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# Large microplastic particle in sediments of tributaries of the River Thames, UK – abundance, sources and methods for effective quantification

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Keywords: Microplastics; freshwater; sediment; sources; pollution; Raman

## Highlights

- Microplastics found at four sites in the Thames River Basin, UK.
- Many fragments derived from road marking paints - a previously undescribed source.
- Efficient methods developed for separating large microplastic particles from sediment.
- Inputs and behaviour of microplastics are varied and complex to predict.

## Abstract

Sewage effluent input and population were chosen as predictors of microplastic presence in sediments at four sites in the River Thames basin (UK). Large microplastic particles (1 mm – 4 mm) were extracted using a stepwise approach to include visual extraction, flotation and identification using Raman spectroscopy. Microplastics were found at all four sites. One site had significantly higher numbers of microplastics than other sites, average 66 particles 100 g<sup>-1</sup>, 91% of which were fragments. This site was downstream of a storm drain outfall receiving urban runoff; many of the fragments at this site were determined to be derived of thermoplastic road-surface marking paints. At the remaining three sites, fibres were the dominant particle type. The most common polymers identified included polypropylene, polyester and polyarylsulphone. This study describes two major new findings: presence of microplastic particles in a UK freshwater system and identification of road marking paints as a source of microplastics.

## Capsule

This study is the first to quantify microplastics of any size in river sediments in the UK and links their presence to terrestrial sources including sewage and road marking paints.

## 1. Introduction

Since the 1960s plastics have become widely manufactured and used, with global production of plastics reaching 311 million tonnes in 2014, 59 million tonnes of which were produced in Europe (PlasticsEurope, 2016). However, only 17.9 million tonnes were recycled or used in energy recovery processes in Europe in 2014 (PlasticsEurope, 2016). Their inherent durability and longevity which make plastics such a favourable commercial material are also the characteristics that allow them to persist in the environment (Barnes et al., 2009). Degradation of large plastic items can be a very slow

1 process therefore plastics may persist in the environment over long timescales (Andrady, 2011;  
2 Hidalgo-Ruz et al., 2012), even in the range of hundreds of years (Barnes et al., 2009). However,  
3  
4 despite the wide-ranging use and disposal of plastic products and the recognised abundance of  
5  
6 plastic litter worldwide, the importance of understanding the fate and impacts of these plastics  
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8 within the environment has only recently started to be addressed.  
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11 Microplastics, plastic particles <5mm in size, are a specific concern given their small scale  
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13 and potential for widespread environmental dispersal. The first reports of synthetic fibres and  
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15 pellets as marine environmental contaminants emerged in the early 1970s (Buchanan, 1971;  
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17 Carpenter and Smith, 1972), however direct research into this field was not pursued until the last  
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19 decade (Thompson et al., 2004). Since then, a growing number studies have investigated the  
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21 presence and effects of marine microplastic debris (Arthur and Baker, 2011; Faure et al., 2012; Law  
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23 et al., 2014; Lusher et al., 2015; Van Cauwenberghe and Janssen, 2014). The majority of plastic  
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25 debris found in the marine environment (70-80%) has land-based sources and rivers are considered  
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27 an important medium for transfer of this debris (Arthur and Baker, 2011; Bowmer and Kershaw,  
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29 2010; Hirai et al., 2011; Jambeck et al., 2015; Sadri and Thompson, 2014; Wagner et al., 2014;  
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31 Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014). Comparatively few studies have actually  
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33 been published on microplastics in freshwater or terrestrial environments, although this field of  
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35 research is growing with a number of papers recently published on microplastics in freshwater  
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37 systems (Corcoran et al., 2015; Klein et al., 2015; Lechner et al., 2014; Sanchez et al., 2014;  
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39 Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014), with the greatest proportion of  
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41 microplastic debris in freshwater environments being observed near to industrialised areas (Dubaish  
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43 and Liebezeit, 2013; Eriksen et al., 2013; Sadri and Thompson, 2014; Zbyszewski and Corcoran,  
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45 2011).

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47 Microplastics fall into 2 categories: primary and secondary. Primary microplastics are those  
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49 which were manufactured with the intention of them being of a micro scale, for example those used  
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51 in cosmetics or exfoliating scrubs (such as glitter and 'microbeads') or virgin pellets used in the  
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1 plastic production industry. Secondary microplastics are those that have formed as a result of  
2 macroplastic degradation, for example breakdown of *in situ* litter (Andrady, 2011; Barnes et al.,  
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4 2009; Rillig, 2012; Shah et al., 2008) or the washing of artificial fabrics in the laundry, which can lead  
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6 to the loss of up to 1900 fibres into wastewater per wash (Browne et al., 2011). Within these  
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8 categories, microplastics are categorised into 2 size brackets: 'large microplastic particles' (LMPP, 1  
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10 mm-5 mm) and 'small microplastic particles' (SMPP, < 1 mm). Over time, LMPPs may become SMPPs  
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12 or even nanoplastics, due to degradation within the environment (Andrady, 2011; Koelmans et al.,  
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14 2015; Lambert and Wagner, 2016).  
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20 Sources of microplastic particles to the environment are numerous and varied. Sewage  
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22 treatment works (STWs) are a critical link in the microplastic transport and distribution web given  
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24 that many plastic particles including microbeads and synthetic fibres will enter these STWs. If not  
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26 physically filtered out within the plant itself then they will be discharged to rivers via effluent or  
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28 incorporated into sludge (Habib et al., 1996; Zubris and Richards, 2005). Sludge may in turn may be  
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30 applied to agricultural land (DEFRA, 2012), leading to direct terrestrial implications, in addition to  
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32 potential for runoff into watercourses. STW outfalls discharge directly into rivers representing a  
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34 point source discharge of particles to freshwater environments. Thus, sewage outfalls have been  
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36 recognised as a likely significant source of microplastic pollution to the oceans (Arthur and Baker,  
37  
38 2011; Browne et al., 2011). Additional sources include degradation of macroplastic debris such as  
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40 sanitary waste from sewage treatment overflows, plastic packaging, particle runoff from roads in the  
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42 form of tyre wear particles or parts of vehicles and runoff from land containing degraded litter  
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44 (Andrady, 2011; Eriksen et al., 2013; Galgani et al., 2015; Hidalgo-Ruz et al., 2012). Another source  
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46 was recently recognised in the form of polymer composite paints. Due to the low polymer  
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48 composition of paints, these are likely to be more brittle than pure polymers and therefore break  
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50 down quickly into smaller particles in the environment (Imhof et al., 2016; Song et al., 2014;  
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52 Takahashi et al., 2012).  
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1 The aim of this study was to investigate the presence, abundance and types of microplastics  
2 within tributaries of the River Thames basin (UK). This study investigated the link between two  
3 expected and related drivers of microplastic input, sewage effluent input and population density,  
4 with the presence of microplastics in river sediments. The River Thames catchment in the UK was  
5 selected as the location for our survey as it is the UK's second longest river and the river basin  
6 supports many large urban areas, receiving effluent from a population of over 13 million (Bengtson  
7 Nash et al., 2006; National Statistics, 2002). Although likely acting as a source of microplastics to the  
8 marine environment, the Thames also has the capability to act as a sink for some plastic particles  
9 due to flow dynamics: in the Thames estuary (and other estuaries), water near the riverbed has a  
10 tendency to flow landward, meaning that some of the debris entering the river may be retained  
11 within estuarine sediments (Board, 1973). Sediment was our selected medium for analysis given that  
12 microplastics can accumulate in sediments at an order of magnitude higher than in the water  
13 column (Hoellein et al., 2016). This indicates the potential for rivers to act as a sink for  
14 environmental microplastics. Studies of macroplastic in the Thames have shown there to be an  
15 abundance of litter being transported down the Thames (Morritt et al., 2014). To our knowledge,  
16 however, with the exception of estuaries this is the first study investigating microplastics in the  
17 Thames catchment or indeed any freshwater system in the UK.

