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The identification and quantification of microplastics in potable water and its sources within Water Treatment Works in England and Wales.

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ABSTRACT:

Microplastics were characterised in 8 water treatment works (WTWs) in England and Wales (UK). Sources included river water, groundwater and an upland reservoir. Water treatment varied from disinfection, filtration, sedimentation and activated carbon techniques. At each WTW, 5 repeat samples of raw and potable water and 2 repeat sludge samples were taken over 5 months. Microplastics in water were captured on 10 µm filters and non-plastic material digested in the laboratory. Microplastics ≥ 25 µm were analysed using Fourier Transform Infra-Red microscopy. Blanks revealed consistent polyethylene (PE), poly(ethylene terephthalate) (PET) and polypropylene (PP) contamination. Spike recoveries for 63-90 µm polyamide microplastic demonstrated 101% (standard deviation, SD 27%) and 113 (SD 15%) recovery for raw and potable waters and 52 (SD 13%) for sludge. Only 4 of the 6 WTW sampled for raw water and only 2 of 8 WTW in their potable water had microplastics above the limit of quantification. Considering only the WTWs with quantifiable microplastics, then on average, 4.9 microplastic particles/L were present in raw water and only 0.00011 microplastic particles/L in potable water (99.99% removal). Values in waste sludge were highly variable. PE, PET and PP were the most common polymers quantified in raw water and sludge, and polystyrene and acrylonitrile butadiene styrene in potable water.

INTRODUCTION

The belated recognition of worldwide plastic and in particular microplastic contamination of the home and the environment raises many more questions than we have answers for. Leaving aside the questions of hazard, it is important to quantify the daily

exposure to humans and wildlife. Microplastics are generally considered to be plastic particles smaller than 5 mm but larger than 1 µm, although a standard definition has yet to be agreed. Whilst the biodegradation of many plastic polymers is seen as negligible [1], they are liable to abiotic decomposition, with the rate being influenced by light and temperature as well as mechanical abrasion [2-4]. Thus, the major source of microplastic particles is considered to be the disintegration of consumer products including packaging and textiles [5-7]. Another challenge are particles released from vehicle tyres and painted road surfaces [8, 9], but these are much more difficult to enumerate as microplastic particles [10, 11].

There has been some effort to understand human exposure to microplastics through food [12, 13] and in the air [14]. However, an important question for the public and Water Utilities alike is whether microplastics are present in tap water and whether this could be a potential route of exposure [15]? There are already studies showing apparently high levels in bottled water [16-18]. However, to date there have been only a few studies quantifying microplastics in treated drinking water.

The processes involved in water treatment are typically designed to reduce if not eliminate biological contaminants such as algae, *Cryptospriridium,* bacteria, chemicals such as pesticides and inert particles. The degree of treatment reflects the nature of the source water, with river water requiring considerably more treatment than groundwater (Table 1). With respect to the question of microplastics contamination, the processes designed to remove particles during water treatment are particularly relevant. The first step is normally the addition of coagulants (usually a salt which neutralises charge) and/or flocculants (usually a polymer which binds to particles) to encourage particles to clump together. Recent research has indicated that whilst an Fe salt could only settle out 20% of <0.5 mm polyethylene (PE) particles, an anionic polyacrylamide could remove 90% of the same material [19]. The next stages can be dissolved air flotation (DAF) or a hopper bottomed clarifier (HBC). With DAF, the floating particles are skimmed off the top, with an HBC, the sediment particles become trapped within the sludge blanket when it is introduced to the bottom of the hopper. It is common to have rapid gravity filters (RGF) where the water is forced into the bottom of a gravel and sand filled tank where particles become trapped before the cleaned water is collected at the surface. Slow sand filters (SSF) collect the water once it has passed through sand containing an active microbial mat at its surface. The majority of the WTWs sampled in this study used combinations of these approaches (Table

1). Such combinations have been recorded as removing around 96% of algal blooms and 99.999% of 1 µm Cryptospiridium oocytes[20, 21]. An alternative to filter bed approaches is the use of a membrane with a 30 nm pore-size such as found at LR1 (Table 1). The filter and water flow have to be cleverly designed to prevent clogging [22]. Other treatments like UV, H_2O_2 disinfection, chlorination and membranes can be employed to tackle organisms and granular activated carbon (GAC) or ozonation can be used to trap or destroy organic contaminants.

There are still few studies on microplastics and water treatment and these have reported very different results. Studies which have focused on recording very small microplastics involving scanning electron microscopes and micro-Raman imaging microscopes have found between 300 and 900 microplastic particles/L down to 1 µm size at different water treatment works (WTW)[23, 24]. However, Mintenig, et al. (2019)[25] only found 0.0007 microplastic particles/L at 6 different WTW, but in this case these were of a size of 20 µm or greater. These contrasting values may simply reflect the very different sizes reported on and the different methods used.

There are similar uncertainties in the numbers of microplastic particles in the source or raw waters used by WTWs. The study of Panno, et al. (2019)[26] reports levels up to 20 microplastic particles/L in North American groundwater but Mintenig, et al. (2019)[25] only found up to 0.007 microplastic particles /L in German groundwater. In surface water Pivokonsky, et al. (2018)[23] reported up to 4000 microplastic particles /L.

