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Characteristics of Nano-plastics in Bottled Drinking Water

Yihe Huang¹, Ka Ki Wong², Wei Li², Haoran Zhao³, Tianming Wang², Sorin Stanescu⁴, Stephen Boulton², Bart van Dongen², Paul Mativenga^{1*}, Lin Li^{1*}

¹Department of Mechanical, Aerospace and Civil Engineering, School of Engineering, Faculty of Science and Engineering, The University of Manchester, Manchester M13 9PL, UK

²Department of Earth and Environmental Science and Williamson Research Centre for Molecular Environmental Science, School of Natural Sciences, Faculty of Science and Engineering, The University of Manchester, Manchester M13 9PL, UK

³Faculty of Biology, Medicine and Health, The University of Manchester, Manchester M13 9PL, UK

⁴ LIG Nanowise Ltd, Unit 15 Williams House, Manchester Science Park, Manchester M15 6 SE, UK

- p.mativenga@manchester.ac.uk
- lin.li@manchester.ac.uk

Abstract

Plastic pollution in water is threatening the environment and human health. Previous relevant studies mainly focus on macro and micro plastic pollutions and their characteristics. Little is known about the extent and characteristics of nano-scale plastics in our drinking water systems, mainly due to difficulties in their isolation and analysis. These nano-plastics may pose higher risk to human health than micro-plastics. Here we report the collection and analysis of organic nanoparticles from commercial bottled water of two brands. Novel nano-plastic particle imaging and molecular structure analysis techniques have been applied. The findings show the existence of organic nanoparticles, and a likely source has been identified to be the degradation of plastic water bottles.

Keywords: plastic, nano, water, pollution, health, environment

1. Introduction

Micro and nano-plastic pollution in water is one of the global environmental and public health concerns. Since 1950s the global plastic product has increased rapidly and reached 360 million tons in 2019[1]. The irresponsible disposal of plastic wastes has led to substantial damages to the environment. According to a World Bank estimation

38 in 2017, there were 1.4 billion tons of plastic waste [2]. Among these plastic wastes,
39 only around 60% plastics, including polyethylene terephthalate (PET), high-density
40 polyethylene (HDPE), low-density polyethylene (LDPE) and polypropylene (PP) were
41 recyclable in 2018. Moreover, only 8.4% in total was actually recycled, while 15.7%
42 was incinerated in 2018 [3].

43 Plastic packaging occupies a dominant proportion of around 35% of all polymer resin
44 products from 2000 to 2015, followed by building and construction plastic materials at
45 16%, textiles at 12%, consumer and institutional products at 10%, transportation at 6%,
46 electrical and electronics at 4%, industrial machinery with less than 1% and other
47 products at 14% [3]. Since PET is non-permeable to water, moisture, and bacteria due
48 to its intrinsic properties, 75% of PET is used in various food and beverage packaging
49 products [4-7]. Over 46% by volume of plastic waste generation resulted from
50 packaging [8-10].

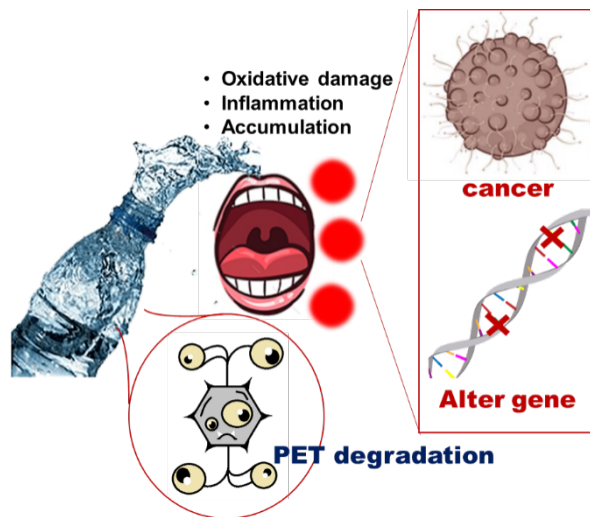
51 There are 7.7 billion single-use plastic water bottles consumed in the UK every year
52 and 391 billion litres of global consumption in 2017[11]. Around 19% of the UK
53 population drank bottled water every day in 2017[12]. On average, 118 litres of bottled
54 water was consumed per person in Europe in 2019[13]. Most single-use plastic water
55 bottles are composed of PET. These PET bottles take 400 years to fully decompose.
56 Ultraviolet light irradiation, heat, mechanical and chemical abrasion can result in the
57 breaking of the chemical bonds in PET polymer. This leads to chain scission and
58 depolymerisation. Therefore, micro and nano-plastics debris can be released inside and
59 outside from plastic water bottles through the degradation of plastics [14, 15]. In
60 addition, 93% of 259 bottled waters across 11 brands were reported to contain
61 microplastics [16-18]. However, the prevalence of nano-plastics in potable water is
62 comparatively unreported because of difficulty in their isolation and analysis [19].
63 Furthermore, standard water treatment processes are unable to remove nano-plastics
64 [20] and may cause their generation from micro-plastics, e.g. during ultraviolet
65 treatment for the removal of natural organic matter.

