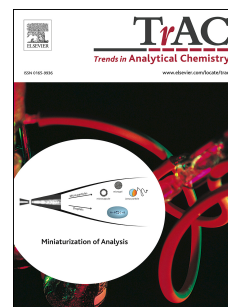


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Expanding Exploration of Dynamic Microplastic Surface Characteristics and Interactions

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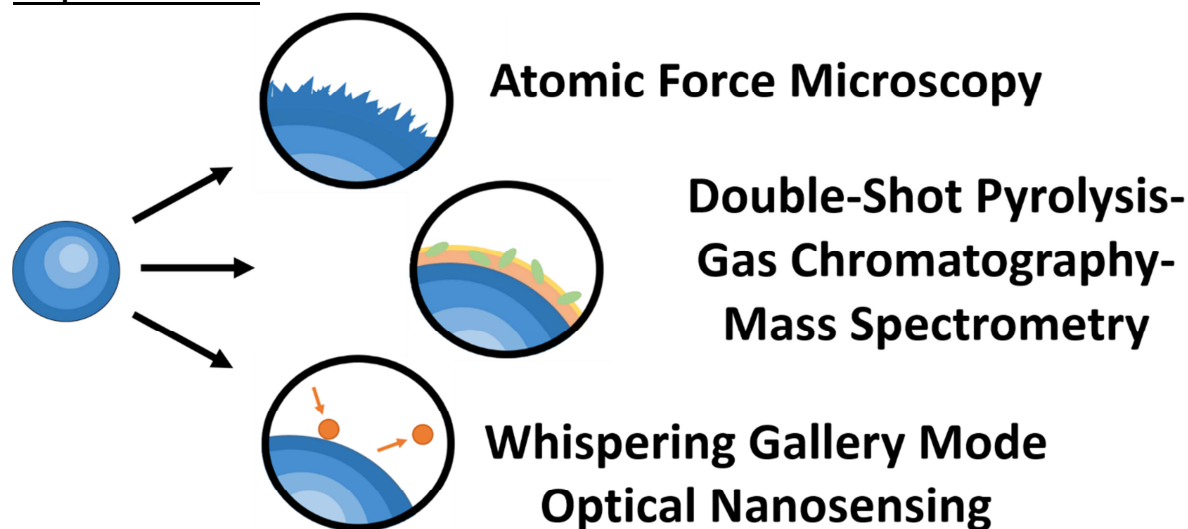
Abstract

Microplastics have been found in all marine ecosystems, raising concern about their potential environmental impacts. Yet relatively little research has focused on surface characteristics, compared to polymer type. The aim of this review is to discuss the importance of microplastic surface properties and how expanded characterisation and more detailed quantification can aid in assessing their behaviours in aquatic environments. Concepts including surface roughness, formation of surface ecocorona and sorptive behaviours of microplastic surfaces are discussed. To address these concepts, three exemplary methods are introduced and their application to the study of microplastic surfaces discussed with the following recommendations; atomic force microscopy should be explored for conducting physical surface characterisation and to examine surface roughness; double-shot Pyrolysis-Gas Chromatography-Mass Spectroscopy should be considered for examining microplastic sorption behaviours in multi-solute media; and finally, Whispering Gallery Mode nanosensing techniques should be explored as a potential means to generate data on microplastic sorption kinetics.

Keywords: Microplastics, Ecotoxicology, Aquatic, Optical Nanosensor, Characterisation

Highlights

- Atomic force microscopy could expand physical characterisation of microplastics.
- A variation on double-shot Py-GCMS could advance research into ecocorona formation.
- Whispering gallery mode methods may enable study of surface interaction kinetics.

42 **Graphical Abstract**43
4445 **1. Introduction**

46

47 Microplastics (generally defined as <5mm particles of synthetic polymer) can now be found
 48 in every marine ecosystem, regardless of distance from human populations [1, 2]. They have
 49 been found from the Mariana Trench to the polar regions of the Arctic and Antarctica [3, 4,
 50 5]. Their wide distribution and prevalence is mostly due to the versatility and strength of
 51 plastic materials lending themselves well to technological advancement and economical
 52 manufacturing [6]. Since the 1950s, when mass production of plastic began, these
 53 properties of plastic materials have facilitated increased production [7]. In 1950, 1.7 million
 54 tonnes of plastic is estimated to have been produced, in 2018 production reached 359
 55 million tonnes, >200 times the level of production 68 years previously. [7, 8, 9]. Significant
 56 resultant pollution has led to a detectable period layer of plastic material in the depositional
 57 record, called the Plasticene [10].