It is important to be aware that given the enormous amount of machine time required to analyse very small particles (<25 µm size) the operator is required to select only a few 'representative' parts of their filter for analysis. This allows the opportunity for bias. Given the apparently high levels of microplastics in the indoor environment, such as a component of dust [14], there is a particular danger of 'false positives' when reporting on microplastics in samples obtained from relatively clean environments. To account for this, a very carefully documented approach to blanks (negative controls) is essential. The lack of standardised methods and quality assurance/control protocols in microplastics analysis in water still retards progress in this field [27].

The aims of this study were to get an indication of the effectiveness of water treatment works (WTW) in Britain in removing microplastics during drinking water

96 treatment, and identify the common polymers present, whilst using robust methods to
97 reduce the impact of environmental contamination of samples.

98

99 ## MATERIALS AND METHODS

100 **Potable water treatment works sampled.** In the selection of eight WTWs, this study
101 attempted to cover a range of different raw water sources as well as different water
102 treatment techniques (Table 1). Three of the sites directly abstracted and treated water
103 from lowland rivers (LR1-3). A further two of the sites abstracted from lowland rivers, but
104 treatment followed reservoir storage (LRS1-2). Two of the sites abstracted from either chalk
105 or sandstone groundwater (GWC and GWS), and finally one abstracted water from an upland
106 reservoir (UR1). For the river and upland reservoir sites, a range of physical treatment
107 processes were employed by the WTW to separate particulate matter, some including
108 activated carbon (LR1-3 and LRS1) to capture dissolved organic molecules. With the
109 groundwater sites, disinfection was the only treatment process for one, and a simple
110 filtration stage at the other.

111

112 **Table 1. Description of WTW sampling sites including volumes of water filtered. Note DAF**
113 **–dissolved air flotation, HBC-Hopper bottom clarifier, RGF-rapid gravity filter, SSF-slow**
114 **sand filter, GAC-granular activated carbon**

Code	Description	Treatment
LR1	Lowland river, direct abstraction	GAC, membrane, UV/H_2O_2, GAC, disinfection
LR2	Lowland river, direct abstraction	HBC, RGF, GAC, disinfection
LR3	Lowland river, direct abstraction	Disinfection, pH balancing, static mixer, clarifier with $FeCl_3$ & polyelectrolyte coagulation, RGF, GAC, microscreen
LRS1	Lowland river, pumped storage	DAF or HBC, RGF, GAC, disinfection
LRS2	Lowland river, pumped storage	Reservoir with SSF, RGF, ozone, SSF, disinfection
GWC	Groundwater, chalk	Disinfection
GWS	Groundwater, greensand	Aeration and pressure, filtration, disinfection
UR	Pristine upland reservoir	$Al_2(SO_4)_3$ coagulation. RGF, disinfection, pH balancing, UV

115

116

Collecting raw water, potable water and sludge from WTWs. The field sampling rigs consisted of metal filter holders (Spectrum Inox economic filter housing for raw water and anodised aluminium filter holder, Pall Life Sciences, Advantec for potable water). These contained either a woven stainless steel 10 µm pore size filter (9 ¾" length tubular cartridge, ca. 500 cm^2 for raw water) or a 47 mm diameter disk, ca. 10 cm^2 filtration area for potable water, both from Wolftechnik Germany. These were connected to sample taps present at the WTWs with Water Regulations Advisory Scheme (WRAS) approved hose (SILEX platinum cured silicone braided hose) and a WRAS approved brass double non-return valve, which was required to protect the drinking water supply from contamination, but contains plastic parts in the non-return mechanism (schematic in SI Figure 1). Before sampling commenced, a minimum of 5 L of sample water were run to waste, bypassing the filter, to flush the tubing, before several hundred litres were passed through the filter over approximately 12 h with the volume being determined by a water meter. Each of the eight WTW were sampled on five separate occasions over a period between August 2018 and May 2019. At four of the WTW it was possible to collect sludge produced during the water treatment process, which was done on two separate occasions each. All sludge was collected in clean 1 L glass Kilner jars with aluminium foil between the jar and the lid, to prevent the samples coming into contact with the rubber coating on the inside of the lids. Sludge samples were initially stored frozen at -18°C.

Controlling microplastic contamination in the laboratory. To minimise contamination from airborne dust, all processing took place in a Class II Microflow Biological Safety Cabinet, (MDH Contamination Control, Hitchings Clinical Services, UK). 100% cotton lab coats were worn at all times. All glassware and equipment were washed thoroughly prior to use, first with diluted dishwashing detergent and a natural bristle brush, then six times with reverse osmosis water (RO). The sampling rigs were only assembled or disassembled within the safety cabinet. All reagents were filtered through a 1.2 µm glass-fibre filter before use and PTFE lined lids were used to seal glass bottles containing reagents. Samples and glassware were covered with aluminium foil.

To avoid contamination between samples, the following precautions were taken with the 10 µm stainless steel filter discs. Following washing thoroughly before and after use, using the method detailed above, the discs were heated between samples in a muffle furnace at 350°C for 180 minutes. This temperature and duration represent a pragmatic

choice, between the desire to eliminate any microplastics through melting (all polymers examined have a melting point <350˚C) and/or ignition of the polymer whilst maintaining the integrity of the stainless steel filter. Finally, filter discs were kept separate according to sample type, so that particular filter discs would only be used for potable samples for example.