66 It has been estimated that on average a person ingests over 5800 micro/nano-particles
67 of synthetic debris each year, and the largest contribution of over 88% is via drinking
68 water [16]. Whilst micro-plastics have been more widely studied, nano-plastics are
69 more likely to have more negative impacts on human health. Cytotoxicity from
70 circulating particles in vivo is related to particle properties, including size, shape,
71 solubility, surface charge, surface reactivity and energy band structure [21, 22]. The
72 surface properties of nano-polymer, including surface energy, charge, and specific
73 affinity for certain biomolecules are capable of adsorbing macromolecules such as
74 proteins and lipids from the surrounding body fluids. The resulting corona will present
75 toxicity to human [23, 24]. Furthermore, a high abundance of reactive surface groups
76 can denature surrounding lipids and proteins and lead to membrane damage and
77 distortion to haemolytic symptoms [25]. Nano-polymer surface charge can modify
78 cationic particles, which leads to higher localisation of cationic particles in the lung and

79 enhanced cellular uptake and pulmonary toxicity [26]. Additionally, the translocation
80 of nano-polymer into cells by endocytes is followed by phagosomes, which leads to
81 accumulation of particles in lysosomes. This becomes a pathway for cellular breakdown
82 of pathogens [27]. These toxicities have the potential for oxidative damage,
83 inflammation and accumulation in diverse tissue types [28, 29].

84 The toxicities of nano-plastics digestion will result in potential oxidative damage,
85 inflammation, and accumulation in diverse tissue types of humans. Figure 1 illustrates
86 the potential impact of nano-plastics in drinking water on human health.

87



88

89 Figure 1: Illustration of impact of nano-plastics in drinking water on human health
90 [30-32].

91 Typically, micro-plastic surveys have proceeded by counting pieces of plastic collected
92 on filters and individually analysing a proportion of them. Results have then been
93 presented as numbers of pieces per volume of fluid which is instructive to demonstrate
94 the existence of contamination. However, as for all other pollutants, assessment
95 and/or prediction of impact requires knowledge of concentration – mass of plastic per
96 volume. This can be determined by bulk analysis of plastics concentrated from a
97 known volume of water.

98 Determination of the concentration of nano-plastics in water samples requires a method
99 able to both reliably isolate the nano-size fraction and to concentrate it sufficiently to
100 be detectable by the chosen method of analysis. Centrifugation and membrane filtration
101 are the commonly used collection methods for nanoscale plastics. Low concentrations
102 of nano-plastics make the processing of large volumes of water necessary and the batch
103 processing of centrifugation inefficient and a flow through process of filtration is
104 necessary [33]. In this work we have developed a method that uses tangential flow
105 ultrafiltration (TFU) and evaporation to isolate and concentrate nano-sized organic
106 material sufficiently that the material can then be identified by direct thermal desorption
107 (TD) into a gas chromatography mass spectrometry (GC/MS) system. TD-GC/MS

108 has already been shown to be able to identify plastics in samples of micro-plastic [34]
109 but combination with TFU is necessary for nano-plastic analysis as it allows particles
110 in retentate fluids to be concentrated: by dewatering; thereby increasing concentration
111 of suspended particulates, and by desalting; thereby preventing dilution of solids by
112 precipitated salts when the fluid is evaporated.