## 2. Materials and methods

### 2.1. Sampling site selection and sample collection

18 Sampling sites within the Thames river basin were selected based on two variables; average  
19 % effluent present in the river as estimated using the Low Flows 2000 (LF2000) WQX (Water Quality  
20 eXtension) model (Williams et al., 2009) and population equivalent density as calculated using  
21 population within the catchment area (of known area) served by the upstream sewage treatment  
22

1 works (Pottinger et al., 2013; Williams et al., 2009). Selected sites comprised three tributaries of the  
2 Thames: the River Leach, the River Lambourn and The Cut (two sites). These rivers are regularly  
3 monitored for a range of water quality and biological characteristics as part of the ongoing Thames  
4 Initiative project and are therefore well characterised (Bowes et al., 2014). Four sampling sites were  
5 selected to represent scenarios ranging from low sewage input and population equivalent density,  
6 Leach (SU228996) and Lambourn (SU429721) through an intermediate site, The Cut site 1  
7 (SU859704, upstream of an effluent outfall) to a site with high sewage input and population  
8 equivalent density, The Cut site 2 (SU855732, downstream of an effluent outfall) (Figures 1 and 2).  
9 Samples were collected between 28<sup>th</sup> August and 3<sup>rd</sup> September 2014 to correspond with seasonal  
10 low flow conditions. At each site four sediment samples were collected at 1 m intervals along a 3 m  
11 transect running parallel to the bank at 1 m distance, therefore giving four replicate samples per site.  
12 The sediment surface was sampled in all cases to approximately 10 cm depth using a stainless steel  
13 scoop, collected to fill a 1L glass Kilner jar, ensuring that minimal excess water was retained.  
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## 35 **2.2. Sample processing**

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38 The sediments were processed in three steps in order to find and separate microplastic  
39 particles: 1) visual inspection of whole sample, 2) flotation and 3) further visual inspection of  
40 unfloated material. This three-step process was designed to remove microplastic particles with  
41 maximum thoroughness and efficiency (without the need for custom-made equipment (Claessens et  
42 al., 2013; Imhof et al., 2012)), based on the assumption that each step would not in itself be  
43 sufficient to recover all microplastics. To determine whether any of the three steps could be  
44 eliminated from future analyses to further streamline the process, the effectiveness of each step for  
45 microplastic removal was compared, based on percentage removal of total microplastic particles. As  
46 methodological limitations prevent accurate determination of small microplastic particles <1 mm,  
47 before undertaking the steps to extract microplastics particles the 1 L sediment samples were each  
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1 wet-sieved to retain two size fractions, 1-2mm and 2-4mm. These sizes were selected for analysis as  
2 indicators of the types and likely sources of microplastics present in this environment while  
3 remaining visible and easily quantifiable. Two fractions were specified in order to differentiate  
4 between abundances of microplastics of different sizes. Both size fractions from each site were  
5 carefully rinsed into individual clean containers and oven-dried at 80°C. This temperature is below  
6 the melting point of all common polymers and wouldn't be expected to alter the inherent particle  
7 shape considered for the analysis (Kalpakjian and Schmid, 2008). Once dry, samples were weighed  
8 and total dry weight calculated, then covered to prevent airborne contamination and stored for  
9 sorting and analysis.  
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### 25 **2.2.2. Extraction step 1: Visual inspection of sieved sediments**

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28 The first sorting step was a visual inspection of the entire sample using a binocular light  
29 microscope at 6x magnification (Wild Heerbrugg, Switzerland, with Photonic PL2000 cold light  
30 source), in order to determine to what extent this step could remove all microplastics and  
31 potentially eliminate the necessity for flotation in future analyses. For each sample, all sediment  
32 from the 2-4mm fraction was inspected for 15 mins and the 1-2mm fraction for 25 mins (subsample  
33 of 40 g where the total 1-2 mm size fraction exceeded this). These time frames were found to be  
34 sufficient based on the time taken to manually skim through sediment of this size and remove visible  
35 microplastic particles from surrounding organic and inorganic matter. In order to be selected, all  
36 particles sorted from sediment were required to conform to the following criteria as outlined by Nor  
37 and Obbard (2014): no visible cellular or organic structures, particles/fibres are not segmented and if  
38 fibres, were equally thick throughout their entire length and should not be tapered at the end. Two  
39 additional criteria were specified by Nor and Obbard, however these were considered unsuitable as  
40 they would have led to dismissal of likely plastics (homogenously coloured and not shiny) (Nor and  
41 Obbard, 2014). Furthermore, based on initial observations these criteria alone were deemed  
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1 insufficient for identifying all potential microplastic particles and eliminating non-plastics, as many  
2 particles in the sample appeared to be anthropogenic in origin while not conforming to the above  
3 conditions. In order to avoid missing/misidentifying particles we therefore employed additional  
4 measures whereby particles were only identified as microplastics if they also met at least two of the  
5 following criteria: 1) unnaturally coloured compared to the majority of other particles in the sample  
6 (e.g. bright blue, yellow etc.) and appear to be a homogenous material or texture, 2) unnaturally  
7 brightly coloured coating on another particle, 3) unnatural shape e.g. perfectly spherical, 4) fibre  
8 that remained intact with a firm tug/poke with tweezers, 5) shiny/glassy, 6) flexible/can be  
9 compressed without being brittle. All particles identified as microplastics according to the above  
10 criteria were removed and stored for subsequent analysis using Raman spectroscopy.

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Particles were identified and quantified as fragments (angular and solid, likely derived of larger items broken down), fibres (likely derived of synthetic textiles) or films (flexible and very thin, likely derived of large packing materials).