58

59 Increased production is not solely to blame for the state of plastic pollution. A culprit of
 60 equal measure would be mismanagement of plastics as a resource, with around 50%
 61 produced being single-use [11]. A recent publication from the United Nations Environment
 62 Programme estimated that 8.28 million tonnes of plastic is released into the environment
 63 each year [12]. The current throw away culture enabled by single-use plastic is being
 64 challenged through developing legislation and public awareness, but this has only just
 65 started to develop in recent years [13].

66

67 While a significant amount of research has been published on microplastic pollution,
 68 questions remain about their associated risk to the environment and human health.
 69 Microplastics are not a single entity, but rather represent a hugely complex mixture of
 70 different polymer types, shapes, and sizes of material, many of which will have aged and
 71 weathered in multiple environmental compartments and under diverse conditions.

72 Significant diversity is hence found in microplastic surface properties, which is of note, as
73 these dynamic characteristics affect their behaviour in aquatic ecosystems [14]. This
74 complexity has rarely been addressed in detail in publications, and further examination of
75 surface characteristics and interactions are needed to address current arguments in the
76 literature [14, 15, 16].

77
78 There is evidence that microplastic physical surface characteristics, such as surface
79 roughness and surface area, affect the reactivity and potential toxicity of microplastic
80 particles [14, 17]. As such, examining physical surface characteristics is relevant to
81 understanding microplastic behaviour in the environment (e.g. sorption). Furthermore,
82 conflicting results in the literature raise the need for further study. For example, sorption of
83 hydrophobic contaminants might be predicted to increase with an increase in surface area,
84 since there is more space available for molecules to bind. This conclusion is based on the
85 mechanisms behind sorption encompassing both absorption and adsorption. Summarised,
86 the former describes uptake of chemicals into the bulk of a material, while the latter, uptake
87 onto material surfaces [18]. As such, surface area is a significant factor in chemical
88 adsorption.

89
90 However, in a study by Wang, *et al.* [19], sorption of phenanthrene decreased with
91 increased roughness of the subject polyethylene (PE) microplastic material at their smaller
92 size fraction (1 mm), while sorption increased in rougher, larger fibre fractions (4 mm and 10
93 mm). This supports our understanding that factors other than surface area alone are
94 important for sorptive behaviours, such as curvature of the sorptive surface, or the
95 hydrophobic nature of the polymer. Guo, *et al.* [20] studied the sorption behaviour of
96 various hydrophobic organic compounds (phenanthrene, naphthalene, lindane, and 1-
97 naphthol) onto polymer surfaces. They found that polyphenylene oxide, despite its polar
98 chemical structure which includes significantly more oxygen than polystyrene (PS) and
99 styrene-divinylbenzene copolymer (these polymers include oxygen surface content due to
100 sorption from the environment), was found to sorb significantly more of the solutes than
101 the latter polymers [20]. This was concluded to be due to the oxygen moieties of
102 polyphenylene oxide being covered by the surface of the material, forming a hydrophobic
103 surface, resulting in the higher uptake [20].

104
105 Relating to the influence of curvature, Farrow, *et al.* [21] modelled adsorption of oil in a
106 solution onto solid surfaces, showing an increase in surface coverage with solute is due to
107 the geometrical effect of increased surface curvature resulting in more free volume for the
108 solute [21]. Summarised further, the effect of curvature on sorption results in smaller
109 particle surfaces receiving significantly greater coverage when compared to the surface of a
110 larger particle in mutual equilibrium between the solutes and solvent [21]. Furthermore,
111 issues with standardisation of published methods (varying results between instruments and

112 difference in applied terminology e.g. plastic size ranges), such potentially confounding
113 variables (such as surface roughness) require attention as the field progresses [1, 22, 23].
114