113 These methods are used in this paper, to report for the first time the characteristics of
114 nano-plastics found in bottled water. Also, super-resolution optical nanoscopy with
115 microsphere lens was used for the first time for the imaging of nano-plastics as these
116 nano-plastics cannot be observed clearly using standard scanning electron microscopy
117 due to surface charges and agglomeration as well as TD-GC/MS to identify the polymer
118 structures (break down products) of the nanoparticles collected.

119

120 **2. Materials and Characterization Procedure**

121 *2.1 Nanoparticle Collection and Concentration Using Tangential Flow Ultrafiltration* 122 *(TFU)*

123 Two brands of bottled water (A and B) were analysed. Both were bottled in PET
124 bottles in August 2020 and analysed 4 months later. During the isolation procedure
125 all open vessels were covered loosely with aluminium foil to prevent deposition of
126 airborne particulates.

127

128 16 L of each water was filtered using a tangential flow ultrafiltration (TFU) system
129 (Figure 2.) A peristaltic pump (Masterflex P/S Precision Console Drive pump)
130 transferred water at 300 ml/min into filters through silicone tubing. In the TFU system,
131 there were two 3 kD molecular weight cut-off (MWCO) (pore size: 1.2 nm) 200 PES
132 filters (Vivaflow, Sartorius, UK) connected in series.

133

134 The TFU system was used to concentrate the retentate (particulates >1.2 nm) by running
135 until a final retentate volume of 200ml was achieved; 80 fold concentration increase.
136 Furthermore, the salt content of the waters was also reduced by continual replacement
137 of retentate volume with DIW (dialysis) until the electrical conductivity of the retentate
138 dropped from that of the original bottled water (A - 709 $\mu\text{S}/\text{cm}$, B – 337 $\mu\text{S}/\text{cm}$) to 13
139 $\mu\text{S}/\text{cm}$. De-salting ensured that the solid sample ultimately prepared for analysis was
140 not diluted by precipitated mineral salts. 16L of DIW was also run through the system
141 to generate a retentate that was a procedural blank, for comparison to retentate A and
142 B.

143

144 0.5ml of the retentate fluid was used for analysis of size distribution and surface
145 morphology (see 2.2 below). The remaining 199.5ml retentate fluids were evaporated
146 to dryness in watch glasses in a closed drying oven at 40°C. The watch glasses
147 increased in mass by 8mg from retentate A and 6mg from B, the solid material was
148 removed by gentle scraping with a steel spatula. Non-destructive nano-particle

149 characterisation by Fourier Transform Infrared Spectroscopy (FTIR) was carried out on
 150 this powder (see 2.3 below) prior to it being recollected and analysed by TD-GC/MS
 151 (see 2.3 below).

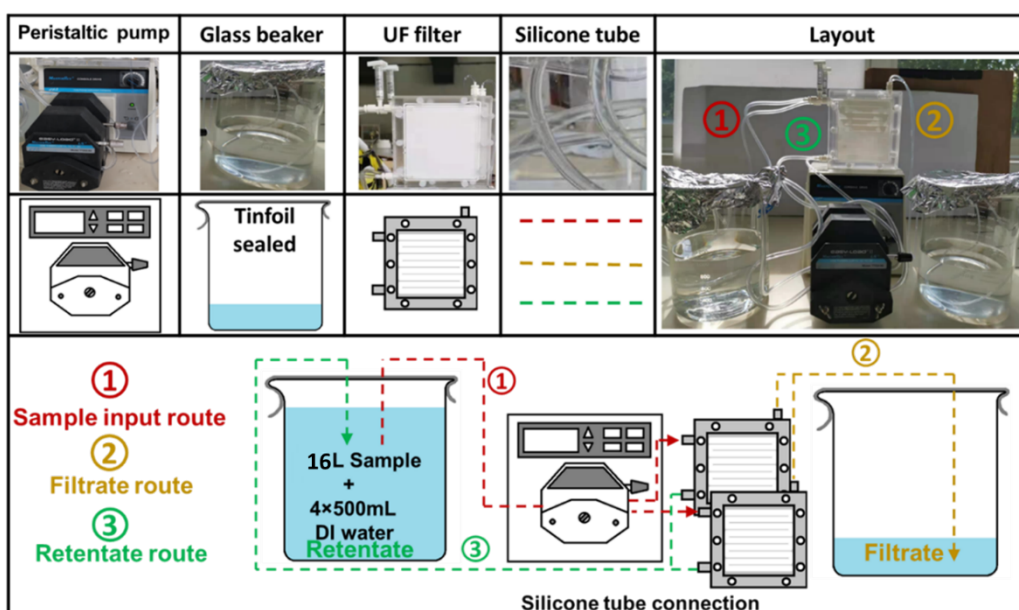
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153 The mass recovered from the procedural blank was <1mg and its solids formed a film
 154 rather than removable powder, therefore, transfer for analysis was done by adding 0.5
 155 ml of DIW to the watch glass to resuspend any particulate. This suspension was then
 156 added dropwise to quartz wool – which had previously been heated and desorbed at
 157 320°C - with intervening drying under an infra-red lamp. This quartz wool loaded
 158 with retentate was then placed in the thermal desorption tube (see 2.3 below).