### 2.2.3. Extraction steps 2 and 3: Flotation and visual inspection of sediments post-flotation

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Following the initial visual sorting, the remaining material from each sample was transferred to 250ml glass beakers, each filled to approximately 75 ml volume, using a sufficient number of beakers to accommodate the whole sample to allow for separation by flotation. A concentrated ZnCl<sub>2</sub> solution (Bonnymans, UK) was prepared to a concentration of 1.7-1.8 kg L<sup>-1</sup>, for use in the flotation. This solution is denser than the plastic particles with the highest expected density in the sediments and should therefore float all plastic particles (e.g. PVC density is ≤ 1.58 g cm<sup>-3</sup> (Nuelle et al., 2014), lower than the density of the ZnCl<sub>2</sub> solution, > 1.7 g cm<sup>-3</sup>). The concentrated ZnCl<sub>2</sub> solution was poured on top of the sediment in the beaker leaving an approximately 1cm gap to the brim of the beaker. The beaker was then covered with Parafilm® to make a watertight seal, and shaken vigorously for 30 seconds. After settling for 2 hours, the beaker was placed into a larger vessel and

1 the Parafilm® removed and any attached particles rinsed back into the beaker. Additional ZnCl<sub>2</sub>  
2 solution was gently poured into the beaker allowing the floating particles to overflow into the larger  
3 vessel. The outside of the smaller beaker was then rinsed into the overflow container to remove any  
4 adhered particles. These shaking and overflow steps were then repeated twice more to maximise  
5 the retrieval of the buoyant particles (Claessens et al., 2013). The remaining sediment was stored for  
6 further visual inspection. The overflow liquid was vacuum filtered through 1.2 µm Whatman GF/C  
7 glass microfibre filter papers (GE Healthcare Life Sciences, UK) to collect floated particles and the  
8 filter was then flushed thoroughly with deionised water to remove all traces of ZnCl<sub>2</sub>. Given that  
9 particles were already size-sieved and > 1 mm, the pore size of these filters allowed for the retention  
10 of particles > 1 mm. The filtered particles were then oven-dried on the filter paper at 60°C before  
11 analysis. These filtered particles were initially inspected using the binocular light microscope varying  
12 between 6-40x magnification (Wild Heerbrugg, Switzerland, with Photonic PL2000 cold light source)  
13 to distinguish plastic from non-plastic using the selection criteria outlined above.  
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31 The third and final step of the process was to visually inspect the material that remained  
32 sedimented following the flotation step. This step was included as a precaution to investigate  
33 whether dense particles such as polymer-based composites had not been originally observed or  
34 floated in the density separation step. The remaining unflouted sediments were rinsed with  
35 deionised water and vacuum filtered through 1.2 µm Whatman GF/C glass microfibre filter papers  
36 (GE Healthcare Life Sciences, UK) to remove ZnCl<sub>2</sub> residues and visually inspected for 25 mins per  
37 sample. Microplastic particles were identified and removed according to the same criteria as before.  
38 This final step, allowed the effectiveness of the previous two steps to be assessed for microplastics  
39 recovery from sediments.  
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54 In order to account for potential handling and airborne contamination three control samples  
55 were also run by passing approximately 400-500 ml of the ZnCl<sub>2</sub> solution through the vacuum filter  
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1 (an equivalent volume to that filtered per field sample) onto 1.2  $\mu\text{m}$  Whatman GF/C glass microfibre  
2 filter papers and analysing under the binocular light microscope for contamination.  
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### 8 **2.3. Sample analysis: Raman spectroscopy** 9

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11 Given the large number of particles extracted overall, 20% of particles were subsampled for  
12 chemical characterisation using Raman spectroscopy (HR800UV, Jobin Yvon Horiba, France, with  
13 integrated Olympus BX41 microscope). To prevent bias in particle selection, all the particles from  
14 each sample were tipped onto a 40 mm by 40 mm grid and a random number generator used to  
15 determine the x and y coordinates from which to take each particle (20% total from each sample).  
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24 Spectra were acquired at 50x magnification using a near infra-red laser (785 nm) to limit  
25 fluorescence and the filter adjusted accordingly with each particle based on colour (to prevent  
26 burning or melting of dark coloured particles). Acquisition time was 30 seconds, accumulation 2,  
27 grating 600 with the range set to 600-3200  $\text{cm}^{-1}$  to ensure the entire fingerprint region was  
28 accounted for. Spectra were analysed using BioRad KnowItAll<sup>®</sup> Informatics System - Raman ID Expert  
29 (2015) software using single and multiple component and functional group analyses to compare  
30 spectra to a database of known compounds. This software carries out optimised corrections for  
31 spectral matching including interdependent corrections of the baseline, intensity distortion and axis  
32 shift with further manual correction possible for noise and baseline correction. The software  
33 matches each sample spectrum to several potential reference spectra. Sample spectra were  
34 compared to matched reference spectra and the most appropriate match was selected based on  
35 matching peak wavenumber positions.  
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### 57 **2.4 Data analysis** 58 59 60 61 62 63 64 65

1 Particle numbers across all the sites were first checked for normal variance structure using a  
2 Kolmogorv-Smirnov test. Where non-normal variance structure was found data were log  
3 transformed and normality confirmed prior to further analysis. Post-normalisation, analysis of  
4 particle numbers, types and sizes across all four sites were carried out using two way analysis of  
5 variance (ANOVAs) using site, size fraction and the interaction term as fixed factors. For comparing  
6 particle numbers between sites, one way analysis of variance (ANOVA) was used. Where significant  
7 differences were found across sites or particle fraction size, a post-hoc Tukey test was used to  
8 identify significant differences between conditions.  
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### 23 **3. Results**

#### 24 **3.1. Sorting method**

25 The three control filters analysed to assess contamination during processing, contained an  
26 average of two fibres per filter paper. These may arise from aerial deposition and from clothing.  
27 Compared to the number of fibres found across all field samples (578 total, with even the least  
28 polluted site, the Leach, containing 69 fibres), this contamination was deemed to be negligible.  
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40 In order to determine the effectiveness of the different sorting methods the proportion of  
41 particles recovered in each step were compared. The most effective method of particle removal was  
42 flotation, which extracted between 51% (The Cut site 1) and 82% (Lambourn) of the total particles  
43 removed combining all three steps. In comparison, number of particles removed in the initial timed  
44 search by eye was between 16% (The Cut site 1 and Lambourn) and 37% (The Cut site 2) of the total  
45 particles. However following steps one (timed search by eye) and two (flotation), 97% of the total  
46 number of particles extracted were found for three out of four sites (excluding The Cut site 1). The  
47 final step which was a search of sediment post-flotation found less than 3% of the total particles  
48 recovered for these three sites. However, for the most polluted site (The Cut site 1) even after these  
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1 two steps of the combined method, 34% particles (of total removed overall) remained in the  
2 sediment (determined by the third step of a search through sediment post-flotation). Overall an  
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4 average 75% of the total recovered particles were extracted by initial sorting and flotation, this being  
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7 98% Cut site 1 was excluded.  
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### 10 11 12 13 **3.2. Particle presence, abundance and size** 14 15