115 The sorption behaviour of microplastic pollution has been a recent source of contention
116 [16]. Despite continuous research, the potential for microplastics to act as vectors for toxic
117 chemicals and to transfer them into the tissues of exposed organisms has not been
118 equivocally proven and the extent to which this occurs in the natural environment is not
119 clear [16]. Teuten, *et al.* [24] studied microplastic material exposed to the waters of Tokyo
120 Bay, where they sorbed PCB content. These microplastics were fed to shearwater chicks
121 supplemented with a diet of fish, which resulted in a spike in PCBs from collected preen
122 gland oil [24]. This spike contained lower chlorinated PCBs which was attributed to their
123 capacity to be metabolised. The fish fed to the shearwater chicks were also contaminated
124 with PCBs, enough that the content outcompeted that sorbed to the microplastics except
125 initially by the lower chlorinated fraction [24]. Lower chlorinated PCBs are less likely
126 biomagnified in ecosystems as they are metabolised more than those that are more
127 chlorinated [24]. As a result the microplastics transported significantly more of the lower
128 chlorinated PCBs into the shearwater chicks than the fish in their diet [24]. Furthermore in a
129 study by Scopetani, *et al.* [25], the authors found that feeding microplastics contaminated
130 with polybrominated diphenyl ether (PBDE) to *Talitrus saltator* resulted in transport of the
131 chemical into the organism tissue. However, the same study also found evidence that
132 feeding uncontaminated microplastics to *T. saltator* contaminated with PBDE resulted in
133 transport of the chemical from the organism [25]. These studies highlight the more
134 complicated involvement of microplastics in toxic chemical pathways, which requires further
135 research for more certain conclusions on their environmental significance.

136
137 Recent studies have explored other ways in which the sorption behaviour of microplastics
138 may have environmental impacts. Dimethyl sulphide (DMS) is formed in the marine
139 environment from the breakdown of a precursor molecule when zooplankton graze on
140 phytoplankton and is widely recognised as an infochemical that triggers and controls
141 foraging cascades. Procter, *et al.* [26] found that the infusing of DMS into microplastic fibres
142 significantly increased their ingestion by copepods. Considering the sorption behaviour of
143 microplastics, this study raises the question of how interactions with environmental
144 chemicals can have other implications relating to organism chemosensory responses. With
145 the complexity of sorption in multi-solute environments only starting to be addressed, a
146 comprehensive understanding of microplastic sorption behaviour to address such questions
147 more fully is still lacking [27]. As such, understanding the sorption behaviour and developed
148 surface layers (ecocorona) of microplastics in more detail is urgently needed to address
149 questions about their environmental impact.

150
151 This short review aims to discuss the above mentioned topics in greater detail and critically
152 review three example novel methods with which to expand chemical and physical

153 characterisation of microplastic surfaces; atomic force microscopy, double-shot pyrolysis
154 gas-chromatography mass-spectrometry and Whispering Gallery Mode optical nanosensors.
155 The application of each of these exploratory methods is discussed in the context of physical
156 characterisation of microplastic material, exploration of ecocorona composition in differing
157 multi-solute environments, and the interactions between environmental chemical factors
158 and microplastic surfaces in greater detail. We do not include a comprehensive review of
159 every method applicable to examine microplastics and instead the reader is referred to
160 reviews by Fu, *et al.* [28] and Pimpke, *et al.* [29]. Additionally, extensive reviews on
161 microbiological interactions with microplastics can be found elsewhere and are not
162 considered in detail here [30, 31, 32, 33].

163

164

165 **2. Quantifying Surface Roughness and Potential using Atomic Force Microscopy**

166

167 Microplastics come in various shapes and sizes, fibres, nurdles and fragments. These
168 physical characteristics of microplastics have significant influence on particle behaviour. For
169 example, properties such as shape, density and size can influence their transport though
170 aquatic environments [34]. As described and tested by Ballent, *et al.* [34], the density of a
171 microplastic particle will significantly affect its vertical transport though the water column as
172 it physically interacts with flow and turbulence (dependent on the density difference
173 between the water and microplastic). Other physical microplastic properties, such as size
174 and shape will also have a significant impact on the degree to which the particle is
175 influenced by water column characteristics such as turbulence. Ballent, *et al.* [34] illustrate
176 this in their investigation into the influence of physical microplastic characteristics on
177 vertical transport, finding larger, more irregular shaped particles were most drawn down by
178 turbulent flow. Microplastics also vary in their physical surface characteristics. In the
179 environment these properties are altered by processes such as UV photo-oxidation, in which
180 C-C and C-O bonds are broken [35], which can affect multiple characteristics including
181 surface roughness, defined here as the amount and extent of deviation of a surface from
182 being perfectly flat [36]. These changes are of note as there is evidence that physical surface
183 characteristics, such as roughness, affect how microplastics interact with their environment
184 [36].