159

160

161



162

163 Figure 2: Schematic diagram of the TFU system used in this research.

164

165 *2.2 Analysis of Size Distribution and Surface Morphology of Nano-plastic Particles*

166

167 The size distribution of the nanoparticle retentate was measured using Dynamic Light
 168 Scattering and Nanoro-M super-resolution optical microscopy with a super-resolution
 169 microsphere amplifying lens - SMAL (LIG Nanowise Ltd, UK)[35, 36].

170 The surface morphologies of nanoscale particles in the liquid samples were imaged
 171 using a novel Nanoro-M model optical nanoscope based on Super-resolution
 172 Microsphere Amplifying Lens (SMAL). The dynamic light scattering recorded and
 173 analysed the significant size distributions in peak diagram using Zetasizer Nano and
 174 associated software tool.

175

176 2.3 Nanoparticle Characterisation

177 FTIR (ALPA II, Bruker) in the transmittance mode was used for the analysis of
178 molecular structures of the retentate nano-plastic samples in powdered form. A pankit
179 (PerkinElmer,UK) was applied to press the sample to ensure flat surfaces on both sides.

180 For TD-GC/MS analyses of nano sized PET degradants from the PET bottled water the
181 samples were analysed using a an Agilent GC-MSD system (Agilent, Technology,
182 Santa Clara, US) interfaced to a UNITY-xr™ Thermal Desorber (Markes
183 International, Bridgend, UK). The advantage of TD-GC/MS is the higher resolution
184 analysis without disruption from organic solvent, thus various low molecular weight
185 plastic additives can be determined [50]. A low volume of nano-PET degradation in
186 retentate can be determined by TD-GC/MS for the first time in this work. This is
187 difficult to be detected by other techniques [51].

188 Prior to the TD-GC/MS analysis, retentate was loaded onto a quartz filter paper which
189 was rolled and placed in an empty stainless steel thermal desorption tube (Markes
190 International, Bridgend, UK) and 2 pieces of 0.01g of quartz wool were inserted into
191 two ends of the tube. The sample loaded tube was sealed by brass storage caps to avoid
192 contaminants before loading into the Thermal Desorber. The tube was desorbed at
193 320°C for 20 mins using nitrogen gas at a flow rate of 100 mL/min. The purged gas
194 was temporarily stored in a 30°C cold trap after which it was desorbed (at 320°C; 3
195 min) and transferred to an Agilent 7980A GC fitted with an Agilent HP-5MS 5%
196 Phenyl Methyl Siloxane column (30m x 250 µm x 0.25 µm) coupled to an Agilent 5975
197 MSD single quadrupole mass spectrometer in electron ionisation mode (scanning a
198 range of m/z 50 to 650 at 2.7 scans s^{-1} ; ionisation energy: 70 eV) using helium as the
199 carrier gas. The heated GC interface was set at 280 °C, the EI source at 230 °C and the
200 MS quadrupole at 150 °C. The oven was programmed from 40 °C (held for 4 min) to
201 200 °C at 8 °C min^{-1} and held at this temperature for 3 min, for a total run time of 27
202 min $sample^{-1}$.