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17 Microplastic particles were found at all of the sampling sites. There were clear and  
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19 significant differences in both the number and types found between the four sites (both ANOVA,  $p$   
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21  $<0.001$ ). However the mass of sediment in the 1-4mm size range varied between sites with total dry  
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23 weights of sediment in the 1-4 mm size fractions being significantly lower in the Leach, Lambourn  
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25 and Cut 2 samples than those from The Cut site 1 (ANOVA,  $p < 0.01$ , Tukey,  $p < 0.05$ ). This was due to  
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27 variation in sediment composition and grain size. For example, total dry weights of sediment  
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29 between 1-4 mm from the total 1 L sample from the Leach (average 128 g) were less than the Cut  
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31 site 1 (429 g) due a greater proportion of sediment particles  $<1$  mm at the Leach (table 1). To  
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33 standardise between sites for comparability, particle numbers were therefore expressed as a  
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35 number of microplastic particles per 100 g dry weight of sediment in the 1-4mm size range for both  
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37 microplastic size fractions and all particle types, and all statistical analysis carried out on these  
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39 corrected data. Total and corrected numbers are reported in table 1, with significant differences  
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41 found between sites for both number and types of microplastics following correction for sediment  
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43 weight (ANOVA,  $p <0.001$ , Tukey,  $p <0.05$ ).  
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51 Site was a highly significant factor determining the total number of microplastics particles  
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53 per 100 g sediment (ANOVA,  $p <0.005$ ). The highest number of particles was recovered from The Cut  
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55 site 1, the second most sewage-impacted site, with an average of  $66 \pm 7.7$  particles per 100 g across  
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57 the four replicates (table 1) found following the three-step extraction method. The high number of  
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1 particles recovered here was, however, not significantly different from the most sewage effluent  
2 impacted site (The Cut site 2) (average  $33.2 \pm 16.1$  particles per 100 g, Tukey,  $p >0.05$ ). The lowest  
3  
4 numbers of microplastic particles were found at the Leach and Lambourn sites, which had the lowest  
5  
6 sewage effluent input and population equivalent density (average  $18.5 \pm 4.2$  particles and  $22.1 \pm 9.5$   
7  
8 particles respectively). Comparisons indicated that total counts from both these sites were  
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10 significantly lower than the more polluted Cut 1 site (Tukey,  $p <0.05$ ), but not significantly different  
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12 from each other (Tukey,  $p >0.05$ ).  
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16  
17 There was a significant difference between the two microplastic particle size fractions found  
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19 across all sites (ANOVA,  $p <0.005$ ), with the number of particles in the 1-2 mm fraction consistently  
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21 being higher on average than in the 2-4 mm fraction (table 1). This difference was consistent across  
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23 all the sites (ANOVA,  $p =0.142$ ).  
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### 31 **3.3. Type of particles**

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34 There was a significant difference between the types of particles found across sites (ANOVA  
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36  $p <0.001$ ). This was due to the significantly lower numbers of films which comprised only 3.3% of  
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38 particles (average 2.2 particles per 100 g) compared to the other two particle forms (Tukey,  $p <0.05$ ,  
39  
40 table 1). The difference between fragments and fibres was not significant (average 17.2 particles per  
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42 100 g, 49.3% overall and average 16.5 particles per 100 g, 47.4% overall respectively, Tukey,  $p$   
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44  $>0.05$ ).  
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49 Site significantly influenced the types of particles found (ANOVA  $p <0.001$ ). The Cut site 1  
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51 was significantly different from all other sites in that the dominant type of particles (Tukey,  $p <0.05$ )  
52  
53 found at this location were fragments, comprising 80.8% of particles (corrected for sediment weight,  
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55 Fig. 3). Fibres were the most abundant particle type at all other sites, although there were no  
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57 significant differences between the numbers of fibres found between sites (Tukey,  $p >0.05$ , table 1).  
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Films were the least abundant particle type and showed no significant differences in abundance between sites (Tukey,  $p > 0.05$ , table 1).

Analysis of fragments from The Cut site 1 identified a specific particle form that was not observed at any of the other sites. These unique fragments were red and yellow and were often found to incorporate glass beads (which themselves were also found independently). As non-plastics these glass beads were not included in overall site microplastic counts, however their presence was observed in all samples from this site. Shards of glass were also easily identifiable due to their brittle nature and were not counted.

### 3.4. Plastic types

A total of 336 particles (20% total) were analysed using Raman spectroscopy with BioRad KnowItAll® Informatics System - Raman ID Expert (2015) software to determine their chemical composition. The particles chosen were evenly distributed across all samples and size fractions. Of the particles analysed, many could not be identified due to poor quality spectra (due to fluorescence/lack of identifiable peaks), or a spectrum was present but was not recognised either using the KnowItAll software or by eye. Therefore 111 out of 335 (33%) particles could be identified to chemical composition.

Of these 111 identifiable particles, eight (7%) were found to be natural substances such as shell or organic matter, while the other 103 (93%) were of anthropogenic origin. The majority of these spectra (62%) related to dyes, as opposed to the plastic materials in which they are impregnated (Fig. 4). Dyes detected included those commonly added to plastics and plastic composites, including copper phthalocyanine, mortoperm blue, hostasol green and chrome yellow (Clariant International Ltd, 2011; Imhof et al., 2016; Lewis, 2005; Okazaki and Suzuki, 1976; Van Cauwenberghe and Janssen, 2014; Van Cauwenberghe et al., 2013). A total of 34 analysed particles

1 could be identified specifically to their polymer composition. The types of polymer identified were  
2 polyester/polyethylene terephthalate (PET, 14 particles) polypropylene (PP, five particles),  
3  
4 polyarylsulphone thermoplastic (five particles), polyethylene (PE, two particles), polystyrene (PS, one  
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6 particle), and poly vinylchloride (PVC, one particle). Additional polymers found include  
7  
8 polycarbonate and composites such as acrylonitrile/PMMA thermoplastic blend and  
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10 polyurethane/resin composite; these were all grouped under 'other polymers' (Fig. 4).  
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#### 18 **4. Discussion**

