



In situ correlation between microplastic and suspended particulate matter concentrations in river-estuary systems support proxies for satellite-derived estimates of microplastic flux

Emma Sullivan^{a,*}, Matthew Cole^a, Elizabeth C. Atwood^a, Penelope K. Lindeque^a,
Pham Thi Chin^b, Victor Martinez-Vicente^a

^a Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, United Kingdom of Great Britain and Northern Ireland

^b Department of Natural Resources and Environment, Da Nang, Viet Nam

ARTICLE INFO

Keywords:

Marine plastic
Remote sensing
Suspended particulate matter
Tamar estuary
Water quality

ABSTRACT

Rivers are key pathways for transporting microplastics from land to the oceans, yet microplastic flux estimates remain uncertain. Remote sensing allows repeated broad-scale measurements and can be used to extrapolate limited *in situ* observations. This study investigated the relationship between suspended particulate matter (SPM), a satellite-observable water quality parameter, and microplastic concentration in a partially mixed estuary (Tamar, UK). Microplastic concentrations ranged from 0.04 to 0.99 microplastics/m³, decreasing downstream. A significant correlation was found between SPM and microplastic concentration over two seasons. This relationship was used to compute a multiyear timeseries of proxy microplastic concentration from satellite imagery and produce estimates of annual proxy microplastic flux. This approach could be applied to investigate microplastic flux in other major rivers worldwide where such a relationship between microplastics and SPM exists. To apply this workflow elsewhere, the establishment of local SPM-to-microplastic relationships from *in situ* observations and local validation of remote sensing SPM algorithms are essential.

1. Introduction

Microplastics (plastic particles <5 mm in size) are pervasive in aquatic ecosystems (Hale et al., 2020). Evidence of microplastic contamination has been found in the water and sediments of marine and freshwater systems across the world, from urban rivers and beaches to remote lakes and oceans (MacLeod et al., 2021). This widespread presence of microplastics is a concern because of their persistence in the environment and the toxicological risks they pose to biota (Hampton et al., 2022). As a result, microplastic pollution has been included in several national and international laws and directives for the protection of the marine environment, including the EU Marine Strategy Framework Directive (MSFD, 2008/56/EC) and the UN Sustainable Development Goal (SDG) 14. Microplastic pollution will also be a feature of the proposed intergovernmental agreement to address plastic pollution – the global plastics treaty, which is hoped to include the prevention and remediation of plastic leakage into the environment. In order to monitor and evaluate progress in reducing plastic pollution, quantitative information on the amount of microplastics entering the marine environment

over time is needed through an integrated observing system (Maximenko et al., 2019).

Rivers have been identified as the major transitional pathway of plastics into the ocean, delivering an estimated 0.4 to 4 million tonnes of plastic annually (Lebreton et al., 2017; Schmidt et al., 2017; Meijer et al., 2021; van Emmerik et al., 2023). Considering microplastics alone, flux estimates range from 6.1 thousand to 1.5 million tonnes year⁻¹ (Boucher and Friot, 2017; Weiss et al., 2021). The current methods available to quantify and monitor microplastic fluxes are based on localised, time and resource intensive *in situ* sampling, laboratory analysis and large-scale modelling approaches (Lebreton, 2017; Schmidt et al., 2017; van der Wal et al., 2015). Significant uncertainty remains in these estimates of the overall scale of microplastic transport and our understanding of how fluxes vary in space and time is incomplete. This is in part because data on the abundance of microplastic in rivers and estuaries are relatively limited, being both spatially and temporally restricted to discrete sampling campaigns in selected rivers concentrated in Europe, North America and South-East Asia (Weiss et al., 2021). Where these measurements are available they show a large range, even

* Corresponding author.

E-mail address: emsu@pml.ac.uk (E. Sullivan).

<https://doi.org/10.1016/j.marpolbul.2023.115529>

Received 3 August 2023; Received in revised form 5 September 2023; Accepted 7 September 2023

Available online 28 September 2023

0025-326X/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

when differences in sampled size ranges are corrected for, from less than one to thousands of particles per m^3 (Weiss et al., 2021; Bai et al., 2022). This range may in part be accounted for by differences in river catchment characteristics such as land use, microplastic sources and sinks, as well as local hydrogeomorphological conditions and weather (Bai et al., 2022). Even within a single river system microplastic concentrations can vary significantly in space and time (Haberstroh et al., 2021; Munari et al., 2021). To capture this spatiotemporal variability in microplastic distribution, repeated and widespread measurements are required, requiring huge investment of time, resources and funding.

Satellite remote sensing can provide regular observations over large areas and therefore has been identified as a tool which could provide insights into the spatiotemporal dynamics of macro- and microplastic litter and fill gaps between *in situ* observations (Martínez-Vicente et al., 2019; Maximenko et al., 2019). However, directly detecting microplastic is challenging because particles are not present at high enough concentrations to alter the water optical reflectance signal (Hu, 2021). In addition, river mouths are often characterised by highly turbid and optically complex waters which makes the accurate detection of water constituent concentrations more challenging. Given these challenges, Piehl et al. (2020) explored the relationship between microplastics and optically active water constituents, including chlorophyll-*a* concentration, coloured dissolved organic matter absorption and suspended particulate matter concentration in three European estuaries to assess their applicability as potential proxies for microplastic distribution. A relationship between water constituents and microplastics ($>300 \mu\text{m}$) could be established for one river, the Trave, however no relationship was present for the Po delta or Elbe estuary. The results suggested that the relationship between water constituents is likely to be unique to each river system due to differences in hydrodynamic conditions and spatiotemporal dynamics of water constituents, as well as the local microplastic sources and sinks. Therefore further investigations are needed to assess the applicability of water constituent proxies for microplastic concentration. The authors also suggest that the lower size limit for microplastic of $300 \mu\text{m}$ may have influenced the results, as microplastic abundance increases exponentially with decreasing size class (Haave et al., 2019; Lindeque et al., 2020).

In large rivers and estuaries, SPM is a commonly retrieved water quality parameter from satellite and is cost-effective and labour-efficient to monitor *in situ*, so is a good candidate for operational monitoring (Nechad et al., 2010; Doxaran et al., 2015; Piehl et al., 2020). SPM comprises particles greater than approximately $0.7 \mu\text{m}$, with a mixture of sizes, densities and morphologies. Particle size and make up of SPM in turbid waters is dynamic and physical and biological processes driving these dynamics are complex (Fettweis et al., 2014). Waterborne microplastics are part of this diverse pool of suspended particles (Rochman et al., 2019), so it is anticipated they will show some correlation with the larger fraction of SPM. Therefore, it is hypothesised that a spatial relationship could exist between the two if they follow similar transport dynamics. Where this relationship can be established, satellite derived maps of SPM could be used to estimate microplastic concentrations and provide a simple technique to monitor and report microplastic concentrations (Piehl et al., 2020).

In this study, we expand the dataset of microplastic concentrations ($200 \mu\text{m} > D > 2.5 \text{ cm}$) in a complex estuarine environment, with sampling focussed on the River Tamar (UK), and determine if a relationship between SPM and microplastic concentration can be established. Encouraged by our results, showing a significant correlation among those variables, we use this correlation as suggested by Piehl et al. (2020), to compute maps of proxy microplastic concentrations, and then propose a prototype methodology to estimate proxy microplastic flux using satellite ocean colour remote sensing. This method allows the extrapolation of limited *in situ* samples to examine the temporal trends of proxy microplastic concentration and flux in an UK estuary. This work highlights the need for further investigation of the dynamics of suspended particulate matter and microplastics in estuarine environments.

While further investigation of the sources of uncertainty is needed, the workflow proposed in this study could be applied to other large rivers globally where a water quality proxy relationship can be established to improve our understanding of the spatiotemporal dynamics of microplastic litter. This approach is cost effective and less time consuming than traditional microplastic sampling used for monitoring.

2. Materials and methods

2.1. Study area: Tamar River

Sampling was conducted in the River Tamar in the Southwest of England (UK; Fig. 1). The Tamar catchment drains an area of 1800 km^2 (Environment Agency, 2012). The estuary extends approximately 22 km inland to Gunnislake (Environment Agency, 2012). At Gunnislake (station 47001 in Fig. 1), the Tamar has an average annual discharge of $23 \text{ m}^3/\text{s}$ (UK CEH, 2022) and in its lower reaches it is also fed by the tributaries Tavy, Lynher and Tiddy. The catchment is primarily rural and agricultural but does contain several major settlements including the city of Plymouth in the lower reaches of the estuary, with a population of over 341,000 people (Environment Agency, 2012).

2.2. In situ sampling

Sampling was conducted at high tide along a 35 km transect, from close to the river's tidal limit (Calstock) to the edge of the riverine plume (L4 station). Sampling was conducted in both dry (Summer; $n = 5$ sites) and wet (Autumn; $n = 5$ sites) seasons (Fig. 1, Supplementary information Table S1). Two research vessels were used to collect samples: (1) RV Quest, a 21.5 m long scientific vessel for deployment in the coastal waters of the Plymouth Sound; (2) RV Explorer, a rigid inflatable boat used to sample in the Tamar estuary. In Autumn 2021, the RV Quest was out of commission for an extended period, and therefore only riverine samples were collected in this campaign. For both campaigns, sampling started in Calstock and followed the ebbing tide downstream. Warm, dry and low wind conditions preceded the sampling date in July 2021, whereas on average cooler temperatures, higher rainfall and stronger winds preceded sampling in October 2021 (Supplementary information Table S2).