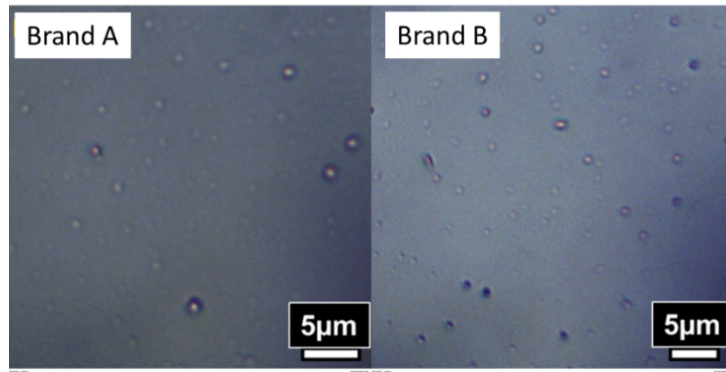
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204 3. Results and Discussion

205 3.1 Surface morphology and size distribution of nano-plastics found in bottled water

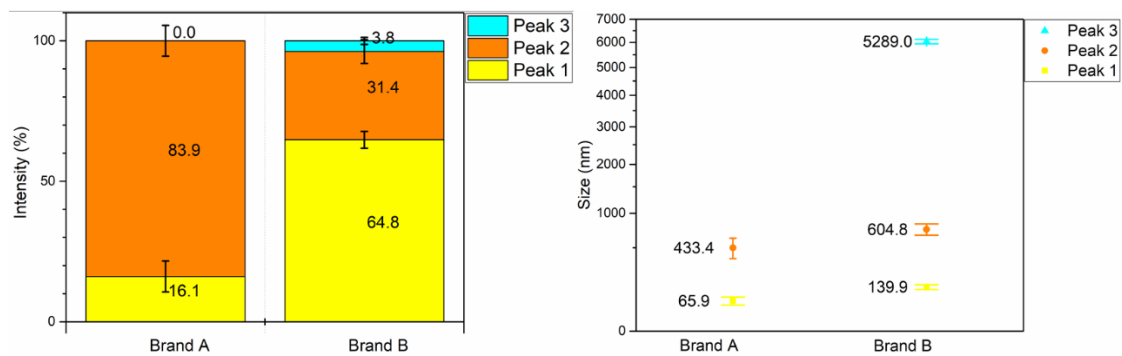
206 The majority of organic nanoparticles from concentrated retentate of Brand A and B
207 bottled water were transparent and spherical (Figure 3). According to the statistics of
208 the DLS analysis, the size distribution of the retentates from the bottled water was
209 uniform (Figure 4). The retentate from brand A bottled water was composed of 83.9%
210 particles with a size around 433 nm, 16.1% particles with a size around 66 nm and no
211 particles were in the microscale. The retentate from brand B bottled water was
212 composed of 64.8% particles with a size around 140 nm, 31.4% particles with a size
213 around 605 nm and 3.8% particles with a size around 5 µm.

214



215
216
217
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Figure 3: Optical microscopic images of organic nanoparticles from concentrated retentate for Brand A and B bottled water.



219
220
221

Figure 4: Size distribution intensity (left) and size distribution peak (right) as measured by DLS.

222

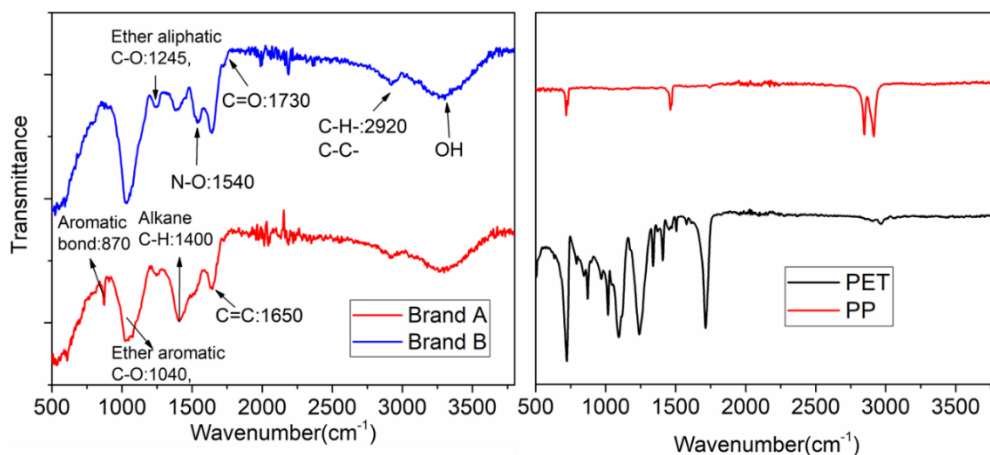
223 3.2 Molecular structures of the submicron and organic nanoparticles from the