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21 In terms of quantification method evaluation, the initial sorting and flotation steps  
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23 combined successfully removed 75% of microplastic particles with the other 25% remaining in the  
24  
25 residual sediment. Recovery would have been at 98% if the particles at The Cut site 1 were excluded,  
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27 as 34% of these could not be floated due to their dense nature. However an initial manual sort by  
28  
29 hand and microscope through an amount of dry sediment alone appears to be ineffective, as a  
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31 maximum of 37% particles were removed in this sorting step. Many of the microplastics manually  
32  
33 sorted would also be expected to float, therefore this suggests that flotation is the most effective  
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35 method for removing microplastics from river sediments, with a subsequent sort through the  
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37 remaining sediment post-flotation to remove dense particles. Given the thorough stepwise process  
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39 of particle extraction, it was considered that these steps carried out in succession were successful in  
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41 removing all microplastic particles from the sediment. However, for efficiency, the initial pre-  
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43 flotation search cannot be considered fully effective on its own and may be eliminated as it can be  
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45 assumed that all particles removed in this step would be extracted in the following two steps. The  
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47 presence of these dense microplastics present in the unfloated fraction highlights the complexity of  
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49 microplastics as an environmental contaminant; these will often likely be polymer-based composites  
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51 and therefore will not behave as the pure polymer would be expected to. This stepwise  
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53 methodology works to extract particles even from complex sediment samples in a cost-effective  
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1 manner. It is necessary to carry out multiple steps of particle extraction to account for dense  
2 particles therefore the suggested protocol for future samples would be to carry out a flotation using  
3 a concentrated ZnCl<sub>2</sub> solution, followed by a timed manual sort of the remaining sediment to  
4 remove any unfloted plastic particles.  
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10 This study shows for the first time in the UK that microplastics are present in river  
11 sediments, with microplastic particles observed at all sites including both urban and rural locations.  
12 Despite being the second most anthropogenically influenced in terms of effluent input and  
13 population equivalent density, the highest sediment microplastic burden was found at The Cut site 1  
14 (although not significantly different from the more highly effluent polluted Cut site 2, Fig. 3). The  
15 dominant type of particle at this site was fragments, as opposed to fibres at the other three sites.  
16 Hence at this site there is the indication of a source of fragment additional to the sources at the  
17 other three sites. The characteristics and chemical nature of particles found (e.g. predominantly  
18 coloured, angular fragments) suggest that many of these particles found were locally-derived  
19 secondary microplastics rather than primary microplastics from consumer products or secondary  
20 artificial fibres introduced by sewage effluent. Factors contributing to the relatively high plastic  
21 fragment input at The Cut site 1 are likely to be the presence of a storm drain immediately upstream  
22 from the sampling location carrying local urban runoff to the watercourse and the urban nature of  
23 the site, on the outskirts of a large town. This implies that, at this site, runoff rather than sewage  
24 effluent is the dominant input. The high sewage-based input at The Cut site 2 may be reflected in it  
25 having the highest number of fibres when calculated per 100 g (Fig. 3).  
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49 Fragments and fibres were both found in significant numbers, with fragments dominating  
50 the particles found at the Cut site 1 and fibres being the dominant particle type at the other three  
51 sites. Films were found only at low numbers. The abundance of fibres at all sites suggests the  
52 influence of sewage effluent, even for the Leach where there is only one upstream STW and  
53 negligible effluent input (Fig. 2). Given that there were still a considerable number of particles found  
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1 at this site there may be an alternative anthropogenic influence, for example airborne  
2 contamination (Peters and Bratton, 2016) or agricultural runoff (e.g. from plastic mulching) (Rillig,  
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4 2012). With UK policy of significant amounts of sewage sludge applied to land in the UK (80% of all  
5  
6 sludge) (DEFRA, 2012), it is possible that such fibres may be derived from sludge applied to  
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8 surrounding arable land entering the watercourses via runoff. Runoff from septic tank systems may  
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10 also be a source (Butler and Payne, 1995).  
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15 Of the particles remaining unfloated throughout the sorting process, a number were  
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17 identified to be dense composites of road-marking paints, aggregates, a painted coating on a dense  
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19 particle or high density mineral-polymer mixtures (Corcoran et al., 2015). These materials are  
20  
21 composites of polymer resin, thermoplastic, bitumen and pigment (often with incorporated glass  
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23 beads for reflectivity) (Conserva and Dupont, 2011; National Association of City Transportation  
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25 Officials, 2014). In addition, key features of the particles identifying road markings as a source  
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27 include their colour (predominantly red and yellow), incorporated glass beads and site location  
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29 downstream of the storm drain input. Raman analysis showed many of these particles to contain  
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31 dyes, for example many yellow particles contained chrome yellow, a yellow pigment commonly  
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33 added to thermoplastic road marking paints (Okazaki and Suzuki, 1976). To confirm this  
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35 identification as road-derived particles, particles were collected from road surfaces upstream of the  
36  
37 Cut site 1 storm drain. Visual inspection and Raman analysis showed that particles collected directly  
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39 from road-based coatings and paints matched those extracted from the sediment samples (Fig. 5).  
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41 Some of these particles appeared to be partially coated in paint indicating that some of the coating  
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43 had degraded and highlighting the potential for small particles to degrade further. The incorporated  
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45 glass beads observed, which are lost to the environment with wear and were also observed  
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47 independently in samples, do not fit the definition of microplastics (Kemsley, 2010).  
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57 Polymers give a weak Raman scatter and therefore an incorporated dye is likely to override  
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59 the polymer spectrum (Imhof et al., 2016; Smith and Dent, 2005). Given the strong dye spectra  
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1 observed in many of the coloured particles, and lack of other peaks, it can therefore be inferred that  
2 the particles identified as pigments are all dyed polymers or polymer composites (Van  
3 Cauwenberghe and Janssen, 2014; Van Cauwenberghe et al., 2013). Unidentifiable particles were  
4 also inferred to be plastics as fluorescence is a common problem when analysing polymer particles  
5 using Raman spectroscopy (Löder and Gerdts, 2015). For the purpose of this study, paints, pure  
6 polymers and composites were all considered as microplastics as per Song et al (2014), although  
7 some authors will distinguish 'micropaints' and microplastics separately due to varying polymer  
8 composition (Imhof et al., 2016). However as all polymers are composites to some extent  
9 (containing fillers, pigments and plasticisers) very few environmental plastics will be 'pure' polymers;  
10 there is currently no threshold of polymer content to distinguish between pigmented polymer and  
11 polymer incorporated within a paint.  
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27 Previous marine studies have identified plastic pellets associated with tarry residues or  
28 attached to tar-based substances (Gregory, 1983). The observations of road-derived particles here  
29 indicate that materials similar in nature are also entering river systems and may add another aspect  
30 to microplastic presence and behaviour in this environment. It has previously been noted that  
31 microplastics can be transported via road surface runoff originating from degraded litter, pieces of  
32 car-related debris such as bumpers or hubcaps, tyre wear particles (Browne et al., 2010; Eriksen et  
33 al., 2013; Galgani et al., 2015; Tibbetts, 2015), however to our knowledge this is the first study to  
34 note the presence of microplastics derived directly from the road surface and associated markings.  
35 Paint particles have previously been found in UK estuarine sediments, however these were not  
36 linked to road surface degradation (Takahashi et al., 2012). Little is known about the long term fate  
37 and behaviours of these materials in rivers. Such releases are likely to be widespread and difficult to  
38 avoid; efforts in infrastructure and civil engineering management would be needed to limit such  
39 emissions.  
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1 Using Raman spectroscopy, polymer types including polypropylene, polyethylene, polyvinyl  
2 chloride, polyester and polystyrene were found at the sites. These were all expected as these are  
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4 among the most widely used plastics in consumer products (PlasticsEurope, 2016). Another polymer  
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6 found in relatively high numbers was polyarylsulphone thermoplastic (Fig. 4), this was found in three  
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8 out of four sites however was not expected as it is not one of the most commonly used polymers.  
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10 This polymer has high thermal resistance and is used to replace ceramics and glass in a variety of  
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12 applications including household goods and electrical equipment (Rosato and Rosato, 2004). One  
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14 expected polymer, nylon was not observed here, although this does not necessarily indicate its  
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16 absence at these sites.  
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22 These findings highlight the ubiquitous nature of plastic as an environmental pollutant, even  
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24 in rural areas with no expected significant inputs. The results presented here can be taken as an  
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26 indicator of microplastic pollution in the Thames Basin. Despite the combination of different sorting  
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28 methods these are not guaranteed to be without error, given that 7% of particles analysed by Raman  
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30 were found to be of natural origin. However, this error is far lower than the 70% predicted by  
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32 Hidalgo-Ruz et al. (2012). To some extent, predictive estimates of microplastic abundances can be  
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34 made based on known site characteristics (including effluent input and population served by  
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36 upstream STWs). However, alternative factors are important to take into account when trying to  
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38 predict microplastic pollution in this size range; other sources such as terrestrial run-off and inputs  
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40 from storm drains cannot be disregarded. Additional factors to take into consideration include  
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42 surrounding land use, population density in the area surrounding the sampling site (as opposed to  
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44 population equivalent served by upstream STWs) and alternative inputs to the watercourse (such as  
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46 storm drains and drainage ditches).  
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52 These results provide evidence of rivers as a source of microplastics to the sea, however the  
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54 factors influencing presence, abundance and behaviour of microplastics in a riverine environment  
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56 are complex and difficult to predict. Within a river, sediment transport and dynamics including flow  
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1 speed and channel depth can control the flow of particles, both natural and artificially produced, *en*  
2 *route* from land to ocean (Phillips et al., 2000; Smith et al., 2003). An accurate assessment of  
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4 microplastics in any environment needs first and foremost knowledge of the range of potential  
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6 sources, behaviour of particles in the environment and an understanding of the factors that mediate  
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8 the inputs. Further research needs to be done at these locations to include the small scale particles  
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10 (<1 mm) and also particles within the water column and on the surface. The density of polymers is  
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12 an important consideration given that the particles observed in sediment are likely to be of denser  
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14 polymers; in flowing waters buoyant particles may have been transported downstream before they  
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16 could become biofouled and dense enough to sink (Andrady, 2011; Van Cauwenberghe et al., 2013).  
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18 Additional studies and modelling of fate and transport of these particles within river systems need to  
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20 be carried out in an attempt to better predict where they will end up. It is also highly likely that  
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22 seasonal changes in river flow will affect the presence and transport of microplastics within riverine  
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24 systems. Therefore sampling in different weather and seasonal conditions would help develop  
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26 understanding of the degree to which rivers act as a sink of microplastics and a source to the marine  
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28 environment.  
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## 40 **5. Conclusions**