At each sampling location, discrete water samples were collected via manual submersion of a stainless steel bucket (RV Explorer) or from the seawater supply system (RV Quest) for SPM and turbidity analysis. These samples were kept in a dark coolbox then transferred to a fridge at the laboratory until further processing. Microplastic samples were collected from surface waters using $200 \mu\text{m}$ mesh plankton nets (0.6 m diameter circular aperture). Nets were trawled for 5–10 min at approximately 0.5–1.5 knots with the net aperture half-submerged to capture surface and sub-surface microplastics. Following the trawls, the outside of the nets were washed with seawater to ensure the sample was fully collected in the cod end then the sample was poured through a $200 \mu\text{m}$ nylon mesh. Any macrodebris (e.g. seaweed) was rinsed with ultrapure water to dislodge adhered microplastics (collected on mesh) and then removed from the sample. The mesh was then folded in on itself to encapsulate the sample, wrapped in aluminium foil and placed in a ziplock bag. In the laboratory, samples were stored in a $-20 \text{ }^\circ\text{C}$ freezer prior to analysis. To limit contamination of samples: (1) nets were deployed to the side of the boat to avoid particles from the ship's hull entering the sample; (2) personnel were advised to minimise sample handling and cover samples promptly to avoid fibres from clothing or airborne dispersal entering samples; (3) equipment was rinsed with seawater and ultrapure water between sampling to avoid cross-contamination. To account for any contamination during sampling and sample processing, procedural blanks ($N = 2$ per research vessel per season), were collected by pouring 1 L of ultrapure water into the cod-end and treating as a standard sample.

To account for the riverine flow in the Tamar estuary, a portable

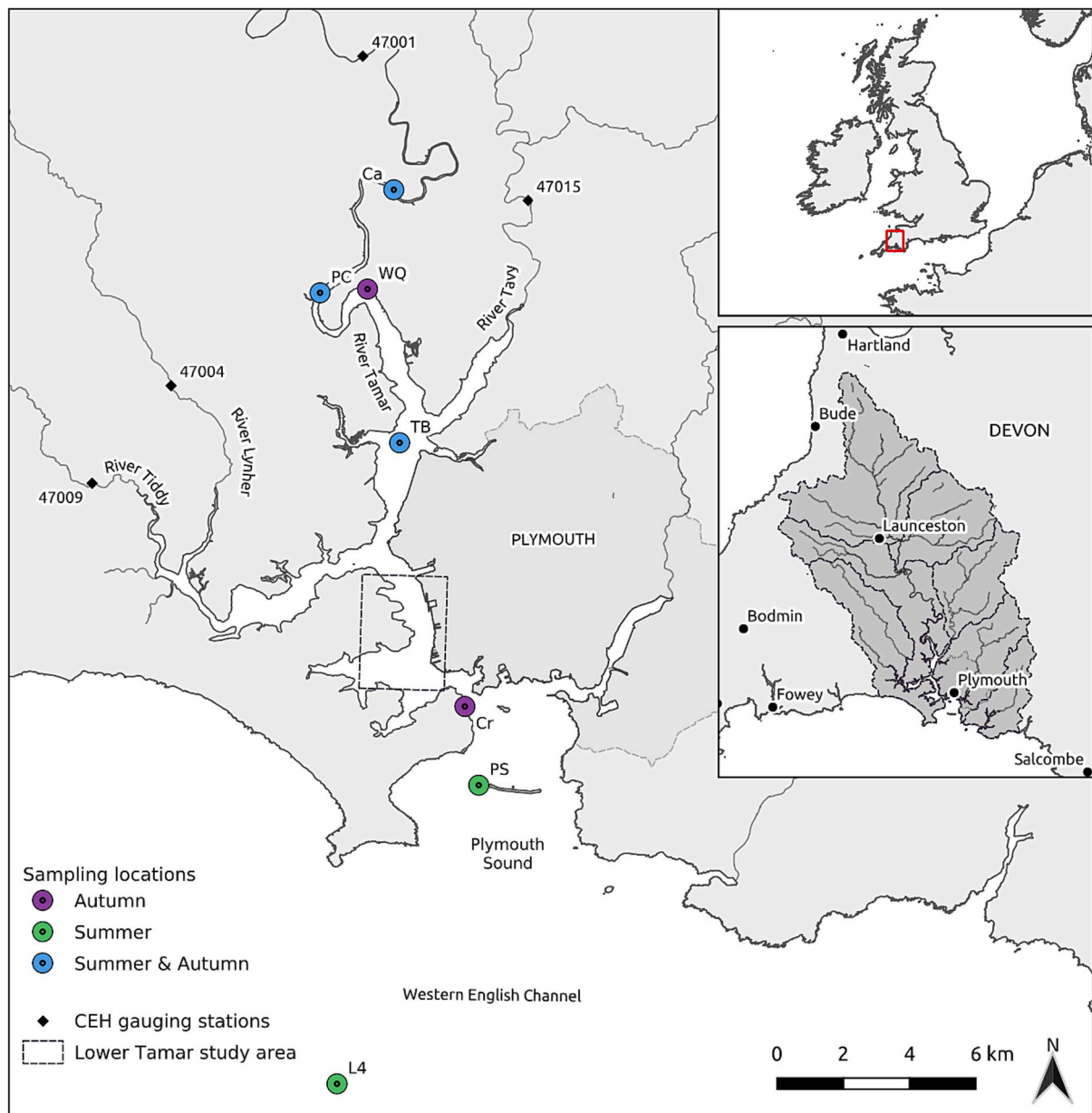


Fig. 1. Map showing sampling locations along the River Tamar and study area used for remote sensing analysis. Site names: Ca - Calstock, PC - Pentillie Castle, WQ - Weir Quay, TB - Tamar Bridge North, Cr - Cremyll, PS - Plymouth Sound, L4 - L4 station. Insets show the catchment location relative to the UK (top) and the Tamar management catchment (below). Source data from OpenStreetMaps and DEFRA.

flowmeter (Valeport Model 801) was deployed from the RV Explorer and mean flow rates recorded three times for each trawl. For coastal samples (*i.e.* L4, Plymouth Sound), where flow rates are very low, tow length was based on start and end coordinates alone. For riverine samples, where flow rates were highly variable depending on direction of travel and state of tidal flow, the tow length (L) was calculated using mean flow rates (Q) and trawl duration (t), where: $L = Q \cdot t$. Per Cole et al. (2014), the volume of water sampled (V) was calculated based on tow length (L) and net aperture radius (r), accounting for the net being half-submerged and applying a 95 % efficiency for using nets, where: $V = (\pi^2 \times 0.5) \times L \times 0.95$.

2.3. Water constituent analysis

Turbidity was measured in the laboratory with a VWR Portable Turbidity meter TIR 500©. SPM was obtained by filtering variable water volumes (0.25 to 4 l per filter) on pre-ashed and pre-weighted 47 mm

GFF Whatman© glass fibre filters in triplicate following methods in Martinez-Vicente et al. (2010), with the modification on rinsing only the filled filtering funnels with de-ionised water (Röttgers et al., 2014). Blanks were obtained for each sample by re-filtering the filtrate. Samples on filters were dried for at least 24 h in a 60 °C oven then weighed on an electronic balance (Oxford, A2205D). The median coefficient of variation of the replicates across all samples for the two days ($N = 13$) was 4 %.

2.4. Microplastic sample processing

Isolation, enumeration and characterisation of microplastics was conducted in Plymouth Marine Laboratory's ultraclean positive-pressure laboratory dedicated to microplastic research. To visualise microplastics in samples, it was necessary to disaggregate and digest the organic material in the samples. An alkaline-surfactant solution containing 0.2 µm filtered 10 % potassium hydroxide (KOH) and 0.01 % Tween 20

surfactant was used to carefully wash samples off the mesh squares into 250 mL conical flasks. Flasks were topped up with ~100 mL of the same alkaline-surfactant solution, then covered with aluminium foil and parafilm to prevent contamination and maintained at 50 °C for 48 h on a shaking incubator (Stuart Scientific S150; 125 rpm). Following digestion, samples were vacuum filtered through 47 mm diameter 200 µm mesh discs; where samples contained copious amounts of undigested materials, multiple mesh discs were used. Mesh discs were stored in pre-labelled Petri dishes and stored at -20 °C prior to microscopic analysis.

Mesh filters were systematically analysed under an Olympus SZX16 stereomicroscope (x25 magnification) by an experienced analyst. Suspected microplastics ($N = 778$) were identified based upon their shape, colour, texture and hardness. All suspected microplastics with distinct characteristics were classified by shape (*i.e.* fibre, fragment, bead), colour and size, with both longest and shortest dimensions measured using CellSens® software (Olympus).