224 retentates

225 FTIR analyses indicate discrete spectra of the submicron and organic nanoparticles

226 from the retentates (Figure 5).

227



228
229
230

Figure 5: FTIR spectra for the retentates from two brand bottled water (left) and bottle cap material (PP) and body material (PET) (right).

231 The IR absorption spectrum of weathering PET and PP has been reported by several
 232 researchers [37-40]. By combining the information and knowledge of IR group
 233 frequencies, most of the bands for retentates observed can be identified (summarised in
 234 Table 1).

235

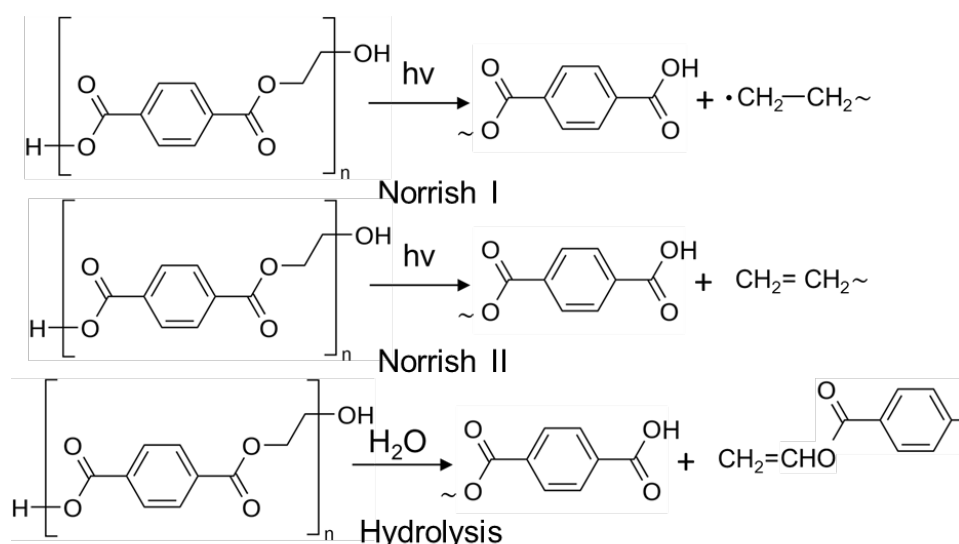
236 Table 1: Responded groups and corresponding compounds to peaks in Figure 5 (left)

| Absorption (cm ⁻¹) | Appearance | Group | Suspended compound |
|--------------------------------|-----------------|--|---|
| 3300 | medium broad | -stretching vibration of O-H | carboxylic acid [41] |
| 2940 | weak | -stretching vibration of C-H -stretching aliphatic vibration in the amorphous region of C-H | -CH ₂ - in ethylene glycol segment [42, 43] |
| 1730 | weak | -stretching vibration of C=O | carbonyl group of carboxylic acids [42-44] |
| 1640 | medium | -stretching vibration of C=C | Conjugated or cyclic alkene [42, 43, 45] |
| 1540 | medium | -stretching vibration of N=O | nitro compound [46] |
| 1375 | weak | -bending vibration of C-C -stretching vibration of ring (C-C) in-plane -bending vibration of ring (C-H) in-plane -aromatic skeleton stretching vibration | carboxylic acid [42, 47, 48] |
| 1245 | weak | -stretching vibration of C-O | carboxylic acid [42-44] |
| 1040 | strong | -stretching vibration of C-O | Anhydride [42-44] |
| 870 | strong | -bending vibration of C=C | Conjugated or cyclic alkene |