However, the use of plastic materials could not be entirely avoided. For example, staff wore nitrile gloves and a plastic wash bottle was used with the RO water. To ensure consistency between samples and blanks, the same distinctly coloured wash bottle was used throughout the project.

Raw water sample processing. On return from the field, the filter holder was opened inside the safety cabinet and the filter disk with attached particles and any particles rinsed off the filter holder were subjected to a Fenton's reaction to remove organic contaminants. This involved topping up the suspension with RO water to 200 ml and placing it in an ice water bath before adding 70 mL 30% hydrogen peroxide and 30 mL Fe(II) solution (0.05 M), acidified with 0.2% sulphuric acid. This was covered loosely with foil and monitored for 1 h to ensure the temperature did not exceed 50°C. The samples were then left in the safety cabinet overnight. If any iron precipitates had formed in the sample, these were removed by pipetting 1% H_2SO_4 drop-wise until they dissolved. The suspension was then filtered through a 10 µm pore size filter disk using a vacuum filtration unit (glass) before submerging the filter in 20 mL cellulase solution (MP Biomedicals, USA, >60,000 U/g powder, made up as a solution of 200 mg/L, in pH 5 phosphate buffered saline solution, which equates to 12,000 enzyme units/L as suggested by Löder, et al. (2017)[28]) and incubating for 48 h at 50°C on a rotating platform at 60 rpm. Particles were filtered again onto the 10 µm stainless steel filter disc and the filter disc placed into 20 mL 5 g/L trypsin (porcine trypsin in 0.9% sodium chloride, Sigma-Aldrich, Germany) for 30 minutes at 37°C and 60 rpm. This solution was filtered again onto the 10 µm stainless steel filter disc, and the filter then washed using 50 % ethanol from a glass pipette to give a 50 % ethanol dispersion for storage prior to analysis by FTIR microspectroscopy.

Potable water sample processing. On their return from the field, the filter cartridges were disassembled within the safety cabinet, the filter placed into a clean 250 mL glass beaker and the filter holders thoroughly rinsed with RO water into the same beaker. The suspension was then filtered through a 10 µm filter disk. The disk was placed in sodium

dodecyl sulphate solution (SDS, ca. 5 g/L) and sonicated for 2 minutes before rinsing the particles from the filter using RO water and a natural hair brush (H G Rant Ltd, UK). Then the suspension was filtered subjecting the sample on the filter disk to cellulase and trypsin digestions and final suspension in 50 % ethanol as described for the raw water.

Sludge samples. Sludge samples were oven dried at 50°C (covered with a glass fibre filter to avoid contamination) for approximately one week, before crushing a sub-sample with pestle and mortar and passing through a stainless steel 1 mm sieve. Per sample, 1 g dry mass of sludge was digested using a Fenton's reaction as described for the raw water samples and re-captured on a 10 µm stainless steel filter disc. The filter was placed in a 1.7 g/cm^3 density $ZnCl_2$ solution and sonicated for 5 minutes before rinsing and brushing. The sample dispersed in $ZnCl_2$ was poured into conical separation funnels and given 20 hours to separate based on recommendations by Wang et al. (2018) [29]. One quarter of the original volume was retained in the separation funnel following removal of dense particulates. This sample was then captured on a 10 µm filter disk and proceeded to the enzyme digestion step and storage as a dispersion in 50 % ethanol as used in the potable and raw water processing.

Final preparation for FTIR microspectroscopy analysis. Samples were vacuum filtered onto 25 mm 5 µm pore size silver metal membrane filters (Sterlitech, USA). For the potable water samples, the whole processed sub-sample (approximately half of the originally filtered amount) could be filtered and transferred onto the silver filter. For the raw water and sludge samples, the presence of residual material (plastic and remaining non-plastic) meant analysis of the whole sample was impossible, so a pre-weighed and re-suspended sub-sample of the 50 % ethanol dispersion was deposited on the filter (SI Tables 3, 6 and 8).

Preparation of blanks. Separate blanks were prepared which simulated the potable, raw and sludge processing steps. For the water samples, these blanks were prepared in the laboratory by setting up the filter rig to sample RO water (400-7,700 L) pre-filtered to 2 µm followed by processing the filters as if they were field samples. This was repeated on ten separate occasions for the potable water protocol and on eight occasions for the raw water protocol. The sludge blanks followed the processing steps exactly as for a real sample, but without including the sludge material. Thus, five 'sludge' replicates for blanks were processed using the Fenton's reaction, $ZnCl_2$ flotation and enzymatic digestion. Separately,