185

186 The term “sorption” includes two modes, accumulation on a surface (adsorption) and within
187 the bulk of a material (absorption) [18]. The capacity for a material to absorb sorbate is
188 dependent on its free volume, i.e. spaces between polymer chains which allow the sorbate
189 to permeate the sorbent material [37]. As such, the capacity of a polymer for absorption is
190 dependent on chemical structure. In contrast, as adsorption is a process which occurs on the
191 surface of a sorbent material. Physical surface characteristics (such as curvature) are more
192 significant to the adsorption of sorbate material [21, 38]. As such, chemical structure and

193 surface characteristics are significant to both a sorbent's capacity for sorption, as well as
194 which mode of sorption is more dominant.

195

196 These concepts are explored further by Mao, *et al.* [36] who found that polystyrene (PS)
197 degraded by UV exposure exhibited increased sorption of heavy metals (Pb, Cu, Cd, Ni and
198 Zn), likely due to shifts in the physicochemical characteristics of the microplastic material of
199 which surface roughness was considered a significant factor [36]. This would agree with
200 previous studies into the influence of surface roughness on sorption. For example, Akkas, *et*
201 *al.* [39] concluded that surface roughness was as significant to sorption of proteins on
202 polyurethane films as hydrophilicity. However, due to variation in modes of sorption with
203 different sorbates, this is not applicable to all interactions [18]. A major example difference
204 between groups of polymers would be between "rubbery" and "glassy" polymers [40].
205 Referring to physical properties, glassy polymers are more rigid and brittle while rubbery
206 polymers are more flexible and have more free volume [18, 41]. This difference in structure
207 (especially the amount of free volume) has consequences for sorption behaviour [41].
208 Rubbery polymers have a heightened capacity for sorption than glassy polymers [18, 40].
209 This difference is primarily due to which mode of sorption is dominant in the polymer. For
210 example in more rubbery polymers (with more free volume), generally, absorption is more
211 likely the dominant mode of sorption [18, 40]. This means different polymers will be
212 affected by surface roughness to a greater or lesser extent depending on their dominant
213 sorption behaviour. Furthermore, these variables in sorption behaviour have significant
214 implications for the strength of bonds between the sorbent and the sorbate, influencing
215 desorption behaviour [42].