A subsample of putative microplastics ($N = 228$; 30 % of total) were analysed using a Perkin Elmer Spotlight 400 imaging system comprised of a PerkinElmer Frontier Fourier transform infrared (FT-IR) spectrometer (MCT detector, KBr window) and PerkinElmer Spotlight 400 microscope, with SpectrumIR software (PerkinElmer, 2017, version 10.6.0.893). Per the method of Cole et al. (2023), in most samples, all putative microplastics were selected for polymeric analysis, however in samples containing a high frequency of particles of consistent morphology, only a representative sub-sample were selected. Resultant spectra were compared against in-house, published and commercially available spectral databases. The FT-IR data was used to determine the analyst's success rate in selecting microplastics from samples, and this metric applied to unidentified particles to more accurately estimate microplastic numbers in each sample. Contamination identified in procedural blanks was used to correct environmental datasets in two ways: (1) in one procedural blank, 4 clear polyethylene fragments were identified; as presence of fragments in blanks is unusual, and their source could not be established, clear fragments present in environmental samples ($n = 4$) were removed from the dataset; (2) plastic microfibrils, which are more common contaminants in blanks, were enumerated ($n = 11$); the average microfibre count per blank (2.2 microplastics per sample) was subsequently used to adjust all microplastic counts in the environmental dataset. Microplastic counts were adjusted to microplastics per cubic metre by accounting for sample volume.

2.5. Satellite data

Satellite ocean colour data was obtained from Sentinel 3A and 3B's OLCI sensors at 300 m resolution for passes between March 2016 to December 2021. Sentinel 3 OLCI was chosen because of its high temporal resolution, which increases the probability of capturing hydrological events and cloud free images. The Level 1 Sentinel 3 OLCI scenes were downloaded and subset to the Tamar area, atmospherically corrected using POLYMER v4.12 and cloud was masked using IdePix. Although it was designed for case-1 waters, POLYMER has been previously tested in optically complex waters and been shown to perform well compared to alternative processors (Qin et al., 2017; Warren et al., 2019). SPM concentration was computed from the atmospherically corrected remote sensing reflectance with the single band algorithm from Nechad et al. (2010) using the 709 nm band.

2.6. Proxy microplastic concentration and microplastic flux

Proxy microplastic concentration was computed from the SPM images using the SPM to microplastic abundance concentration relationship derived from the *in situ* sampling. It is assumed here that this relationship is valid for the entire period of satellite observations. Proxy microplastic concentration was computed for a study area defined in the lower Tamar (Fig. 1). S-102 bathymetry data from the UK Hydrographic

Office were used to select pixels in this area with a water column depth >5 m for analysis. Note that although this selection excludes any pixels partially over land or shallow water, due to the narrow width of the Tamar, adjacency effects may remain. The selected pixels were averaged to compute a daily median proxy microplastic particle concentration for the Lower Tamar. Scenes with <10 % valid pixels in the study area were excluded from the analysis.

The microplastic flux (or microplastic transport) was computed for each month by multiplying the month-averaged proxy microplastic concentration (particles/m³), the month-averaged river discharge (m³/s) by the duration (in seconds) of the month following the methodology proposed by Doxaran et al. (2015). This is a simplified approach to give an estimate of the average microplastic flux without requiring the measurement of vertical profiles of current velocities (Doxaran et al., 2015). The month-averaged proxy microplastic concentration was calculated by creating monthly median composite images, then taking the median pixel value in the study area to give a single value per month. Numerical concentrations (particles/m³) were converted to a mass concentration (g/m³) by multiplying an average microplastic mass 0.09 mg, calculated using the percentage fraction of plastic fibres and non-fibres from the *in situ* samples and average mass conversion factors from Weiss et al. (2021) (Supplementary information Eq. S1). Daily mean river discharge was obtained from the Environment Agency for four gauging stations upstream of the river mouth and summed to give an estimate of the daily mean river discharge for the lower Tamar (Supplementary information Fig. S2). The median of these daily river discharge values for each month was used as the month-averaged river discharge. Estimates of annual microplastic flux were calculated by taking the sum of the monthly median microplastic mass fluxes for each complete year.

3. Results

Microplastics were identified in all samples, with concentrations ranging from 0.04 to 0.99 microplastics m⁻³ with a mean value of 0.42 m⁻³. Microplastic concentrations were found to be higher in the upper reaches of the Tamar in both seasons (Fig. 2a). The samples covered a broad salinity range, from 0.1 psu at Calstock to 34.9 psu at L4. Microplastic concentration was found to have a significant negative relationship with salinity in both sampling campaigns (Summer $R^2 = 0.788$ $p = 0.04$, $N = 5$; Autumn $R^2 = 0.775$ $p = 0.05$, $N = 5$) and a positive relationship with distance from the Plymouth Sound, measured as the distance along river from Devil's Point (Summer $R^2 = 0.91$ $p = 0.01$, $N = 5$; Autumn $R^2 = 0.627$ $p = 0.11$, $N = 5$) (Fig. 2b). At the three sites where samples were collected in both seasons, microplastic concentrations were all notably higher in the Summer (Fig. 2a).

Of particles confirmed to be plastic, 60 % were fibres, 39 % were fragments and only a single bead (1 %) was identified; the majority were black (36 %), clear (19 %) or blue (18 %) (Fig. 3). Particles were highly variable in size, with smallest dimensions ranging 15 µm - 3.5 mm.

SPM in the Tamar estuary samples ranged from 0.65 g/m³ to 49.81 g/m³. SPM also generally decreased with distance downstream along the Tamar estuary and demonstrated a negative bilinear relationship with salinity. Turbidity also conforms to a similar decreasing trend towards offshore. There is a strong positive correlation between SPM and turbidity ($R^2 = 0.99$, $p < 0.01$, $N = 10$). Seasonally, the linear regression model explains a similar amount of variance in both seasons (Summer $R^2 = 0.96$, $N = 5$, Autumn $R^2 = 0.95$, $N = 5$).

A significant relationship was found between log transformed *in situ* microplastic and SPM concentration from the Tamar (Fig. 4, $N=10$, $F=22.8$, $P=0.001$, $R^2=0.74$) and is formulated with the equation:

$$\log_{10}(\text{MP}) = -1.081 + 0.7811 \log_{10}(\text{SPM}) \quad (1)$$

When analysed by season, the relationship was stronger in the summer samples ($R^2: 0.80$, p -value: 0.04, $N = 5$) than in the autumn samples ($R^2: 0.68$, p -value: 0.085, $N = 5$) (Fig. 4). However, this should