213 several silver filters (used for the final presentation of the sample to the FTIR) were taken
214 straight from the pack and also tested for contamination (no particles were found).
215 **Limit of detection (LOD), limit of quantification (LOQ), and blank correction.** For
216 each polymer, the mean blank value was subtracted from the raw count for a sample. This
217 correction was done on the basis of the whole processed sample, not per litre, because it
218 seemed likely that contamination might occur during the various processing steps (rather
219 than occurring in the 2 µm pre-filtered water or entering at the very last steps of depositing
220 the sample on the silver filter). Both counts per sample and calculated concentrations per
221 litre of blanks are provided in the supplementary information. The LOD for the blank-
222 corrected sample was defined as 3.3 x the standard deviation of the blank as recommended
223 by AOAC International [30] or one particle detected, if no particles were found. The LOQ was
224 expressed as 10 x the standard deviation of the blank or 3 particles detected. If the blank-
225 corrected value was above the LOD it counted as detected and if above the LOQ value it was
226 considered quantifiable. For each sample, the LOD and LOQ were expressed by referral to
227 the original volume (or weight in the case of sludge) of sample used for processing and the
228 proportion of the final processed sample that was transferred to the silver disc used in the
229 FTIR. Thus, if only a small sample volume was collected in the field and only a fraction of the
230 processed sample was placed on the silver filter for FTIR, these gave the highest (least
231 sensitive) LOD and LOQ values.
232 **Polymers quantified.** This study reported on the following plastic polymers; buta-1,3-
233 diene;prop-2-enenitrile;styrene commonly known as acrylonitrile butadiene styrene (ABS);
234 polyamide (actually a family of amide linked polymers) (PA); polyethene (PE); poly(ethylene
235 terephthalate) (PET); poly(methyl 2-methylpropenoate) commonly known as poly(methyl
236 methacrylate) (PMMA); Poly(1-methylethylene), commonly known as polypropylene (PP);
237 poly(1-phenylethene-1,2-diyl) commonly known as polystyrene (PS); poly(1-chloroethylene)
238 commonly known as polyvinylchloride (PVC); and ethylurea commonly known as
239 polyurethane (PU). The selection made for reporting was based on their ubiquity and
240 reported presence of these polymers by others in water [31].
241 **Spike recovery.** A stock dispersion of polyamide (PA) particles, 1131 +/- 198
242 particles/ml (63-90 µm diameter) was prepared in RO water and Tween (0.025%). Recoveries
243 of this stock were performed in triplicate for the potable water protocol and with 5
244 replicates for both raw water and sludge recovery protocols. Filtered RO water represented

245 the potable or raw water, whilst for sludges, 1 g replicates of a single spiked sludge sample
246 were used. At the time of this research project the most suitable standard available for
247 spiking we could obtain was 63-90 µm diameter PA. As a flotation step was utilised in the
248 sludge processing, density was considered an important parameter which could result in
249 differing recoveries between polymer types. With a density of 1.14 g/cm^3, PA was
250 considered representative of most polymers under investigation. This density is greater than
251 that of PU foams (0.05 - 0.8 g/cm^3), PP (0.946 g/cm^3), PE (0.975 g/cm^3), PS (1.06 g/cm^3), and
252 ABS (1.07 g/cm^3), thus is representative of a worst case for these polymers based on
253 extraction from the environmental matrix based on density separation. Another advantage
254 of using PA for the spike recoveries was that it was not normally found up as a laboratory
255 contaminant as shown in the blank studies (SI Tables 3,6,9). The volume of PA spiked for
256 each sample type was tailored to attain >100 particles on the final filter. The analysis
257 followed the same procedure as for a field sample, including correcting for filter area (see
258 below), blank correction and proportion of sample analysed under FTIR.
259 **Microplastic analysis.** Fourier Transform Infrared (FTIR) microspectroscopy was
260 performed on a Perkin Elmer Spotlight^{TM} 400 (Perkin Elmer, UK) in transflectance mode.
261 Spectral imaging was carried out at a resolution of 8 cm^{-1} using 4 accumulations (i.e. four
262 scans per spectra) at a pixel resolution of 25 µm and an interferometer speed of 2.2 cm/s,
263 which reflects a trade-off between mapping time and spectral quality. Scans were carried
264 out from 4000 cm^{-1} to 700 cm^1. Constraints on the file size generated meant that only 92% of
265 the filtration area could be scanned, so the counts were adjusted to account for this.
266 The software programme, MPhunter [32] was used to quantify and identify particles, by
267 comparing spectra to a custom polymer database comprising reference spectra of target
268 plastics. Spectra were matched against this database using a Pearson's correlation
269 coefficient threshold of 0.65 (where 1.0 is a perfect match and 0 is a complete mismatch)
270 against the first and second derivative spectra. Whilst there is currently no established
271 practice for thresholds in the literature, it is essential to report these thresholds and how the
272 score for matching spectra is calculated (the weights assigned to the raw, first and second
273 derivative spectra), to allow for comparison between approaches [33] in this case weights of 1
274 being assigned to the first and second derivative spectra. The 0.65 threshold was chosen as a
275 compromise between allowing for spectral modifications that occur when microplastics
276 weather in the environment and having a reasonable confidence in the polymer assignment.

The second and third thresholds for particle building (i.e. for pixels adjoining a pixel already identified as the polymer in question) were set using a Pearson's correlation coefficient thresholds of 0.4 and 0.3.

RESULTS AND DISCUSSION

It must be recognised that the results presented in this study of microplastics in the water treatment network consider nine common plastic polymers and report on only those larger than 25 µm in diameter. A rigorous approach to correcting for contamination in blanks was taken and particle number concentrations are reported as both those greater than the limit of detection, and those greater than the limit of quantification. Because we were unable to obtain standards for all of the polymers, the spike recovery was conducted only with the PA polymer. Recovery averaged 101% (standard deviation, SD 27%) and 113% (SD 15%) recovery for raw and potable water protocols and 52% (SD 13%) for the sludge protocol (SI Table 11). Recovery of the PA spike from sludge was lower at 52%, probably reflecting the greater degree of sample manipulation and higher matrix complexity of the sample. Variation observed between replicates was similar to the variation inherent in the PA stocks that were spiked (Levene's test was not significant, $F(3,12) = 1.6065$, $p = 0.239$). These spike recoveries may be indicative for the other polymers. Although no correction for recovery was made for the sludge samples, (the recovery for all polymers being unknown) it is probable that they underestimated the amount of microplastics present in this material.