237

238 The typical FTIR fingerprints for PET are composed of peak positions of: 1716 cm⁻¹,
 239 1408 cm⁻¹, 1342 cm⁻¹, 1282 cm⁻¹, 1257 cm⁻¹, 1246 cm⁻¹, 1122 cm⁻¹, 1099 cm⁻¹, 1015
 240 cm⁻¹, 870 cm⁻¹ and 725 cm⁻¹ (Figure 5 right) [41, 48]. Compared with bands for typical
 241 PET, the retentate from bottled waters were found to be degraded PET compounds.
 242 PET is the typical material used as the bottle material in these bottled waters. The
 243 bending vibration of C=C generate the absorption of 1640 cm⁻¹ and partially 870 cm⁻¹
 244 from the retentate of bottled water showed a ring structure. The 1716 cm⁻¹ absorption
 245 peak is attributed to C=O stretching. A relatively weaker absorption peak can be found
 246 from both bottled water retentates. Compared with absorptions for typical PET, the
 247 (C=O)-C stretching of ester on 1246 cm⁻¹ was found as a ring ester in the plane mode
 248 left from the retentate sample, thus the existence of carboxyl acid end group as shown

249 in Figure 6 could be formed from the degradation of PET. Additionally, the low
 250 intensity of 1246 cm^{-1} and 1716 cm^{-1} absorption peaks was the result from the C=O of
 251 nanoscale-carboxylic acid generated from Norrish I, II and released into water[42, 49].
 252 The 1375 cm^{-1} absorption peak was attributed to the vibration of -CH₂- in the ethylene
 253 glycol segment, which was believed to be a gauche conformer of ethylene glycol
 254 segment. This was also coming from the aging of PET with conformational changes as
 255 illustrated in Figure 6 [43, 48, 50]. The intensity of asymmetry stretching aliphatic
 256 vibration of C-H at 2940 cm^{-1} was increased due to the time of weathering (UV
 257 exposure and hydrolysis[41, 45]). The remaining absorption from the retentates may
 258 come from weathering and aging of PET resulting in the absents of 1342 cm^{-1}
 259 attributing to CH₂ wagging, 1099 cm^{-1} attributing to symmetric glycol C-O stretch, and
 260 725 cm^{-1} attributing to C-H and C=O out of plane.
 261



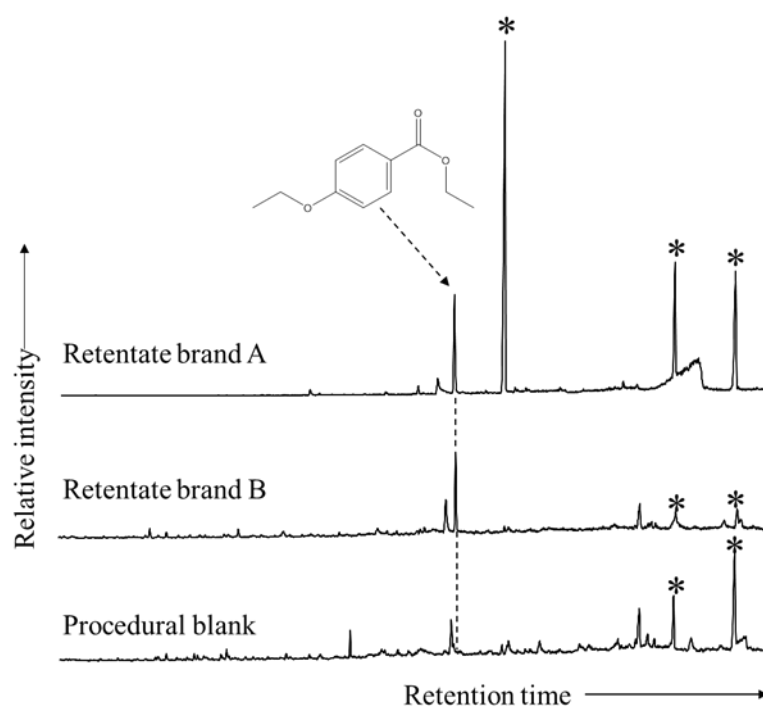
262
 263 Figure 6: Norrish I, II reactions of PET degradation (derived from [47, 48, 51])

264

265 3.3 Mass spectrum of submicron and organic nanoparticles from the retentates

266 The selection of secondary-ion mass spectrometry (SIMs) for TD-GC/MS result was
 267 based on Norrish I, II reactions of PET degradation and results in derivatives from PET
 268 or plasticizer with m/z of 121 (benzoic acid) and 149 (fomyl benzoic acid) moieties [52].
 269 These m/z values were therefore used to select specific peaks for suspended suspected
 270 derivatives from aged PET.