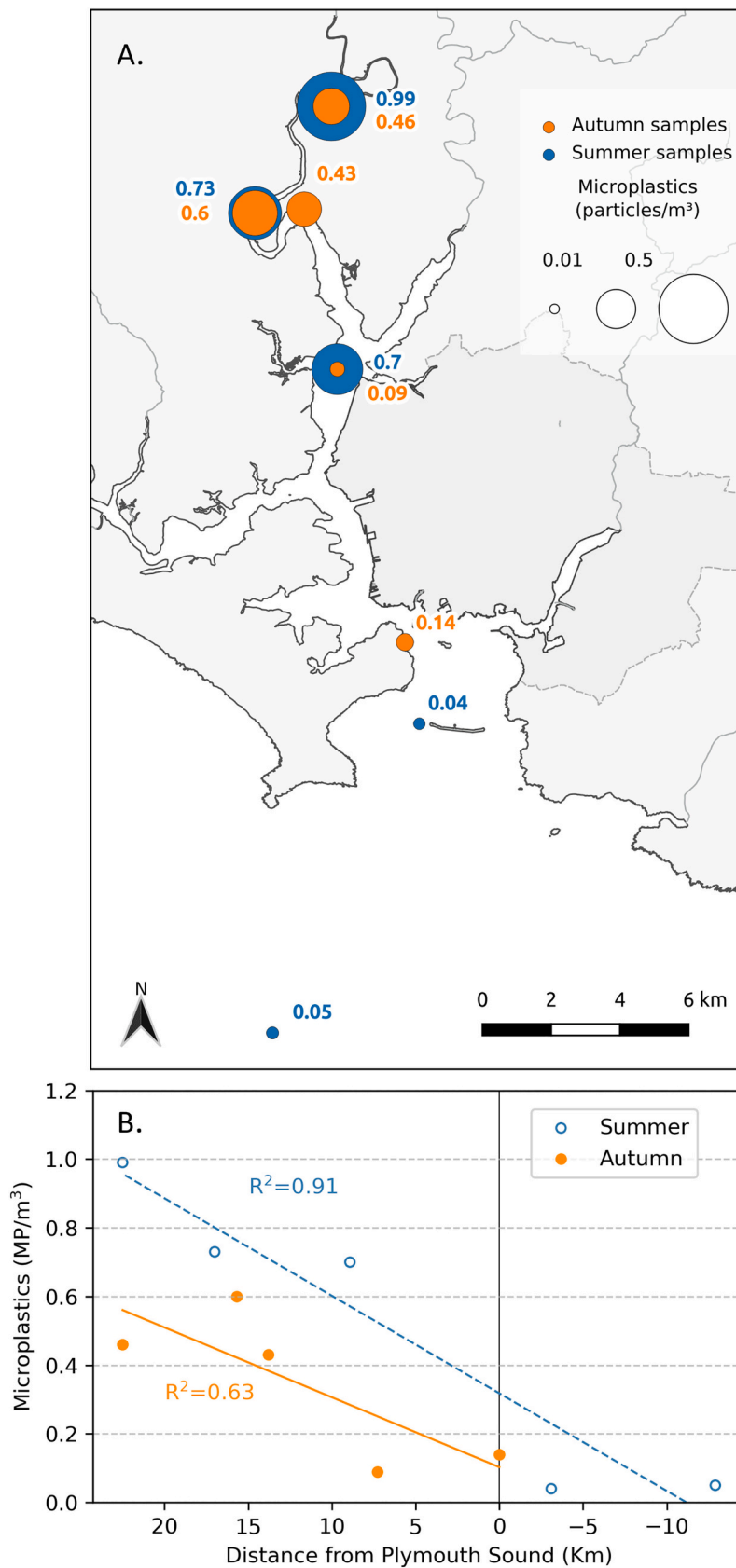


Fig. 2. Microplastic concentrations: (A) mapped at the different stations, for the Summer (•) and Autumn (•) 2021 campaigns. (B) With respect to distance to Plymouth Sound. Positive x-axis values are upstream of Plymouth Sound, negative values are towards offshore.

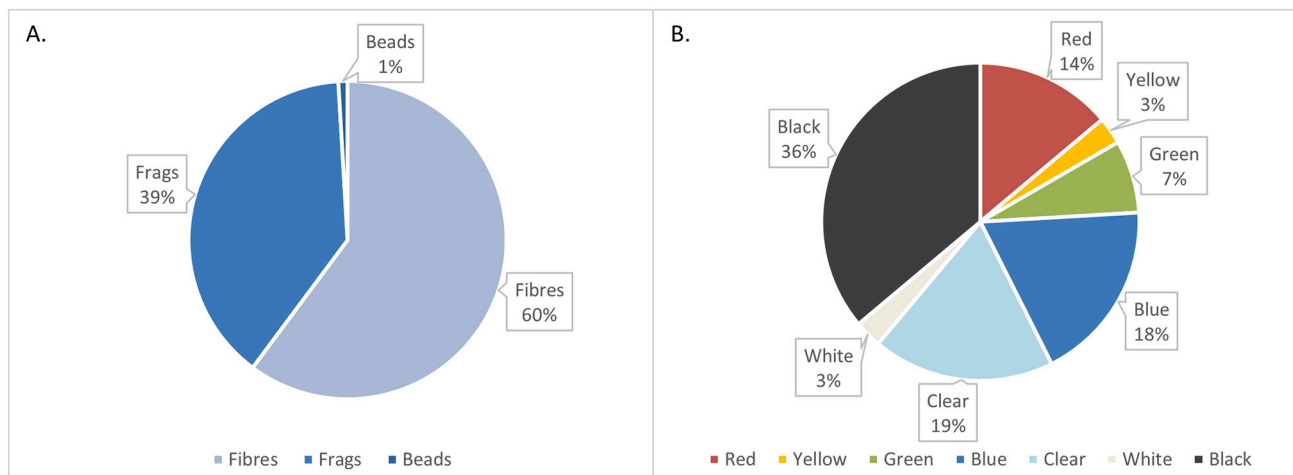


Fig. 3. Microplastic (A) shape and (B) colour composition from all confirmed plastic samples.

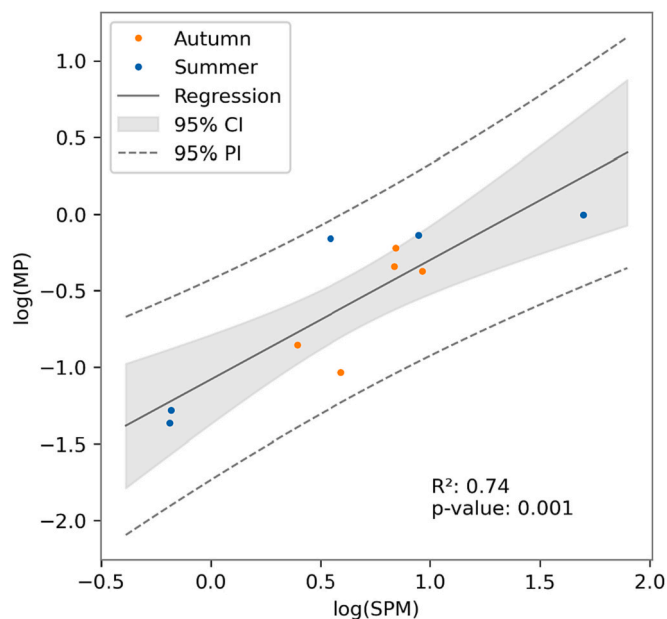


Fig. 4. The SPM to microplastic relationship from all samples from the Tamar, UK coloured by sampling campaign.

be interpreted with caution due to the limited number of samples in each season, differences in sites sampled and on the ranges of SPM.

To illustrate how this relationship could be used to provide an insight into the spatial and temporal variations in proxy microplastic concentrations in the Tamar estuary, Eq. 1 was used to convert satellite-derived SPM concentration maps to microplastic concentration maps. The daily median microplastic particle concentration values over the study area were plotted against time to produce a timeseries for the lower Tamar (Fig. 5). The nearly 6-year timeseries indicates proxy microplastic concentration displays a seasonal pattern, with concentrations generally lowest from May to September and highest between December to March. The daily median proxy microplastic particle concentration ranged from 0.002 to 1.028 microplastics/m³.

Data on freshwater discharge from the Environment Agency showed a seasonally variable discharge rate, with the highest average flows in October to March and lower values between April to September (Supplementary information Fig. S2). Over the study period discharge varied between ~4 and 484 m³/s. The daily median proxy microplastic concentration and river discharge were positively correlated (Fig. 6), with

river discharge accounting for 48 % of the variability in proxy microplastic concentration.

The monthly proxy microplastic flux from the lower Tamar to the ocean was estimated following the methodology proposed by Doxaran et al. (2015). The proxy microplastic flux timeseries revealed large seasonal variations, with generally low flux rates in the late spring to summer and higher in winter, which can largely be explained by the seasonal variability in the Tamar River's discharge. The estimated microplastic flux ranged from 0.78×10^6 to 166.64×10^6 particles/month, or approximately 0.07 to 15.0 kg/month, for the lower Tamar over the period of Sentinel 3 observations (Fig. 7). The annual microplastic flux estimates range from 304×10^6 – 477×10^6 particles (or 0.027–0.043 t).

4. Discussion

In situ observations of microplastics abundance and SPM have shown a positive correlation in a UK estuary. From these observations, >70 % of the variability in microplastics is explained by the variability in SPM, using a bi-log regression model. We have used this model to propose a workflow to map proxy microplastics concentrations from satellite remote sensing and provide some initial estimates for monthly and annual fluxes. This approach has several important caveats and limitations that are discussed hereafter, but opens up questions for future research.

4.1. Microplastics in the Tamar

To the authors' knowledge this is the first study providing waterborne microplastics data for the transitional waters of the Tamar estuary, with prior studies having focussed on estuarine sediments and waterborne concentrations at the river mouth, within the Plymouth Sound and western English Channel (Browne et al., 2010; Cole et al., 2014; Sadri and Thompson, 2014). The marine sites had microplastic concentrations of 0.04–0.14 microplastics m⁻³, which is of a similar magnitude to previous studies in this area. For example, Sadri and Thompson (2014) found concentrations of 0.03 microplastics m⁻³ collected using a 300 µm manta net near Cremyll in May–July 2012 and Cole et al. (2014) identified concentrations of 0.26 and 0.31 microplastic m⁻³ at Plymouth Sound and L4 collected using 200 µm nets in October 2013. Lindeque et al. (2020) identified higher concentrations of 2.4–3.6 microplastics m⁻³ using 333 µm nets across Plymouth Sound in August 2015. Differences in plastic concentrations may be explained by: (1) the spatio-temporal variability in microplastic concentrations, influenced by weather, riverine outflow, tidal cycle and inputs from point-sources

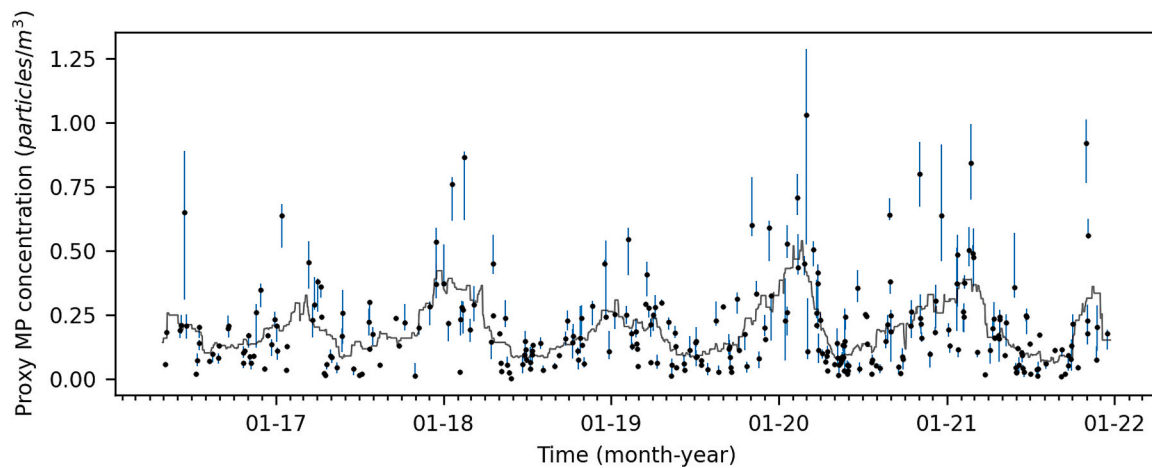


Fig. 5. Daily values of proxy microplastic concentration for the lower Tamar. Central values are median of predicted proxy microplastic concentration over the area selected in Fig. 1. Vertical lines show the interquartile range over the area, the grey line shows the 60-day rolling mean.