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42 This study is the first to report relative amounts and types of microplastics present across  
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44 different locations both in the Thames basin, and also in any low-lying river catchment in the UK.  
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46 Despite the uncertainties and complexities with predicting and analysing microplastic pollution,  
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48 microplastics were observed at all sites and inference can be made as to sources. While it is clear  
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50 that the number and types of microplastics observed in this study are not the entirety of  
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52 microplastic pollution at these sites, these results give a representative indication of the proportions  
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54 of plastics between these sites and the factors that influence their presence and abundance,  
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56 specifically sewage and road-derived input, plus in situ degradation of litter, especially in urban  
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1 areas. The majority of microplastics from this study were deemed to be secondary microplastics i.e.  
2 broken down from larger items. To some extent, different types of particles could be attributed to  
3 different sources i.e. road surface markings made of thermoplastic composite paints, fibres derived  
4 from synthetic textiles and fragments of large litter items such as plastic bottles (polypropylene) and  
5 packaging materials (polystyrene). Sewage and effluent input is also a likely significant source given  
6 that many of the particles found were fibres, especially in the most polluted sites that receive a high  
7 volume of effluent such as those at The Cut sites 1 and 2. However these results indicate that  
8 despite the evidence for sewage influences at these sites, in certain locations sewage effluent may  
9 be a less significant source of large microplastic particles than direct runoff from land. This study  
10 highlights the importance of rivers as a source of microplastics and other anthropogenic litter to the  
11 ocean, but also as a sink for dense plastics and anthropogenic particles with potential for  
12 environmental and ecological impacts.  
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39 Environment Research Council through National Capability funding of the Centre for Ecology and  
40 Hydrology Pollution and Environmental Risk Program.  
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Table 1. The average ( $\pm$  St Dev) sediment weight (g in 1-4 mm size range from 1 L samples,  $n=4$ ), total number of microplastic particles for four 1 L sediment samples and average ( $\pm$  St Dev) number of microplastic particles per sample ( $n=4$ ) reported both as total particles extracted per 1 L sediment and weight-corrected to particles per 100 g sediment (1-4 mm fraction) from sediment samples from four sites in the Thames basin, namely two rural sites Leach and Lambourn (with low population equivalent densities and low sewage input) and the urban sites Cut 1 and Cut 2 (with high population equivalent density and high sewage input). Average ( $\pm$  St Dev) numbers of microplastic particles per site ( $n=4$ ) are reported for both totals and within the categories of particle size distribution split into two size ranges (1-2mm & 2-4mm) and three particle types (“fragments”, “fibres” and “films”); averages that do not share a common letter are significantly different (Tukey  $p < 0.05$ ).

Site	Average dry weight of sediment in 1-4mm size fraction (g) from 1 L total sample	Total actual number of particles between 1-4mm at site (total of 4 replicates)	Average actual number of particles between 1-4mm	Average number of particles per 100g between 1-4mm	Size distribution (particles per 100g)		Particle types (per 100g)		
					Average number of particles (1-2 mm) (A)	Average number of particles (2-4 mm) (B)	Average number of fragments (A)	Average number of fibres (A)	Average number of films (B)
Leach	128.1 $\pm$ 50.8 (B)	88	22 $\pm$ 5.2 (A)	18.5 $\pm$ 4.2 (A)	10.2 $\pm$ 3.1	8.3 $\pm$ 1.9	3.2 $\pm$ 0.6 (CDE)	14.7 $\pm$ 3.8 (BCD)	0.6 $\pm$ 1 (E)
Lambourn	191.1 $\pm$ 62.7 (B)	149	37.3 $\pm$ 5.8 (A)	22.1 $\pm$ 9.5 (A)	14.1 $\pm$ 5.4	8.1 $\pm$ 5.3	3.1 $\pm$ 3 (CDE)	16.9 $\pm$ 5.7 (BC)	1.7 $\pm$ 1.6 (DE)
The Cut site 1	459 $\pm$ 148.4 (A)	1190	297.5 $\pm$ 85.5 (B)	66 $\pm$ 7.7 (B)	41.9 $\pm$ 3.4	24.1 $\pm$ 5	53.3 $\pm$ 7.8 (A)	12.1 $\pm$ 4.5 (BCDE)	0.6 $\pm$ 0.3 (E)
The Cut site 2	225.8 $\pm$ 88.6 (B)	252	63 $\pm$ 25.4 (A)	33.2 $\pm$ 16.1 (AB)	20.5 $\pm$ 12	12.7 $\pm$ 4.6	9.1 $\pm$ 9.6 (BCDE)	22.3 $\pm$ 7.1 (B)	1.7 $\pm$ 1.3 (DE)

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Figure captions:

