–4000	–	185 ± 42–660 ± 77*	–
Hurley et al. (2017)	Salford Quays, UK	Size range not discussed but observed microplastics ranged between 50 and 5000	914 ± 844	55.9–2543	–
Klein et al. (2015)	Rhine and Main, Germany	63–5000	–	228–3763 (Rhine), 786–1368 (Main)	21.8–932 (Rhine), 43.5–459 (Main)
Peng et al. (2017)	Changjiang Estuary, China	1–5000	121 ± 9*	20–340*	–
Rodrigues et al. (2018)	Antuã River, Portugal	55–5000	–	18–629	2.6–71.4
Tibbetts et al. (2018)	Tame, UK	63–4000	165*	20–350*	–

possible that these conditions also affected the microplastic deposition in similar ways (Fagherazzi et al., 2015; Kwon et al., 2023).

4.2. *Microplastics shape and composition*

Dominant microplastic shape varies between studies of microplastics in rivers, although in studies of estuarine environments, fibres often slightly dominate over fragments (as reviewed in Harris, 2020). However, a lack of statistical difference between microplastic fibres and fragments in either river within this study is perhaps indicative both of diverse sources of microplastics, and high levels of mixing, across surface sediments in both the Thames and Medway. Alternatively, other studies have suggested that sieve-based methods such as that used herein are preferentially biased toward fragments as compared to fibres, therefore it is possible that the similar yields of fibres and fragments presented herein is in part driven by the separation method.

Similarly, the types of microplastic material identified via FTIR did not significantly vary between sites on the Thames or Medway, indicating also that the microplastic material inputs were well mixed and of varied sources across the respective river basins. The Blackwater sample contained several polystyrene particles which were not present in any samples from the other basins; more study sites would be required for a clearer comparison but could indicate a different source of microplastic on this river. Despite this difference, the dominant plastics found in all samples were those that are most frequently manufactured, suggesting that microplastics in the sediment samples were a good reflection of plastics in circulation (Plastics Europe, 2023). This is in agreement with several other studies of microplastics in river sediments (Nor and Obbard, 2014; Peng et al., 2017; Tibbetts et al., 2018; Enders et al., 2019).

In a previous study of the upper Thames estuary, large plastic items flowing along the riverbed were found to be dominated by single-use plastics such as food packaging and sanitary towel components which were suggested to be of likely sewage-related origin (Morritt et al., 2014). Single-use plastics are typically made of polymers like polyethylene and PET, matching the most commonly identified polymer types in this study. It may be that a large portion of the secondary microplastics found in this study are therefore of a similar origin, having broken down from larger plastic waste items either before or after they entered the estuary and were incorporated into the sediment. In agreement, a study of microplastic abundance in the water column of the Thames estuary also found a dominance of polyethylene microplastics (Rowley et al., 2020), although another instead found a dominance of polyvinyl chloride (PVC) and polystyrene (Devereux et al., 2023).

4.3. *Microplastics, particle size and organic matter*

Relatively few studies investigating microplastics in sediments have examined the relationship between microplastic abundance, particle size and TOC. Conclusions so far have been conflicting, with some finding a clear relationship between the factors where fine-grained sediments and organic matter abundance increased microplastic concentrations, while others have been unable to confirm one (Vianello et al., 2013; Alomar et al., 2016; Maes et al., 2017; Peng et al., 2017; Enders et al., 2019; Haave et al., 2019). The current study was unable to find a strong correlation between microplastic abundance and particle size, which may in part be due to the complex tidal hydrodynamics of the Thames estuary, with marine influences affecting the particle sizes.

There was, however, a positive correlation found between the microplastic abundance and the TOC, through which microplastic abundance increased as the TOC increased. Organic matter (range of densities between approximately 1.2–1.4 g cm^{-3}) has a bulk density range more similar to microplastic particles (range of densities between approximately 0.89–1.6 g cm^{-3}) than sediment particles (approximate density of quartz = 2.65 g cm^{-3}) (Haan et al., 1994; Enders et al., 2019). The organic matter in the Thames was also primarily of terrestrial origin (similarly to the majority of microplastics), which in combination with the overlapping bulk density may lead it to behave more similarly to microplastic particles than sediment particles, generating a covarying correlation between the two variables. Other comparisons of microplastic and organic matter behaviour in rivers have described similar relationships (Enders et al., 2019; Hoellein et al., 2019). Further understanding of this relationship could therefore help to refine understanding of microplastic behaviour, particularly in complex hydrodynamic conditions.

5. Conclusions

This study indicates for the first time the extent of microplastic pollution in Thames estuary, river Medway, and river Blackwater sediments, falling within the range of concentrations found in other tidal estuaries around the world. Urban regions were identified as particular hotspots of microplastic contamination, while the influence of Beckton STW on the abundance in sediments was not found to be significant. However, a CSO in Rochester was identified as a possible significant source of microplastics (especially fibres) to sediments in the river Medway. Differences between individual sites on all rivers were attributed to a range of site hydrodynamic conditions, from proximity to the river mouth, to turbulence, and dilution events. It is therefore likely that microplastic abundance was affected by both by large- and small-scale processes and conditions, highlighting that both should be considered when investigating microplastic behaviour and consequences in these environments.

Fragments and fibres were found in similar abundance at each site, indicating mixed microplastic sources and/or internal mixing of microplastics within the river. Similarly, most sites had a trend of polyethylene, PET, and polypropylene dominating the microplastic record, indicating that microplastics in these sediments are a good reflection of plastics in circulation. While the concentration of microplastics did not correlate with the sediment particle size, a possible relationship between microplastic abundance and TOC was established, which may in future help to develop understanding of microplastic behaviour in complex hydrodynamic environments.

CRediT authorship contribution statement

Megan M. Trusler: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Vicky L. Moss-Hayes:** Formal analysis. **Sarah Cook:** Writing – review & editing, Supervision, Conceptualization. **Barry H. Lomax:** Writing – review & editing, Supervision, Conceptualization. **Christopher H. Vane:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2024.116971.

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