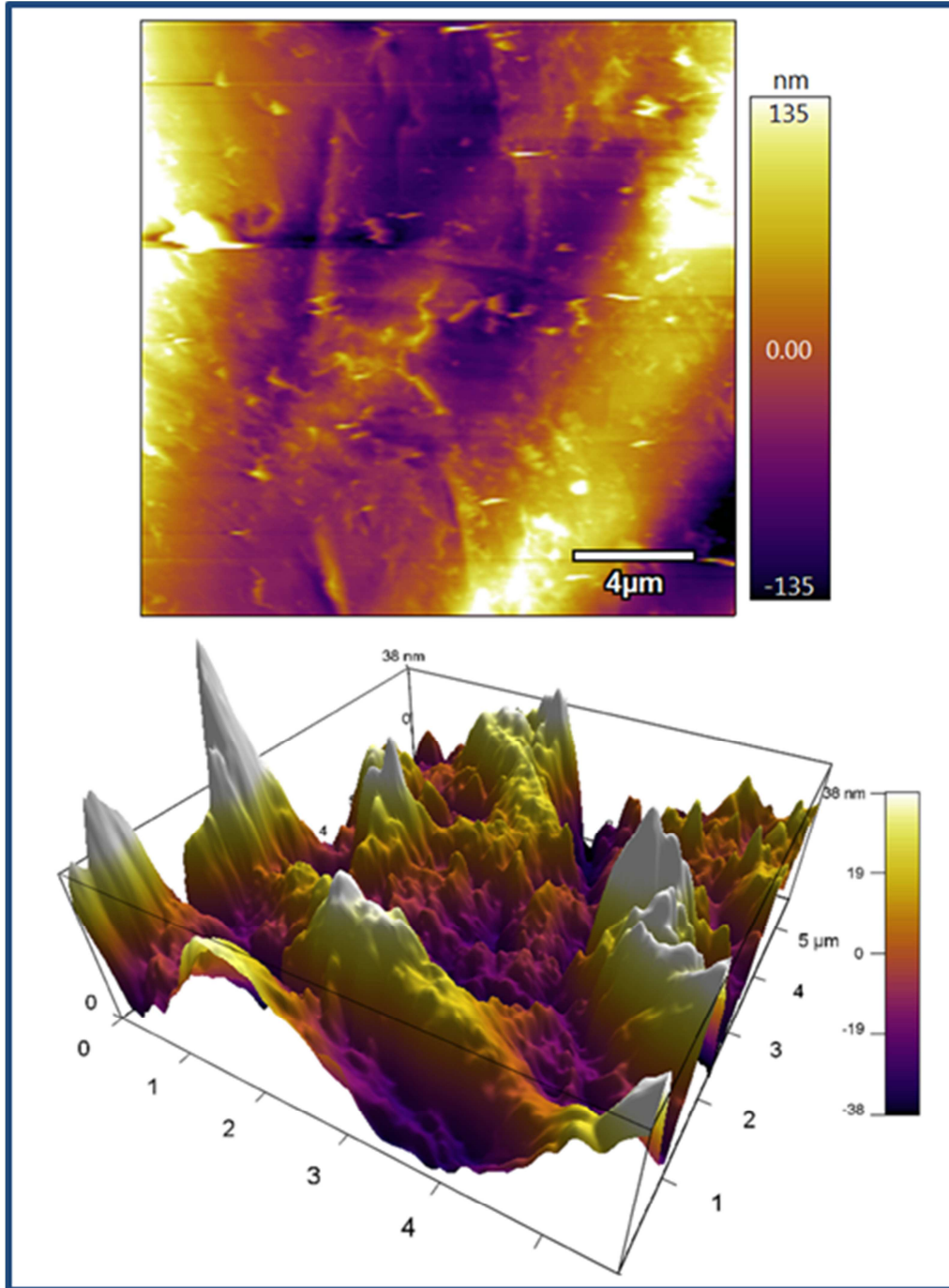
216

217 As the involvement of physical surface characteristics is yet to be fully understood in regards
218 to its influence on microplastic behaviour (sorption and fate), more extensive surface
219 characterisation is important for a range of related studies (e.g. sorption and degradation).
220 Characterisation of surface roughness is most often presented in the form of imaging with
221 scanning electron microscopy (SEM). This method, while practical in producing qualitative
222 data on microplastic surface structure, is limited in terms of quantitative analysis [43]. Other
223 methods, such as optical profilometry (OP) and atomic force microscopy (AFM), can enable
224 quantified analysis of surface structures [43, 44]. The former was applied to microplastic
225 material in a study by Murrell, *et al.* [43], in which the authors presented the practical
226 application of OP to quantify the surface roughness of microplastic material as an
227 improvement from solely qualitative characterisation with SEM. The potential of the latter
228 method is discussed below.

229

230 Atomic force microscopy (AFM) is a physical measurement of topography down to an
231 atomic resolution [45, 46]. It allows for the measurement of various surface characteristics,
232 including surface roughness, by physically interacting a cantilever with a specialised tip (of
233 nanoscale diameter) with the sample surface [44]. The resultant rise and fall of the

234 cantilever is measured by the monitoring of a laser aimed at the cantilever with a photo
235 detector [44]. There are three modes of AFM: a contact mode in which the cantilever tip is
236 drawn along the surface of the sample, an intermittent-contact mode in which the tip is
237 tapped at regular intervals along the sample, and a non-contact mode in which the tip does
238 not come into contact with the sample itself, but with liquid on its surface from which it
239 measures topography [44].
240



241
242

243 Figure 1 - 2D and 3D scans of a virgin PS microplastic nurdle surface generated using an
244 Asylum Research MFP-3D Cypher S AFM in contact mode.