Blank results. No contaminating particles from the polymers PMMA and PU were found in any blank type, PVC-U was only found in one blank (sludge) and there was limited contamination by ABS, PA and PS (mean 1-2 particles in raw blanks, 0-1 particles in potable blanks and 0-9 particles in sludge blanks). Whilst considerable efforts were taken to limit contamination of the samples (e.g. limiting use of plastic materials in equipment in contact with samples, SI Table 1), there was still persistent contamination (although the levels could be quite variable) for PE, PET and PP (mean 11-18 particles for raw, 5-17 for potable and 10-208 for sludge blanks). These contamination results showed the method would be very sensitive to the presence of PMMA, PVC-U and PU microplastics but less so (higher LODs/LOQs) for PE, PET and PP (SI Tables 3,6, and 9).

A number of sources suggest themselves for this contamination. The cotton lab coats worn by staff perhaps acquired microplastics generally within the laboratory and transferred these to our vessels within the safety cabinet. Alternatively, the glassware cleaning may not be completely effective or the 1.2 µm glass fibre filters used to prepare the reagents were themselves contaminated (SI Tables 3, 6, and 9). This outcome indicates that preparation of blank samples that capture the entire processing procedure are essential.

Microplastics found in raw water. The raw water of the three WTWs that directly abstract water from lowland rivers (LR1, LR2 and LR3), as well as the pumped storage site at LRS1, all had quantifiable microplastics present on at least one sampling occasion (Figure 1). When found, the numbers were typically around 15 microplastic particles/L, with the highest result being 113 PE microplastic particles/L found at LRS1. However, with the exception of LR2, microplastics were not a consistent presence in the raw water at any site. The polymers most often detected or quantified were PE, PET and PP (SI Table 5). The polymers PMMA, PS, PU and PVC were occasionally detectable but remained below the LOQ. If one polymer was quantifiable on one sampling day then others would often be detected too.

The analysis of the raw water was somewhat hampered by obscuring matrix material (despite the processing efforts) preventing full examination of the entire sample. In these cases only a small proportion of the sample was transferred to the silver disc for FTIR microspectroscopy analysis (SI Table 5). Whilst placing a small fraction of the processed sample on the silver disc reduced the obscuring material, this in practice meant also a reduction in sensitivity. The highest microplastic numbers were usually linked to occasions when only a small amount of the sample was collected or could be analysed due to matrix effects. In other words, on these occasions, there was more obscuring material present. However, a possible explanation is that situations where the WTW is abstracting water with high turbidity, with a high contaminating matrix, were the same occasions when high concentrations and ranges of microplastics were also present. This would be consistent with the possibility of runoff events depositing material from urban hard surfaces into surface waters.

The cleanest raw water samples came from LR1, LRS2 and UR, where typically all the sample could be examined, but no microplastics were quantifiable. Both LRS1 and LRS2 WTWs abstract surface water which is then stored in a reservoir before being treated (Table

1). Given that LRS2 is using a major river as its source water, the virtual absence of quantifiable microplastics in the raw water may be a testament to the effective settlement in the reservoir being employed there.

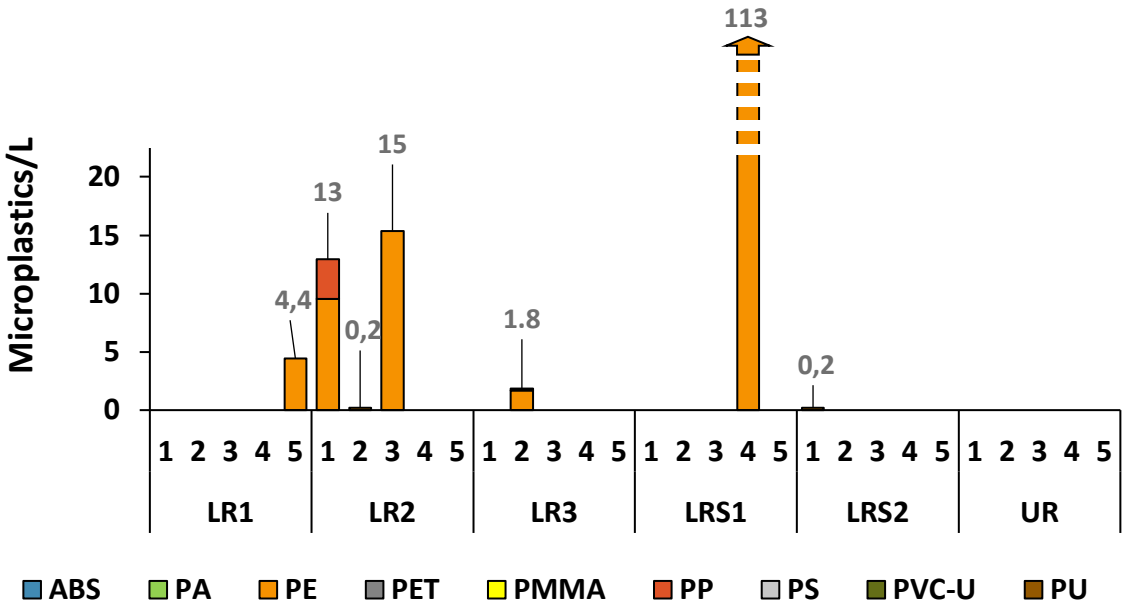

Figure 1. Quantifiable (>LOQ) microplastics in raw water, broken down by polymer type found on five repeat visits to six different WTWs having a non-groundwater raw water source. Labels refer to the sum of polymers.