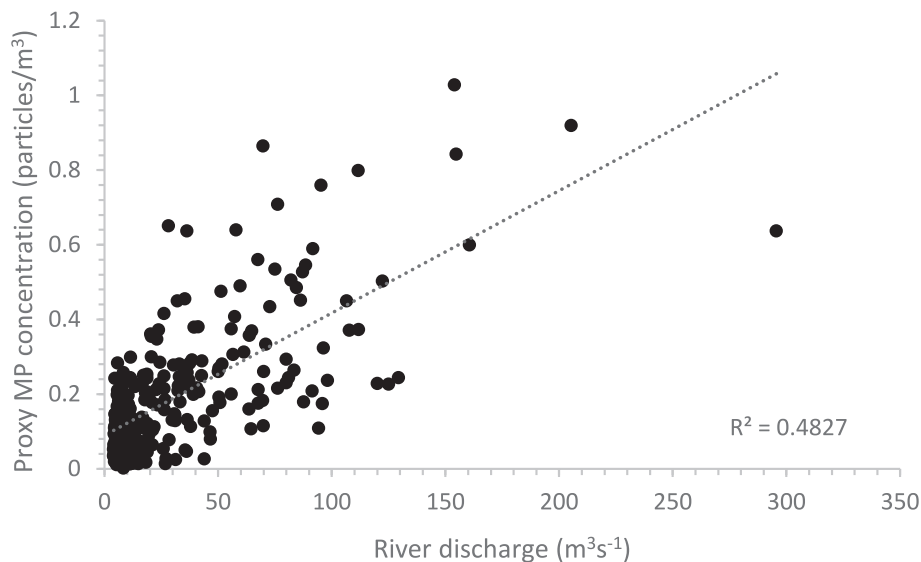


Fig. 6. Daily proxy microplastic concentration as a function of the river daily mean flow.

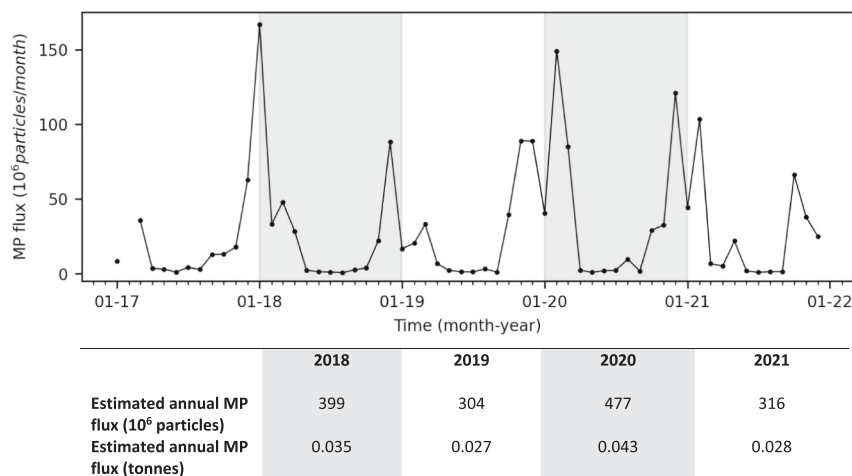


Fig. 7. Top: monthly median proxy microplastic flux computed for the lower Tamar. Bottom: annual estimated microplastic flux from the Tamar calculated for each complete year.

such as sewage and wastewater treatment plants (Skalska et al., 2020); (2) methodological differences, for example Cole et al. (2014) and Lindeque et al. (2020) used an enzymatic digestion protocol to remove organic material from the sample, which while more time-consuming, may reduce loss of some polymers via chemical degradation (Lusher et al., 2017), as well as including cellulosic microfibrils within their microplastic counts. The microplastic concentrations observed upstream in the Tamar estuary ($0.09\text{--}0.99\text{ m}^{-3}$) are within the lower end of the range of values reported for other European rivers (Table S3) and orders of magnitude lower than have been recorded in major river systems elsewhere in the world (Weiss et al., 2021; Bai et al., 2022).

Although the relationships are often not straightforward, previous studies have shown densely populated urban areas can contribute to higher microplastic concentrations in nearby rivers via wastewater and sewage outflows, industry, highway drainage, run-off and littering (Yonkos et al., 2014; Mani et al., 2016; Tibbetts et al., 2018; Luo et al., 2019; Yan et al., 2019). Given this, it would be expected that the conurbations of Saltash, Torpoint and Plymouth on the lower reaches of the river Tamar would result in relatively high microplastic concentrations at the mouth of the river. However, our results demonstrate microplastic concentrations decrease from the tidal limit near Calstock (~23 km upstream of the river mouth) to the edge of the riverine plume near L4 (~12 km off-shore) in line with SPM concentrations. In the Tamar estuary, this trend may be explained by three main factors: (1) increased microplastic settlement due to salinity gradients and converging currents that effectively reduce hydrodynamic flow and facilitate particle aggregation and settlement resulting in microplastic deposition throughout the estuary. This theory is supported by a prior study which evidenced high- and low-density micro- and macroplastics are prevalent in sediments throughout the Tamar estuary (Browne et al., 2010). (2) The dilution effect of mixing with incoming tidal waters and additional freshwater inputs downstream. (3) The accumulation effect in the upper reaches of the estuary from a tidal intrusion front. On a flooding tide, the inflow of seawater into an estuary, particularly estuaries with a narrow entry point such as the Tamar, can create a salinity driven, tidal intrusion front, easily distinguished by a change of colour and trapping of foam (Largier, 1992). These tidal fronts have been associated with trapping of flotsam, bivalve larvae (Shen et al., 1999), and presumably microplastics too, which would result in their transport up the estuary at high tide (when the sampling in this study occurred). This hypothesis is supported by a field study demonstrating highest microplastic concentration at the mouth of the River Tamar were associated with peak flows during ebbing and flood tides (Sadri and Thompson, 2014). Future work should consider concurrent water and sediment sampling along source-to-sea estuarine transects at consistent tidal conditions (we suggest ebbing tide) to better understand the flux of microplastics in transitional ecosystems.

Previous studies have identified that high rainfall can result in higher microplastic loads in rivers (Campanale et al., 2020; Napper et al., 2021), lakes (Xia et al., 2020) and coastlines (Lattin et al., 2004), likely as a result of plastics being “flushed out” from tributaries and drainage systems and via run-off from land. Given the precipitation levels prior to sampling and the average river flow, higher microplastic concentrations were expected in the Autumn samples, however we found the opposite. We suspect this might be due to the time-lag between an extreme weather event (e.g. storm, monsoon, heavy rainfall) and sampling. In other studies, sampling typically occurred in the day(s) following extreme rainfall, whereas here we sampled 7 days after heavy rainfall; as evidenced by Cheung et al. (2019) and Hitchcock (2020), waterborne microplastic concentrations can spike and subsequently decline by orders of magnitude in the hours and days immediately following a storm. Observed differences in microplastics concentrations between Summer and Autumn samples might be explained by dilution effects (based on overall riverine water volume), supply exhaustion following rainfall events, as well as tidal cycle, flow rates and differences in anthropogenic inputs across seasons. This pattern has also been noted in several other

ivers, where greater concentrations of microplastic are found in the dry season sampling campaigns compared to the wet season and this has been attributed to flushing and dilution effects (Fan et al., 2019; Napper et al., 2021; Oo et al., 2021).

The microplastics found in the Tamar samples were primarily fibres and fragments, with only one bead detected. This indicates they are likely to be secondary microplastics derived from the breakdown of larger plastic items from a variety of sources including from agricultural materials, packaging, rope and synthetic textiles (Piehl et al., 2018; Schell et al., 2021; Yang et al., 2021). As primary microplastics are usually associated with industrial production, the absence of primary particles could be explained by the primarily agricultural and rural nature of much of the catchment (Eibes and Gabel, 2022). It may also reflect that pellets and beads are likely to settle out from flows first due to their density, whereas fibres are most easily entrained and carried in suspension. This finding is consistent with a review by Bai et al. (2022) who found fibres were the dominant shape of MPs in rivers.