245
246 Quantitative measurements of the surface roughness of a microplastic can be produced
247 using AFM, while producing qualitative data in the form of nanoscale resolution images of
248 sample surfaces (Figure 1) [44, 47]. Another specific benefit of using AFM is the scanning
249 resolution in three dimensions, AFM is able to reach resolutions ≤ 1 nm, dependent on the
250 size of the cantilever tip used [48, 49]. This high resolution allows for quantified examination
251 of physical surface structure at a range not yet explored in microplastics. In addition, the
252 capacity of AFM to scan in three dimensions is not possible at the same resolution in SEM,
253 meaning AFM is able to detect more detailed changes in surface roughness [48].

254
255 Furthermore, AFM is able to image a surface with significantly less pre-preparation
256 compared to SEM [48]. Due to the risk of a sample's secondary electron signal being
257 interfered with by external factors, imaging is required in a sealed vacuum, a feature not
258 required by AFM [48]. In addition, changes to the physical surface of a microplastic sample
259 can be caused by the heat generated by an SEM electron beam, melting the sample [50].
260 This is significant as any processing has the potential to impact the nanoscale surface of a
261 microplastic sample. This change is not required in AFM and presents the opportunity to
262 measure a more accurate surface roughness [48].

263
264 Quantification of microplastic surface roughness using AFM provides an avenue to address
265 the issues stated earlier in this section. However AFM is not limited to quantification of
266 surface roughness, it has also been used to measure characteristics including
267 hydrophobicity, adhesiveness (in regards to microbial interactions) and conductivity [51,
268 52]. Fu and Zhang [51] demonstrated how measurement of hydrophobicity was possible
269 with AFM, which was used to measure adhesion forces between the AFM tip and self-
270 assembly monolayers (SAMs). A linear relationship was found between the measured
271 adhesion force and water contact angles (a measurement of hydrophobicity based on the
272 continuum thermodynamic approach) of the subject nanoparticles (NPs), which included,
273 CuO, ZnO and TiO₂. This relationship enabled measurement of hydrophobicity with adhesion
274 force measurement by AFM. It is of note that the accuracy of these measurements differed
275 depending on the NP material, which is theorised by the authors to be due to difference in
276 surface roughness and hydration [51]. Zhang, *et al.* [52] used AFM to calculate the
277 interaction forces between NPs (hematite and corundum) and bacterial (*E. coli*) cells. These
278 interaction forces were used as a measurement of adhesion between the NPs and the
279 bacteria [52]. This AFM measurement was used by Zhang, *et al.* [52] to investigate the
280 relationship between NP size and microbe adhesiveness, in which they found a decrease in
281 adhesion force with increased NP size. This was presumed due to the effective contact area
282 between the NP and the cells increasing with decreasing NP size [52].

283
284 Furthermore, the development of hybrid AFM techniques (AFM-Raman and AFM-infrared
285 spectroscopy (AFM-IR) have extended the minimum size range threshold of chemical

286 characterisation techniques into the nanoscale [53, 54]. In these advances there is
287 significant evidence that AFM can contribute more to the development of characterisation
288 in microplastic research. AFM-IR is a method which combines the chemical characterisation
289 of infrared (IR) spectroscopy with the resolution of AFM [53, 55]. The method exposes a
290 sample to an IR laser, which causes photothermal expansion, the degree of which is
291 dependent on the IR absorbance properties of the sample material [53]. This expansion is
292 monitored by measuring the oscillation of an AFM tip in contact with the sample as a
293 wavelength, and this wavelength is converted into an IR absorbance spectra [55]. This
294 development has expanded IR spectroscopic chemical characterisation into the nanoscale
295 resolution, previously not possible with methods such as FT-IR [55]. As plastic research
296 expands into nanoplastic pollution, development of such methods may become increasingly
297 important to the field.

298
299 While the potential benefit in using AFM is significant, there are considerations which need
300 to be taken into account in regards to its use. Physical contact in AFM has the potential to
301 cause damage to the surface of samples potentially affecting results and preventing
302 accurate and reliable physical characterisation of the sample [56]. This contact can be
303 minimised by using intermittent-contact or non-contact AFM, however this can be a trade
304 off with the resolution of the acquired image [56].