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6 Fig. 1. Map to show locations of sampling sites within the Thames basin and the UK.  
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12 Fig. 2. Site characteristics including average percentage effluent in the river at the sampling sites  
13 and population equivalent density of upstream sewage treatment works.  
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21 Fig. 3. Total number of microplastic particles at each site per 100 g dry weight of sediment, and  
22 number of different types of particles (fragment, fibre and film) within this total. Different letters  
23 indicate significant differences between the number of microplastic particles per 100 g at each site.  
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32 Fig. 4. Proportional compositions of 111 identifiable particles characterised by Raman analysis (of an  
33 original 336 analysed particles) across all sites including polymers, dyes (inferred to be polymers)  
34 and particles misidentified as plastics (natural substances)  
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44 Fig. 5. Photographs comparing particles collected directly from coloured road surfaces/road marking  
45 paints (top row) to particles extracted from sediment samples at The Cut site 1 (bottom row). These  
46 particles all fit within the 2-4 mm size range. Photos were taken using a Nikon Coolpix 4500 camera  
47 with a Nikon Coolpix MDC lens attachment on a Nikon SMZ800 stereo microscope with Photonic  
48 PL2000 cold light source at varying magnifications. Arrows highlight incorporated glass beads,  
49 present both in particles taken from road marking paints and in environmental samples.  
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Figure 1 (2-column)  
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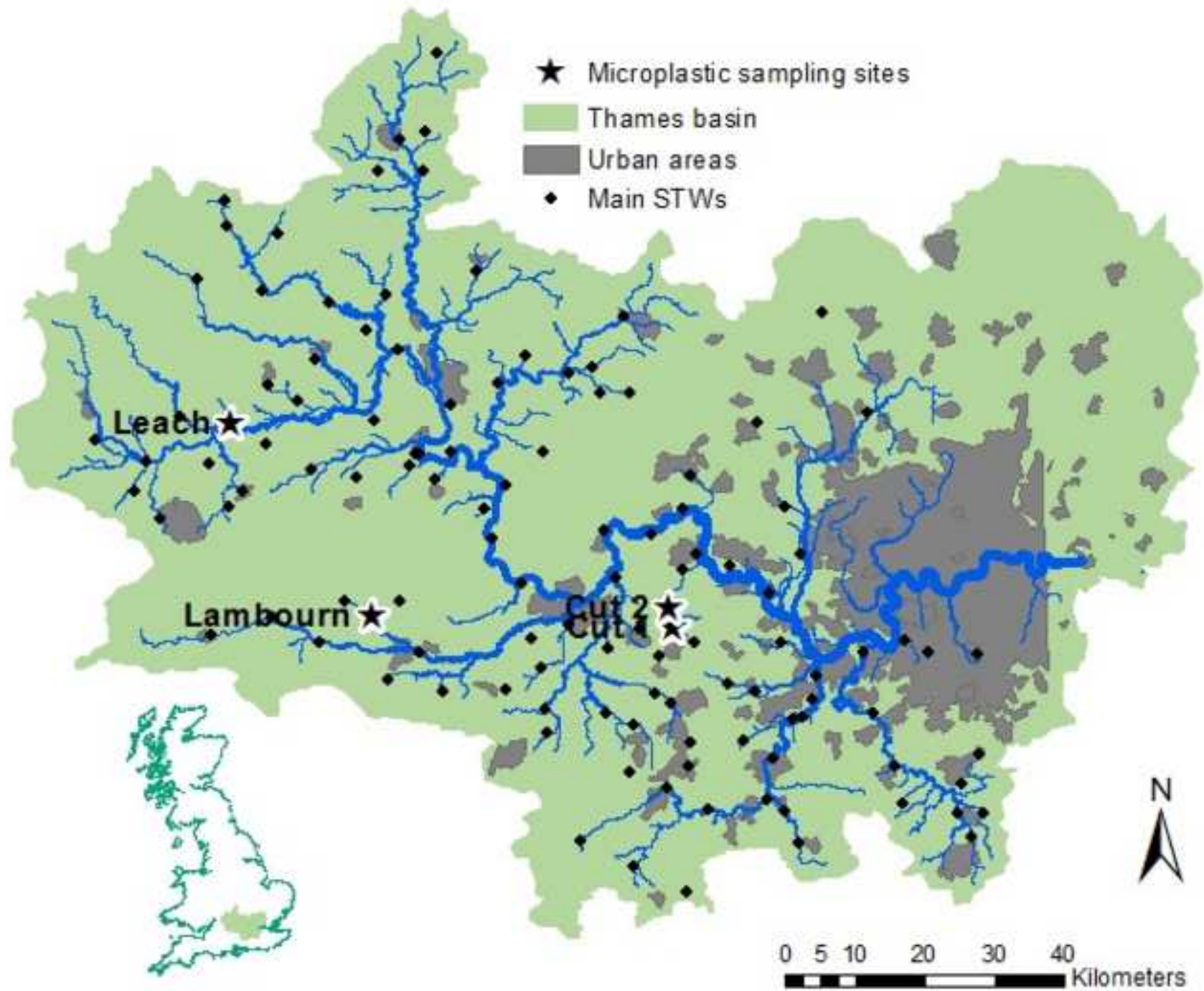


Figure 2 (1-column)

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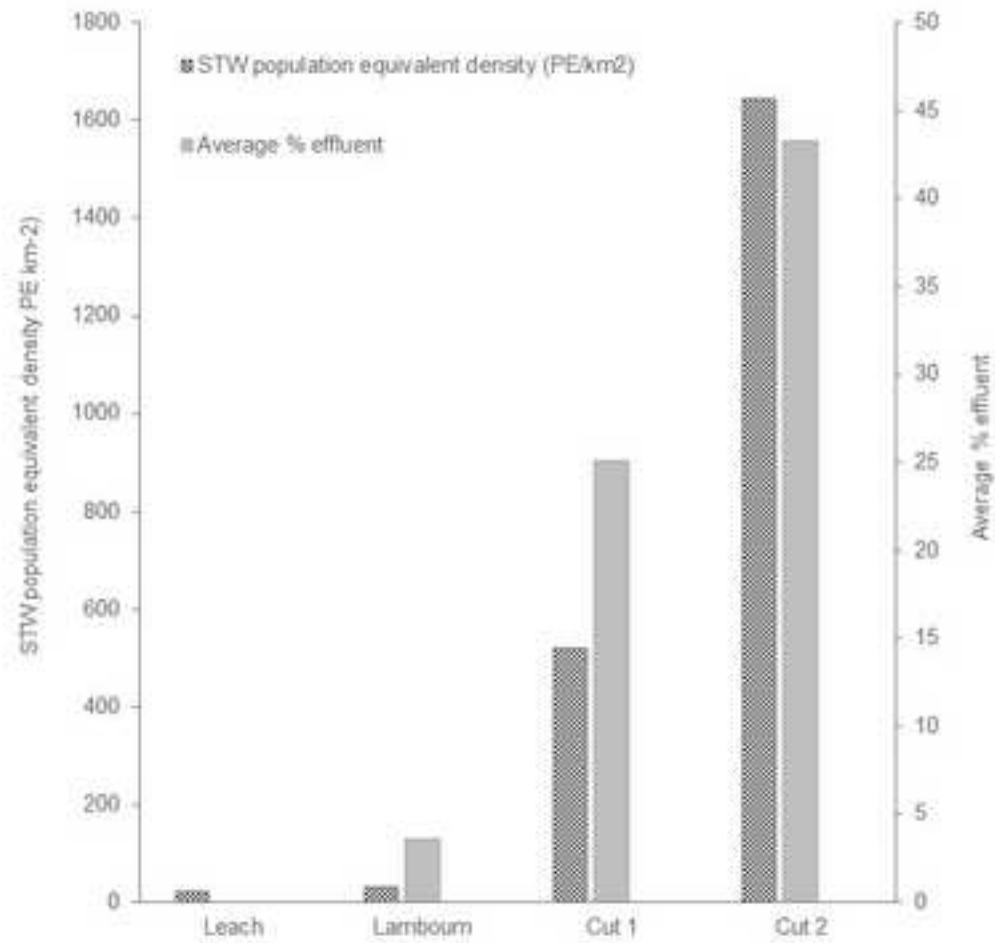