4.2. The relationship between *in situ* microplastics and SPM concentration

In both seasons, microplastic concentrations were correlated with SPM concentrations in the Tamar estuary. Measured surface SPM concentrations in the Tamar estuary had a wide range ($0.6\text{ to }49.8\text{ g/m}^3$) and followed a pattern of decreasing concentration from the turbidity maximum zone at the fresh-seawater interface ($0.5\text{ to }10\text{ psu}$ salinity) in the upper reaches of the estuary, downstream to Plymouth Sound which is consistent with previous studies in the area (Uncles and Stephens, 1993; Uncles et al., 2015). Previous investigations by Piehl et al. (2020) found a significant relationship between SPM and microplastic abundance for only one out of three locations studied, the Trave river in Germany. The Trave has a similar catchment size to the Tamar (1804 km^2) and, compared to the other two rivers in the study, has a relatively small annual discharge of $7.37\text{ m}^3/\text{s}$. The authors suggested a possible reason for the relationship between SPM and microplastic concentration in the Trave was the proximity to emissions sources, in this case a wastewater treatment plant. In the Tamar there are also wastewater treatment plants distributed along the estuary which could be sources of microplastic, however the plant upstream of Calstock (at the head of the estuary) has the lowest population equivalent of all the estuary, despite having the highest recorded microplastic abundance. We speculate that rather than distance to wastewater treatment plants, the observed relationship between SPM and microplastic in the Tamar may be due to similar physical mechanisms of tidal resuspension and transport. At the turbidity maximum/fresh-seawater interface particles are resuspended by erosion of the bottom by tidal currents then carried by surface flushing of less dense riverine freshwater downstream by the ebbing tide where the suspended sediment load is diluted when it reaches the coastal area. This process, which has been observed for SPM (Uncles and Stephens, 1993), may be similar for deposited microplastics as a component of SPM, although the original sources of the two are different. This would align with studies which found that microplastics accumulate in the river seabed and are resuspended by winter runoff events (Hurley et al., 2018). Though a relationship between SPM and microplastics has been found for both the Trave and the Tamar, this method would benefit from further exploration, particularly in larger rivers with higher microplastic abundances. More generally, studies targeting microplastics transport in tidal estuaries are required to investigate their dynamics in these complex environments, as focus has been so far in transport of plastics in coastal and open ocean (van Sebille et al., 2020).

4.3. Satellite-derived estimates of proxy microplastic concentration and flux

Using the relationship established by the *in situ* measurements, an approach to derive proxy microplastic concentration and flux from

satellite ocean colour measurements of SPM has been demonstrated. The daily satellite-derived proxy microplastic concentrations in the lower Tamar study area (0.002 to 1.028 microplastics m^{-3}) were similar in magnitude to the *in situ* measurements. The results indicated a correlation between daily river discharge and SPM concentration, and thus proxy microplastic concentration, but whether this is due to the impact of runoff, inputs of wastewater or resuspension of bed sediments is unknown. This relationship has also been observed in *in situ* measurements of microplastics, for example Campanale et al. (2020) found a strong positive correlation between the concentration of MPs and river flow for the Ofanto river when monitored over a year. However, in the *in situ* samples from the Tamar, the Autumn sampling campaign followed higher rainfall and had higher average river flow rates, but was found to have lower microplastic concentrations than the summer sampling campaign. This may possibly be due to particle exhaustion or dilution after a rainfall event (discussed above) and highlights the complexity of dynamic estuarine systems over different timescales and the challenges of sampling few points in time.

Existing estimates of plastic emissions from the Tamar and its tributaries have a large range and uncertainty: from 0.052 t/year (Lebreton et al., 2017) to 2.78 t/year for macroplastics only (Meijer et al., 2021). The satellite-derived annual microplastic flux estimates (Fig. 7) provide a first approximation of the microplastics transported downstream through the defined area of the Tamar river. Other processes such as particle settling will impact the microplastic concentration downstream, so estimating the actual emissions to the marine environment is more complex. That being said, the microplastic flux estimates in this initial demonstration are similar in magnitude to the estimate of all plastic emissions from Lebreton et al. (2017) and they show a similar seasonal pattern to these modelled results, where microplastic flux is typically highest in the winter months with an order of magnitude difference between the microplastic flux in the winter and summer (Fig. S3). The annual microplastic mass flux estimate computed for the Tamar is lower than the ranges reported for other European rivers (Table S3). However, these studies have predominantly focused on larger rivers (by catchment size and average discharge) with different levels of urbanisation and industrial activity. Also, the mass concentration is highly dependent on the value chosen for representative mass of microplastic particles, in this study 0.09 mg, so the absolute magnitudes should be treated with caution. When looking at the annual particle fluxes, the estimates are also lower than the reported values found for other European sites such as the Warnow Estuary ($152\text{--}291 \times 10^9$ particles a year) and the top layer of the Ebro River (2.14×10^9 particles a year) (Simon-Sánchez et al., 2019; Piehl et al., 2021).

4.4. Limitations to the proposed approach

This study has demonstrated how point microplastic measurements could be extrapolated using ocean colour remote sensing to produce a timeseries of microplastic concentration and estimates of flux. However, it is important to consider the limitations and caveats of the approach when interpreting the results described above. These limitations indicate important areas for future research to enhance our understanding of microplastic dynamics in estuaries and improve the accuracy of the flux estimates presented here.

A major assumption of the workflow is that the satellite derived SPM measurements are an accurate reflection of the *in situ* SPM. Estuarine and coastal waters are complex in their composition and optical properties and it should be stressed that accurate SPM retrievals from satellite in these transitional waters is challenging. In this study we have used a standard algorithm used for moderately turbid coastal waters in the southern North Sea from (Nechad et al., 2010). However, few matchups with *in situ* measurements were available so we were unable to assess the accuracy of this SPM algorithm in our study location, and it is anticipated this would introduce significant uncertainty in the proxy microplastic concentration figures. Regionally calibrated algorithms for

SPM are always preferred if the *in situ* data are available, as significant variations occur in specific inherent optical properties in estuarine and coastal environments (Babin et al., 2003; Tilstone et al., 2012). Future work to quantify this uncertainty would be valuable and the generation of regionally calibrated SPM algorithms where this monitoring method is applied in future is encouraged (Piehl et al., 2021).

In this demonstration we have also assumed that the relationship between SPM and microplastic is constant over time and space. However, it is likely that the concentration of microplastics as a component of SPM will vary over both short and longer timescales with changes in relative supply of plastic due to changes in human activities or due to changes in the relative importance of input pathways of plastics and SPM. As a result, this relationship would benefit from further validation over a range of hydrological and meteorological conditions and over long and event timescales.

Microplastics are also heterogeneously distributed throughout river systems, depending on the distribution of inputs, particle sinks and there is dilution and mixing of water masses. Therefore, it is important where we place our geographical zone of interest for the flux calculation. The values obtained by the flux calculation in the Tamar do vary depending on the area over which this is computed. In this study the location was largely determined by the narrow width of the Tamar, as further upstream would have been too narrow compared to the sensor pixel size, however this area is also influenced by tidal dynamics and therefore is likely to be subject to dilution and particle settling, which may lead to a reduction in the SPM concentration in the upper layer of water measured by ocean colour satellites and therefore an underestimation of particle flux. The flux calculation also does not attempt to account for vertical or horizontal differences in current velocities or differences in microplastic concentration with depth. Previous studies have shown plastic concentrations and fluxes are highly variable over two orders of magnitude within a river cross-section (Haberstroh et al., 2021). For example, a study on the Nakdong river showed the microplastic concentration in surface river water was 3 times higher than that 1 m from the riverbed (Eo et al., 2019). To calculate more accurate fluxes high-frequency current velocity and microplastic abundance measurements across the river cross section and high spatial resolution modelling would be needed (Torres and Uncles, 2012). In addition, as mentioned above, the final microplastic mass flux estimates are highly dependent on the mass conversion calculation and additional uncertainty is introduced in the use of month-average microplastic concentration and river flow. However, while this method has its limitations, it can start to give us an indication of microplastic loads and fluxes which are challenging to quantify, particularly in hard to access and sample locations.

5. Conclusion

This study explored the spatial patterns of microplastic concentrations and SPM in the Tamar estuary. Microplastics were reported in all samples, but recorded concentrations were relatively low compared to previous studies in other European rivers. The concentrations of microplastics in marine samples are consistent with previous investigations in the area. Both SPM and microplastic abundance displayed a pattern of decreasing concentration with distance downstream and a strong relationship between these variables was found. It is hypothesised this relationship is due to physical mechanisms of tidal resuspension and flushing. This suggests for the Tamar SPM may be a good proxy for microplastic concentration, although further investigation is needed into how this relationship varies seasonally and with hydrological and meteorological events.