271 TD-GC/MS analyses of both bottled water retentates indicated besides the presence of
 272 a series of phthalate derivatives the presence of substantial amounts of ethyl p-
 273 ethoxybenzoate, which was notably absent in the procedural blank derived from DI
 274 water retentate (Figure 7). The similarity of ethyl p-ethoxybenzoate to partial break
 275 down segments from PET (Figure 6) indicates the existence of decomposed
 276 components from PET (the bottle material for the bottled water) in the bottled water
 277 retentates.



278
 279 Figure 7: Partial TD-GC/MS m/z 121 mass chromatograms of both brands of bottled
 280 water retentates and the procedural blank. Stars indicated the presence of phthalate
 281 derivatives. Ethyl *p*-ethoxybenzoate was identified based on the characteristic
 282 fragments in its mass spectrum (m/z 194 (molecular ion peak), 166, 149, 138 and 121
 283 (base peak))

284 The Norrish degradation of PET may have been caused by light exposure, particularly
 285 UV light exposure during packaging, transportation, storage, and shelving in the
 286 supermarket and stores for 4 months before our water collection.

287

288 3.4 Limitations of the study

289 In this study the bottled water was only from two commercial water suppliers. The
 290 occurrence of the nano particles reported in this study is specific to the locations
 291 covered. While the study on the bottle and cap materials has provided strong evidence
 292 that some nano particles in bottled water shows similar TD-GC/MS spectrum signatures
 293 from PET nano plastics, and plasticizer, this work demonstrates the presence of PET
 294 breakdown products in bottled water quantification of the amount is not possible. To
 295 quantify the amount of nano-sized PET breakdown products in water samples there is
 296 a requirement for a standard – a material of known mass that can be put through the
 297 analytical procedure – that must also behave identically to the retentate during TD-GC-
 298 MS. Such a material could be generated by keeping PET under the same conditions as
 299 that collected in the retentates; kept in water at same temperature and UV exposure –
 300 but it would also be necessary that all this material was also <10kD. Preparation of such

301 standards should be the object of further studies in order that quantification of nano-
302 plastics that have now been demonstrated to be detectable.

303 It, however, suggests a careful consideration of the use of plastic containers for drinking
304 water given the possibility of degradation by thermal mechanism and light exposure.
305 The study provides a warning for the need for more systematic, controlled, and
306 randomised studies to understand the occurrence of plastic nanoparticles in our water
307 systems. The possibility that this is an existing risk makes this of urgency.

308

309 **4. Conclusion**

310 In this research, a relatively high volume of organic nanoparticles (dominated by
311 precursors of PET plastic) from the bottled water were collected effectively through a
312 specially designed tangential flow ultrafiltration system. Spherical transparent organic
313 nanoparticles were detected in bottled waters. Most of those retentates were in the
314 nanoscale, which were not removed by current municipal water plants. Decomposed
315 segments from PET were identified as ethyl p-ethoxybenzoate by FTIR and TD-GC-
316 MS. These may come from the degradation of the PET bottles containing the water.
317 These nano-plastics are unable to be metabolized and can be absorbed by people
318 causing various damage to health. Therefore, it is strongly recommended that more
319 systematic quantification of occurrence of nano-plastic particles be done, and national
320 and international standards need to be established to limit the amount of nano-plastics
321 in drinking waters. Given the possibility of cumulative impact, timely action is of
322 paramount importance.

323

324 **Acknowledgment**

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327 Recycling”, Ref: EP/S025200/1.

328

329 **Data Statement**

330 The data generated by this research is reported in the Tables and Figures.

331

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