Figure 3 (1-column)

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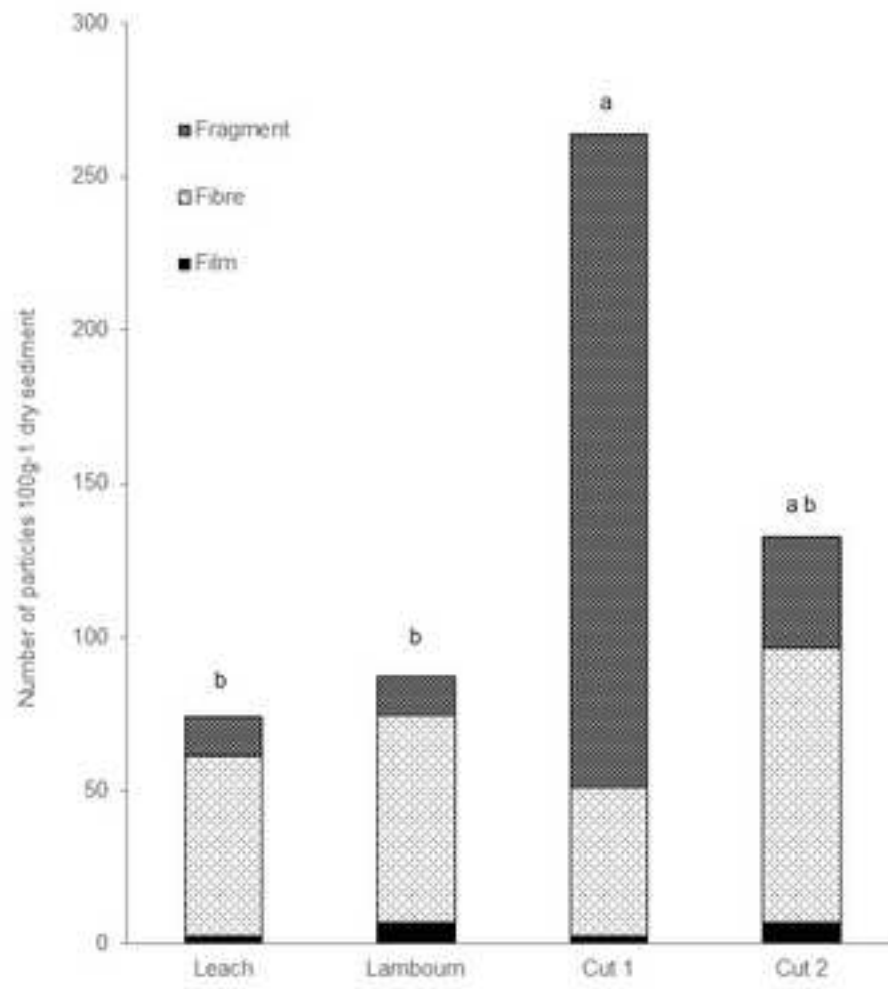


Figure 4 (1-column)

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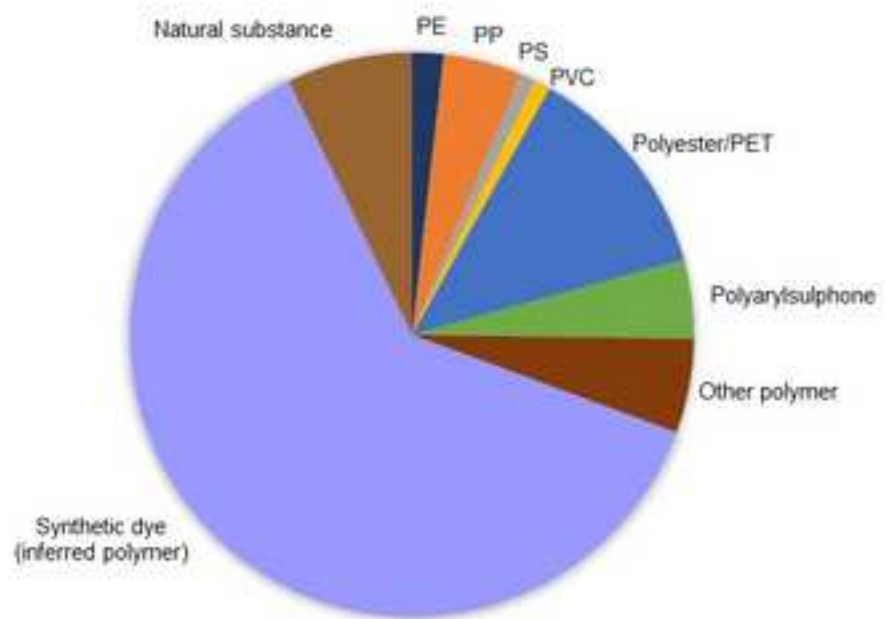
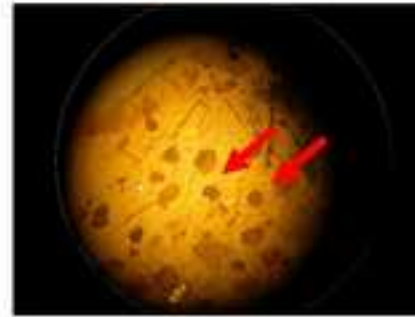
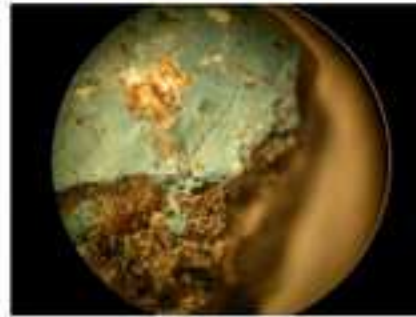
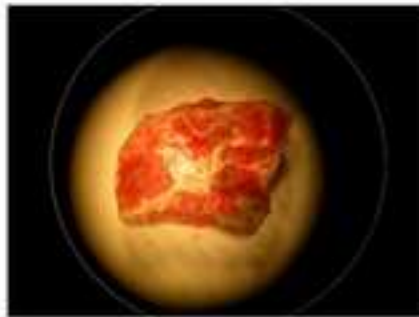


Figure 5 (2-column)  
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Particles collected  
from road surface



Particles extracted  
from sediment