Microplastics found in potable water. Despite obtaining 39 separate potable water samples and filtering very large quantities of potable water, it was very rare to find microplastics above the LOQ (Figure 2) although a range of polymers were present above the LOD (Figure 3). With a range of 0.001 to 0.024 microplastic particles/L detected no WTW could be said to be routinely under-performing. Although LR1, LR2 and LR3 directly abstract from a lowland river, their potable water product was comparable to the other WTWs. Although a Y-axis scale is given in the Figure 3, showing values above the LOD, it should be stressed that these polymers can only be discussed as detected and not accurately quantified. The raw data for the particles found by the FTIR and attributed to different polymer groups are shown in SI Table 5.

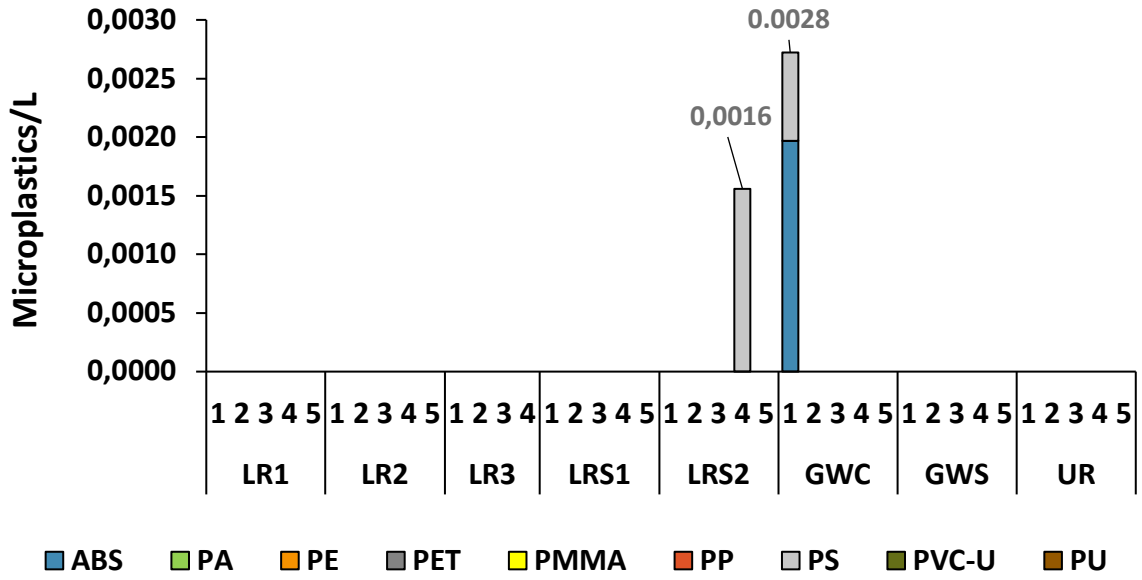

Figure 2. Quantifiable (>LOQ) microplastics in potable water, broken down by polymer type found on five repeat visits to eight different WTWs. Labels refer to the sum of polymers.