305
306 Further needed consideration when using AFM comes from its limited depth of field [48].
307 Compared to SEM, AFM has a significantly shorter depth of field, where SEM can show a
308 depth of field at a magnitude of mm, AFM is limited to that of μm [48]. In the context of
309 imaging a surface, if a surface is particularly rough in regards to height differences in a given
310 area, then AFM will be limited in the vertical information it is able to collect [48]. This has
311 implications for the scan size used to measure the surface roughness of a microplastic
312 particle, significant due to the effect scan size has on measured surface roughness [57]. This
313 is illustrated by Mwema, *et al.* [57] whose found that surface roughness of aluminium films
314 was increased by increasing the scan size used ($1\mu\text{m}^2$, $3\mu\text{m}^2$, $30\mu\text{m}^2$). These limitations being
315 considered, developing use of AFM holds significant potential to expand microplastic
316 physical surface characterization and to contribute to the development of characterisation
317 techniques regarding other microplastic properties.

318
319

320 **3. Exploring Sorption in Multi-Solute Media with Double-Shot Pyrolysis-Gas** 321 **Chromatography-Mass Spectrometry**

322

323 As microplastics are exposed to the environment they sorb various chemical and biological
324 factors, eventually forming a surface layer called an ecocorona [11]. The composition of
325 these ecocoronae is dependent on the nature of the particle, the environment the particle
326 has been exposed to and potential to interact with the surrounding ecosystem [58]. Such

327 interactions can range from influencing organism behaviour to increasing or decreasing the
328 toxicity of sorbed chemicals [26, 59].

329

330 There are in addition questions to be addressed around the effects of polymer degradation
331 and multi-solute media on sorption behaviour, for which the exploration of microplastic
332 surface layers is imperative [18, 26, 27, 60]. Ho and Leung [27] studied the sorption to
333 microplastics (LDPE and PS) of UV filters (benzophone-3 (BP-3), 4-methylbenzylidene
334 camphor (4-MBC) in a multi-solute environment containing ethylhexyl methoxycinnamate
335 (EHMC) and octocrylene (OC). They found that although most interactions between co-
336 solutes appeared antagonistic, sorption of 4-MBC by PS increased in the presence of the
337 other UV filters [27]. Laterally attractive interactions between the adsorbed co-solute UV
338 filters (BP-3, EHMC and OC) and the 4-MBC were proposed to explain the subsequent
339 increase in adsorption by the PS [27]. The study highlights the complexity of sorption
340 behaviours concerning microplastics in multi-solute environments.

341

342 Wang, *et al.* [60] exposed microplastic polyethylene terephthalate (PET) material to 313nm
343 wavelength UV light (from 50W/m² lamps) for up to 500 hours, finding an increased
344 sorption capacity for metal ions Cu²⁺ and Zn²⁺. The authors conclude that the increased
345 sorption with UV degradation was likely due to increased surface area with microplastic
346 material becoming more irregular in shape (which was highlighted by changes in surface
347 structure shown by SEM images), in addition to the increased number of oxygen groups on
348 the PET surface caused by photooxidation [60]. Furthermore, both increases in temperature
349 and pH are noted as being significant to the sorption rate, the former due the endothermic
350 characteristic of adsorption of the metal ions by PET, and the latter due to resultant
351 increased charged sites on the microplastic surface and the positive charge of the subject
352 ions [60]. This highlights the complexity brought by variation in conditions such as pH and
353 temperature, as well as the physical degradation of the microplastic material, which all have
354 consequences for subsequent sorption behaviours.