Where a water quality proxy relationship can be established, satellite imagery has the potential to improve our knowledge of microplastic concentration over time and allows us to extrapolate from *in situ* data. In the Tamar we have shown how the relationship found in the *in situ* samples could be used to compute a timeseries of proxy microplastic concentration and to calculate first approximations of microplastic flux

in the lower Tamar. However, we caution the reader against indiscriminate use of the local relationship found in this study. These results pioneer a new line of research and require further investigation into the described potential sources of uncertainty, including the assessment of the accuracy of the SPM algorithm used and the quantification of the uncertainties in flux values.

In addition to posing some fundamental research questions about the dynamics of SPM and microplastics in estuaries, the practical implication of this study, is that the workflow has been designed to be scalable to other rivers, particularly in areas where regular monitoring of riverine plastic fluxes *in situ* is challenging. This could be a valuable tool for authorities wishing to understand, monitor and report plastic fluxes in their jurisdiction. It is likely that within each river system these relationships are unique, as each river is likely to have a unique assemblage of plastics (particle sizes, composition and concentration) and SPM. Therefore, further investigations are needed to assess this method, particularly on larger rivers with higher microplastic concentrations, to test the applicability of this method elsewhere.

CRedit authorship contribution statement

Emma Sullivan: Software, Data Curation, Methodology, Investigation, Formal analysis, Writing - Original Draft; **Matthew Cole:** Conceptualization, Methodology, Investigation, Data Curation, Formal analysis, Writing - Original Draft; **Elizabeth C. Atwood:** Conceptualization, Methodology, Software, Writing - Review & Editing; **Penelope K. Lindeque:** Conceptualization, Methodology, Investigation, Writing - Review & Editing; **Pham Thi Chin:** Conceptualization, Methodology, Writing- Reviewing and Editing; **Victor Martinez-Vicente:** Conceptualization, Investigation, Methodology, Writing- Reviewing and Editing, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare no competing interests.

Data availability

Data are available at <https://doi.org/10.5281/zenodo.8319399>.

Acknowledgements

This work was funded by ESA contract no. 40000123928/18/I-NB 'SIMPLER: Sensing Marine Plastic Litter using Earth observation in River outflows'. Support from EU Horizon 2020 CERTO (Grant Agreement #870349). We express our sincere thanks to Oban Jones, Georgina Ramm and Gaia Gleratti at PML for their support during field sampling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2023.115529>.

References

- Babin, M., et al., 2003. Variations in the light absorption coefficients of phytoplankton, nonalgal particles, and dissolved organic matter in coastal waters around Europe. *J. Geophys. Res. Oceans* 108 (C7). <https://doi.org/10.1029/2001JC000882>. Available at:
- Bai, M., et al., 2022. Controlling factors of microplastic riverine flux and implications for reliable monitoring strategy. *Environ. Sci. Technol.* 56 (1), 48–61. Available at: <https://doi.org/10.1021/acs.est.1c04957>.
- Boucher, J., Friot, D., 2017. Primary microplastics in the oceans: A global evaluation of sources. IUCN International Union for Conservation of Nature. <https://doi.org/10.2305/IUCN.CH.2017.01.en>. Available at:
- Browne, M.A., Galloway, T.S., Thompson, R.C., 2010. Spatial patterns of plastic debris along estuarine shorelines. *Environ. Sci. Technol.* 44 (9), 3404–3409. Available at: <https://doi.org/10.1021/es903784e>.
- Campanale, C., et al., 2020. Microplastics and their possible sources: the example of Ofanto river in Southeast Italy. *Environ. Pollut.* 258 <https://doi.org/10.1016/j.envpol.2019.113284>, 113284. Available at:
- Cheung, P.K., Hung, P.L., Fok, L., 2019. River microplastic contamination and dynamics upon a rainfall event in Hong Kong, China. *Environmental Processes* 6 (1), 253–264. Available at: <https://doi.org/10.1007/s40710-018-0345-0>.
- Cole, M., et al., 2014. Isolation of microplastics in biota-rich seawater samples and marine organisms. *Sci. Rep.* 4 (1), 4528. Available at: <https://doi.org/10.1038/srep04528>.
- Cole, M., et al., 2023. Mussel power: scoping a nature-based solution to microplastic debris. *J. Hazard. Mater.* 453 <https://doi.org/10.1016/j.jhazmat.2023.131392>, 131392. Available at:
- Doxaran, D., Devred, E., Babin, M., 2015. A 50% increase in the mass of terrestrial particles delivered by the Mackenzie River into the Beaufort Sea (Canadian Arctic Ocean) over the last 10 years. *Biogeosciences* 12 (11), 3551–3565. Available at: <https://doi.org/10.5194/bg-12-3551-2015>.
- Eibes, P.M., Gabel, F., 2022. Floating microplastic debris in a rural river in Germany: distribution, types and potential sources and sinks. *Sci. Total Environ.* 816 <https://doi.org/10.1016/j.scitotenv.2021.151641>, 151641. Available at:
- Environment Agency, 2012. Tamar Catchment Flood Management Plan. Exeter: Environment Agency, p. 24. Available at: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/294033/Exe_Catchment_Flood_Management_Plan.pdf.
- EO, S., et al., 2019. Spatiotemporal distribution and annual load of microplastics in the Nakdong River, South Korea. *Water Res.* 160, 228–237. <https://doi.org/10.1016/j.watres.2019.05.053>.
- Fan, Y., et al., 2019. Distribution, sedimentary record, and persistence of microplastics in the Pearl River catchment, China. *Environ. Pollut.* 251, 862–870. <https://doi.org/10.1016/j.envpol.2019.05.056>.
- Fettweis, M., et al., 2014. Seasonality of floc strength in the southern North Sea. *J. Geophys. Res. Oceans* 119 (3), 1911–1926. Available at: <https://doi.org/10.1002/2013JC009750>.
- Haave, M., et al., 2019. Different stories told by small and large microplastics in sediment - first report of microplastic concentrations in an urban recipient in Norway. *Mar. Pollut. Bull.* 141, 501–513. Available at: <https://doi.org/10.1016/j.marpolbul.2019.02.015>.
- Haberstroh, C.J., et al., 2021. Effects of hydrodynamics on the cross-sectional distribution and transport of plastic in an urban coastal river. *Water Environ. Res.* 93 (2), 186–200. Available at: <https://doi.org/10.1002/wer.1386>.
- Hale, R.C., et al., 2020. A global perspective on microplastics. *J. Geophys. Res. Oceans* 125 (1). <https://doi.org/10.1029/2018JC014719>. Available at:
- Hampton, L.M.T., et al., 2022. Characterizing microplastic hazards: which concentration metrics and particle characteristics are most informative for understanding toxicity in aquatic organisms? *Microplast. Nanoplast.* 2, 20. Available at: <https://doi.org/10.1186/s43591-022-00040-4>.
- Hitchcock, J.N., 2020. Storm events as key moments of microplastic contamination in aquatic ecosystems. *Sci. Total Environ.* 734 <https://doi.org/10.1016/j.scitotenv.2020.139436>, 139436. Available at:
- Hu, C., 2021. Remote detection of marine debris using satellite observations in the visible and near infrared spectral range: challenges and potentials. *Remote Sens. Environ.* 259 <https://doi.org/10.1016/j.rse.2021.112414>, 112414. Available at:
- Hurley, R., Woodward, J., Rothwell, J.J., 2018. Microplastic contamination of river beds significantly reduced by catchment-wide flooding. *Nat. Geosci.* 11 (4), 251–257. Available at: <https://doi.org/10.1038/s41561-018-0080-1>.
- Largier, J.L., 1992. Tidal intrusion fronts. *Estuaries* 15 (1), 26–39. Available at: <https://doi.org/10.2307/1352707>.
- Lattin, G.L., et al., 2004. A comparison of neustonic plastic and zooplankton at different depths near the southern California shore. *Mar. Pollut. Bull.* 49 (4), 291–294. Available at: <https://doi.org/10.1016/j.marpolbul.2004.01.020>.
- Lebreton, L.C.M., et al., 2017. River plastic emissions to the world's oceans. *Nat. Commun.* 8 (1) <https://doi.org/10.1038/ncomms15611>, 15611. Available at:
- Lindeque, P.K., et al., 2020. Are we underestimating microplastic abundance in the marine environment? A comparison of microplastic capture with nets of different mesh-size. *Environ. Pollut.* 265 <https://doi.org/10.1016/j.envpol.2020.114721>, 114721. Available at:
- Luo, W., et al., 2019. Comparison of microplastic pollution in different water bodies from urban creeks to coastal waters. *Environ. Pollut.* 246, 174–182. Available at: <https://doi.org/10.1016/j.envpol.2018.11.081>.
- Lusher, A.L., et al., 2017. Sampling, isolating and identifying microplastics ingested by fish and invertebrates. *Anal. Methods* 9 (9), 1346–1360. <https://doi.org/10.1039/C6AY02415G>.
- MacLeod, M., et al., 2021. The global threat from plastic pollution. *Science* 373 (6550), 61–65. Available at: <https://doi.org/10.1126/science.abg5433>.
- Mani, T., et al., 2016. Microplastics profile along the Rhine River. *Sci. Rep.* 5 (1) <https://doi.org/10.1038/srep17988>, 17988. Available at:
- Martinez-Vicente, V., et al., 2010. Particulate scattering and backscattering related to water constituents and seasonal changes in the Western English Channel. *J. Plankton Res.* 32 (5), 603–619. Available at: <https://doi.org/10.1093/plankt/fbq013>.
- Martinez-Vicente, V., et al., 2019. Measuring marine plastic debris from space: initial assessment of observation requirements. *Remote Sens.* 11 (20), 2443. Available at: <https://doi.org/10.3390/rs11202443>.
- Maximenko, N., et al., 2019. Toward the integrated marine debris observing system. *Front. Mar. Sci.* 6, 447. Available at: <https://doi.org/10.3389/fmars.2019.00447>.
- Meijer, L.J.J., et al., 2021. More than 1000 rivers account for 80% of global riverine plastic emissions into the ocean. *Sci. Adv.* 7 (18) <https://doi.org/10.1126/sciadv.aaz5803>, eaz5803. Available at:

- Munari, C., et al., 2021. Temporal variation of floatable plastic particles in the largest Italian river, the Po. *Mar. Pollut. Bull.* 171 <https://doi.org/10.1016/j.marpolbul.2021.112805>, 112805. Available at:
- Napper, I.E., et al., 2021. The abundance and characteristics of microplastics in surface water in the transboundary Ganges River. *Environ. Pollut.* 274 <https://doi.org/10.1016/j.envpol.2020.116348>, 116348. Available at:
- Nechad, B., Ruddick, K.G., Park, Y., 2010. Calibration and validation of a generic multisensor algorithm for mapping of total suspended matter in turbid waters. *Remote Sens. Environ.* 114 (4), 854–866. Available at: <https://doi.org/10.1016/j.rse.2009.11.022>.
- Oo, P.Z., et al., 2021. Horizontal variation of microplastics with tidal fluctuation in the Chao Phraya River estuary, Thailand. *Mar. Pollut. Bull.* 173 <https://doi.org/10.1016/j.marpolbul.2021.112933>, 112933. Available at:
- Piehl, S., et al., 2018. Identification and quantification of macro- and microplastics on an agricultural farmland. *Sci. Rep.* 8 (1), 17950. Available at: <https://doi.org/10.1038/s41598-018-36172-y>.
- Piehl, S., et al., 2020. Can water constituents be used as proxy to map microplastic dispersal within transitional and coastal waters? *Front. Environ. Sci.* 8, 92. Available at: <https://doi.org/10.3389/fenvs.2020.00092>.
- Piehl, S., et al., 2021. Combined approaches to predict microplastic emissions within an urbanized estuary (Warnow, southwestern Baltic Sea). *Front. Environ. Sci.* 9 <https://doi.org/10.3389/fenvs.2021.616765>, 616765. Available at:
- Qin, P., Simis, S.G.H., Tilstone, G.H., 2017. Radiometric validation of atmospheric correction for MERIS in the Baltic Sea based on continuous observations from ships and AERONET-OC. *Remote Sens. Environ.* 200, 263–280. Available at: <https://doi.org/10.1016/j.rse.2017.08.024>.
- Rochman, C.M., et al., 2019. Rethinking microplastics as a diverse contaminant suite. *Environ. Toxicol. Chem.* 38 (4), 703–711. Available at: <https://doi.org/10.1002/etc.4371>.
- Röttgers, R., Heymann, K., Krasemann, H., 2014. Suspended matter concentrations in coastal waters: methodological improvements to quantify individual measurement uncertainty. *Estuar. Coast. Shelf Sci.* 151, 148–155. Available at: <https://doi.org/10.1016/j.ecss.2014.10.010>.
- Sadri, S.S., Thompson, R.C., 2014. On the quantity and composition of floating plastic debris entering and leaving the Tamar Estuary, Southwest England. *Mar. Pollut. Bull.* 81 (1), 55–60. Available at: <https://doi.org/10.1016/j.marpolbul.2014.02.020>.
- Schell, T., et al., 2021. Spatio-temporal distribution of microplastics in a Mediterranean river catchment: the importance of wastewater as an environmental pathway. *J. Hazard. Mater.* 420 <https://doi.org/10.1016/j.jhazmat.2021.126481>, 126481. Available at:
- Schmidt, C., Krauth, T., Wagner, S., 2017. Export of plastic debris by rivers into the sea. *Environ. Sci. Technol.* 51 (21), 12246–12253. Available at: <https://doi.org/10.1021/acs.est.7b02368>.
- Shen, J., Boon, J.D., Kuo, A.Y., 1999. A modeling study of a tidal intrusion front and its impact on larval dispersion in the James River estuary, Virginia. *Estuaries* 22 (3), 681–692. Available at: <https://doi.org/10.2307/1353055>.
- Simon-Sánchez, L., et al., 2019. River deltas as hotspots of microplastic accumulation: the case study of the Ebro River (NW Mediterranean). *Sci. Total Environ.* 687, 1186–1196. Available at: <https://doi.org/10.1016/j.scitotenv.2019.06.168>.
- Skalska, K., et al., 2020. Riverine microplastics: behaviour, spatio-temporal variability, and recommendations for standardised sampling and monitoring. *J. Water Proc. Eng.* 38 <https://doi.org/10.1016/j.jwpe.2020.101600>, p. 101600. Available at:
- Tibbetts, J., et al., 2018. Abundance, distribution, and drivers of microplastic contamination in Urban River environments. *Water* 10 (11), 1597. <https://doi.org/10.3390/w10111597>.
- Tilstone, G.H., et al., 2012. Variability in specific-absorption properties and their use in a semi-analytical ocean colour algorithm for MERIS in North Sea and Western English Channel coastal waters. *Remote Sens. Environ.* 118, 320–338.
- Torres, R., Uncles, R.J., 2012. Modelling of estuarine and coastal waters. In: Wolanski, E., McLusky, D.S. (Eds.), *Treatise of Estuarine and Coastal Sciences*. Academic Press, Waltham, pp. 395–427.
- UK CEH, N.R.F.A., 2022. 47001 - Tamar at Gunnislake. Available at: <https://nrfa.ceh.ac.uk/data/station/meanflow/47001>.
- Uncles, R.J., Stephens, J.A., 1993. Nature of the turbidity maximum in the Tamar Estuary, U.K. *Estuar. Coast. Shelf Sci.* 36 (5), 413–431. Available at: <https://doi.org/10.1006/ecss.1993.1025>.
- Uncles, R.J., Stephens, J.A., Harris, C., 2015. Estuaries of Southwest England: salinity, suspended particulate matter, loss-on-ignition and morphology. *Prog. Oceanogr.* 137, 385–408. Available at: <https://doi.org/10.1016/j.pocean.2015.04.030>.
- van der Wal, M., et al., 2015. *SFRA0025: identification and assessment of riverine input of (marine) litter*, p. 186. Available online at: <https://mcc.jrc.ec.europa.eu/documents/201606244356.pdf>.
- van Emmerik, T.H.M., et al., 2023. Focus on plastics from land to aquatic ecosystems. *Environ. Res. Lett.* 18 (4), 040401. <https://doi.org/10.1088/1748-9326/acc086>.
- van Sebille, E., et al., 2020. The physical oceanography of the transport of floating marine debris. *Environ. Res. Lett.* 15 (2) <https://doi.org/10.1088/1748-9326/ab6d7d>, p. 023003. Available at:
- Warren, M.A., et al., 2019. Assessment of atmospheric correction algorithms for the sentinel-2A MultiSpectral imager over coastal and inland waters. *Remote Sens. Environ.* 225, 267–289. Available at: <https://doi.org/10.1016/j.rse.2019.03.018>.
- Weiss, L., et al., 2021. The missing ocean plastic sink: gone with the rivers. *Science* 373 (6550), 107–111. Available at: <https://doi.org/10.1126/science.abe0290>.
- Xia, W., et al., 2020. Rainfall is a significant environmental factor of microplastic pollution in inland waters. *Sci. Total Environ.* 732 <https://doi.org/10.1016/j.scitotenv.2020.139065>, 139065. Available at:
- Yan, M., et al., 2019. Microplastic abundance, distribution and composition in the Pearl River along Guangzhou city and Pearl River estuary, China. *Chemosphere* 217, 879–886. Available at: <https://doi.org/10.1016/j.chemosphere.2018.11.093>.
- Yang, L., et al., 2021. Microplastics in freshwater sediment: A review on methods, occurrence, and sources. *Sci. Total Environ.* 754 <https://doi.org/10.1016/j.scitotenv.2020.141948>, p. 141948. Available at:
- Yonkos, L.T., et al., 2014. Microplastics in four estuarine rivers in the Chesapeake Bay, U.S.A. *Environ. Sci. Technol.* 48 (24), 14195–14202. Available at: <https://doi.org/10.1021/es5036317>.