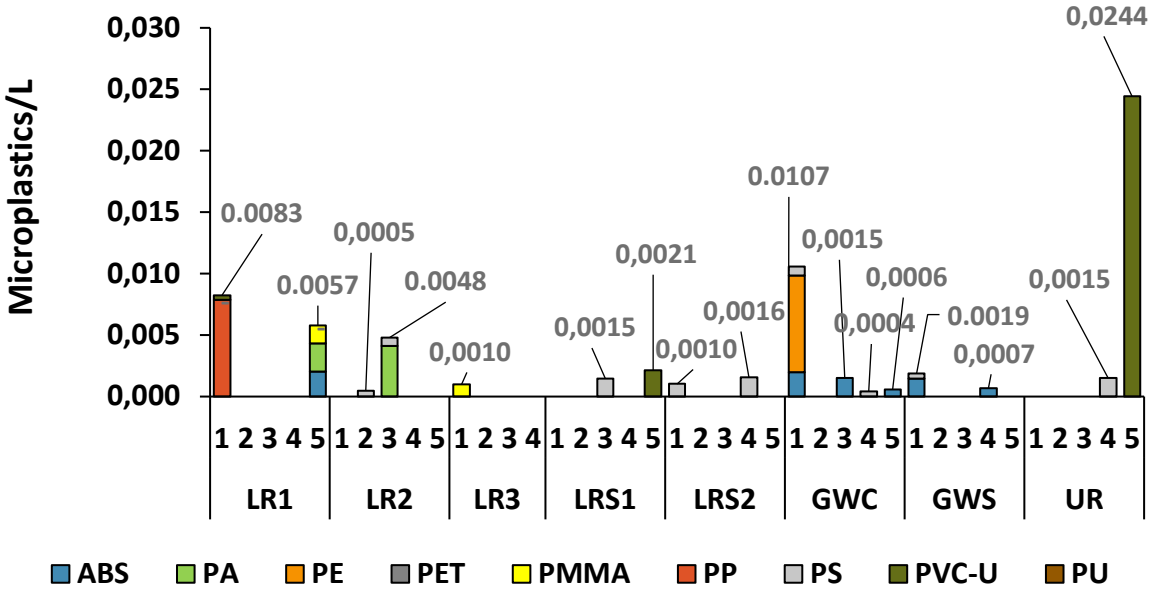

Figure 3. All detected (> LOD but often <LOQ) microplastics in potable water. Results broken down by polymer type found on five repeat visits to eight different WTWs. Labels refer to the sum of polymers.

The microplastic levels found in potable water (remembering sampling typically takes volumes of 1.5 to 3 m^3) were extremely low. For example, in 14.2 m^3 of all the potable water from GWC after five visits, only one particle of PS and two of ABS were quantified (SI Table

8). No individual microplastic polymer has been quantified at greater than 0.002 microplastics/L. The highest value for all polymers combined in a sample was 0.003 total /L if only polymers above the LOQ are counted (Figure 2).

With the GWC, GWS (groundwater) and UR (rain-fed upland reservoir some microplastics were occasionally detected above LOD in their potable water. ABS was detected six times, five of these were at the groundwater sites (Figure 3). PS was detected nine times. The most common quantifiable polymer was PS but the quantities found were very low. Despite the most common polymer in raw water being PE, this was not found in potable water above LOQ, and was rarely found above LOD (Figures 1-3). It will be noted that ABS and PS were not detected in the raw water of the WTWs (SI Table 5). This raises the possibility that microplastics found in potable water may have been, on some occasions, generated within the WTW itself (possibly due to losses from pipes or valves). However, given the difficulties in detection and quantification it is not a certainty that this occurred.

Overall ability of WTWs to remove microplastics. Only 4 of the 6 WTW sampled for raw water and only 2 from 8 WTW in their potable water had quantifiable microplastics. If only the WTWs with quantifiable microplastics are considered, the average value for microplastic particles in the raw water was 4.9/L (n=7/30) and in potable water 0.00011/L (n=2/39). Thus, these WTWs were extremely effective at preventing microplastics in the raw water from reaching potable water, with an overall value of 99.99% removal.

Presence of microplastics in WTW sludge. The values for microplastics found in waste sludge were extremely variable, from below the LOD to 86,000 microplastics/g DW (SI Table 10). Given the limited number of samples taken it is hard to explain this variability. Although LR2 had quite a high microplastic presence in its river raw water, this did not translate to high values in its sludge other than the relatively high concentration of 808 microplastics/g DW PE on the second visit (SI Table 10). The other direct pumped site at LR3 had high quantifiable values for PE, PET and PP (5000-60,000 microplastics/g DW) only on the second sample. PE and PP were detected but not quantifiable at the pumped storage river water site at LRS1. The upland impounding reservoir at UR had low but detectable PE and PP which was sufficient to be quantified at 404 microplastics/g DW on one of the two occasions. It will be recalled that with the raw water, PE, PET and PP were also the most common polymer forms detected. Given the spike recovery with a PA standard recovered a

mean of 52% particles, it must be considered that these sludge values may be under-estimates.

Size distribution. With the FTIR, 25 µm resolution was chosen as a pragmatic choice between resolution and time to analyse (and file size generated). The MPhunter software is able to provide an output of the size distribution of plastic particles found. When reviewing this output, it is clear that whilst a few larger particles exist, a logarithmic distribution is apparent, with numbers vastly increasing as particle size decreases (Figure 4, the small bars at the very left of each graph are likely to be an artefact of very small particles not always being detected). This distribution was the same for the contamination in the blanks as for the field samples.

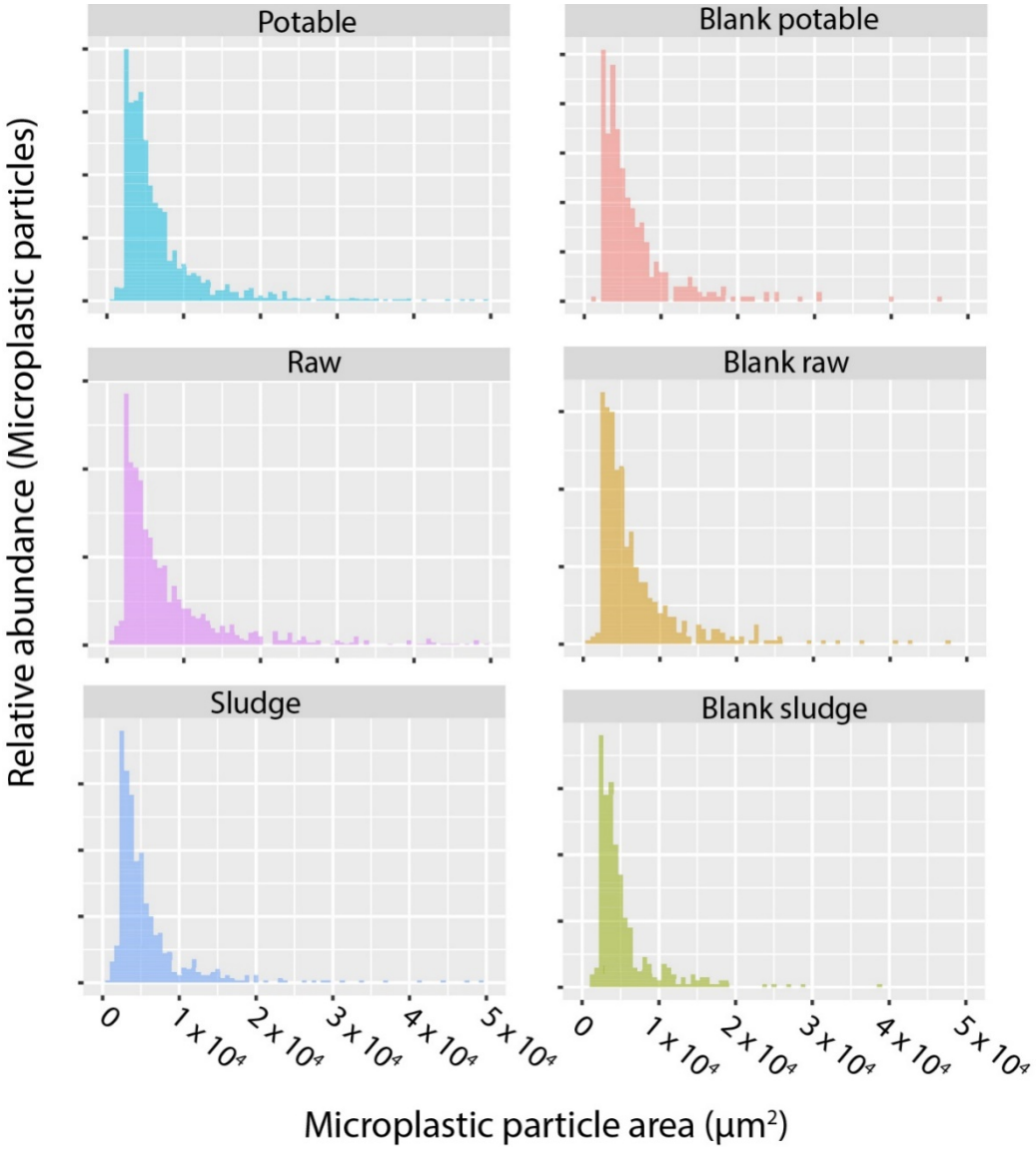

Figure 4. Size distribution of the microplastics found in the different sample types

The implication of these size distribution graphs is that it is very likely that large numbers of microplastics, less than 25 µm, were present but they have not been quantified due to both the FTIR pixel size (25 x 25 µm) and the spectral sensitivity of the system.

The analytical approach was not able to specifically distinguish microfibres from other non-microfibre plastic particles. Although FTIR images are generated of the particles for each polymer type, currently no reliable method of distinguishing the type of particles based only on shape is available.

Quality control and inter-comparability of studies. A difficulty in microplastic research is the poor inter-comparability between different studies. Early research relied on microplastics being spotted by eye down a microscope [34, 35] which focused on particles of 100 µm and above and thus fibres were relatively easy to spot and gained a lot of attention. Non-imaging Raman microspectroscopy or ATR-FTIR approach, also tends to focus on large particles and relied on the skill (and bias) of the operator to find and identify them. Given the enormous effort required to identify <25 µm microplastics in a sample, only very few samples can be analysed and of those some report only quantifying a small 'representative' part of the filter from which they extrapolate their results. Another issue hampering inter-comparability is the lack of clarity in studies regarding their controls and LOD/LOQ approach [27]. It may be possible over time to reduce or eliminate laboratory contamination and so lower the LODs and LOQs, but for the moment it would be wise to accept that microplastics are ubiquitous contaminants of any laboratory and this can compromise studies of 'pristine environments'. The most comprehensive review to date of studies in the field of microplastics and water used a checklist to evaluate the quality of papers [31]. Use of this checklist to evaluate the output from this research suggests this study would have met most of the elements listed by Koelmans, et al. (2019)[31].

Overview. The values for microplastics found in potable water here were extremely low (typically less than 0.002 microplastics/L where quantifiable) and are not dissimilar from those found in German potable water sourced from groundwater [25].

For the raw water, the processing was less successful in providing clear, non-plastic contaminant-free images. However, notwithstanding the methodological limitations, it would appear that where challenged, the WTW are succeeding in eliminating over 99.9% of microplastics from their source water leading to a transfer to the waste sludge.

It is likely that there are many microplastic particles present in the environment which are smaller than 25 µm. Whilst this < 25 µm particle fraction may be numerous, its contribution to the total mass is likely to be trivial. Thus, if the question was how effective are the range of water treatment approaches in England and Wales at removing microplastics particles >25 µm in size then the answer would appear to be they perform well. It would be more difficult to give an answer as to how successful the Water Industry is at removing all microplastic particles including the ultra-small varieties. The current methodology puts severe constraints on the ability to quantify such small <25 µm particles. Until more is known about the relevance of particle numbers, size or concentration to any hazardous properties of microplastics, it is too early to comment on risk.

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