355

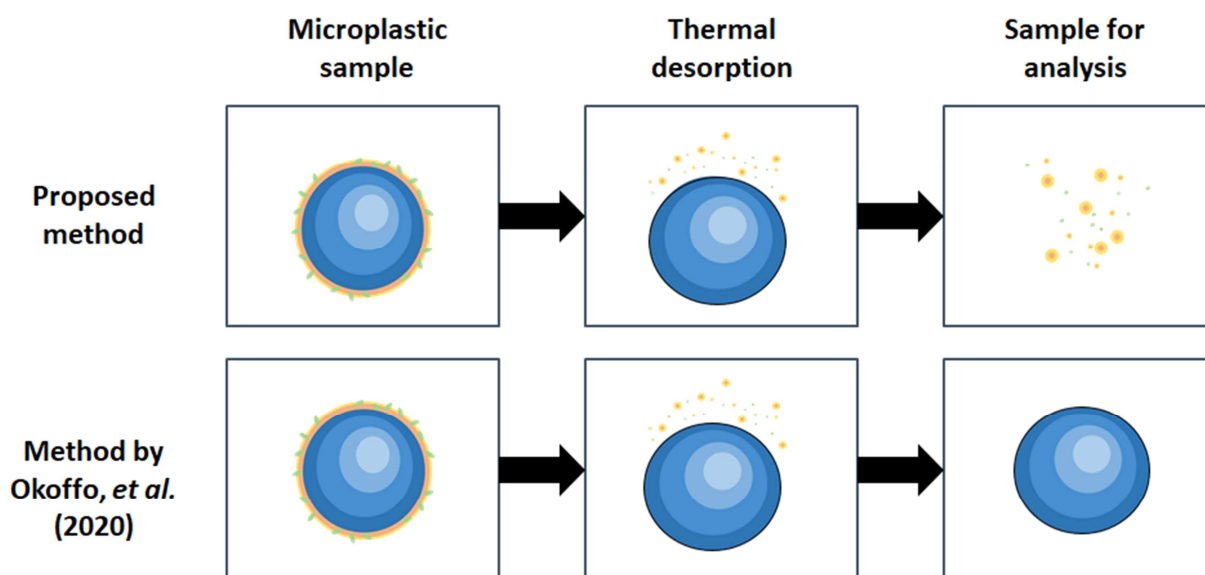
356 Studies into the sorption behaviour of microplastics in single solute media, in which one
357 chemical contaminant in solution is studied at a time, are numerous in the literature.
358 Despite the use of such studies to understand sorption behaviour and the different affinities
359 for sorption with varying sorbates, in the environment microplastics are exposed to
360 chemically diverse media [18, 27]. This is significant, as sorption in multi-solute media
361 involves factors such as competitive sorption, which would affect the composition of
362 microplastic surface layers [27, 61]. Therefore, in looking to address how microplastic
363 surface layers form in different environments, analysis of the sorbed contents of
364 microplastics in multi-solute experimental media, with quantification of the formed
365 ecocorona composition, would be effective.

366

367 Such analysis of the sorbed content of microplastics has been achieved with a number of
368 different methods in the literature, with numerous variations in liquid and gas-
369 chromatography mass-spectrometry [19, 62]. However, we focus here on one method in
370 particular; based on recent advances in microplastics quantification in pyrolysis-gas
371 chromatography-mass spectrometry (Py-GCMS). In Py-GCMS, materials are thermally
372 degraded, and the volatile products that are produced are subsequently identified through
373 mass spectrometry [63]. To achieve this, samples are raised to between 500-1400°C in an
374 inert gas, transforming the sample into a volatile product [64]. This volatile product is
375 chromatographically separated and identified through mass spectrometry based on
376 reference spectra libraries [64].

377
378 This method has been modified in a number of ways to analyse both microplastic material
379 and their additives [2, 65]. Sequential Py-GCMS is an example, where the temperature is
380 raised at intervals, which has been used to separate additives (e.g. organic plastic additives:
381 diethylhexyl phthalate, dibutyl phthalate and dimethyl phthalate) from microplastics (e.g.
382 PE, polypropylene and PS) for analysis [65]. Thermo-extraction and desorption with GCMS
383 (TED-GCMS) would be another example [2]. This technique combines thermogravimetric
384 analysis with desorption GCMS for practical chemical analysis of relatively high quantities of
385 microplastic material [2]. Progress in Py-GCMS has now enabled the separation of
386 microplastics from environmental material (such as biosolids) for subsequent analysis [66].
387 Okoffo, *et al.* [66] described a so-called double-shot technique, where interfering
388 environmental material is thermally desorbed from the sample before pyrolysis of the
389 microplastic content. The authors apply this method to process biosolid material, with a
390 combined use of solid phase extraction and double-shot Py-GCMS resulting in separation of
391 microplastic material from biosolid samples [66]. However, in using Py-GCMS to look at the
392 associated chemical content, as previously published by Fries, *et al.* [65] sequential Py-GCMS
393 to quantify organic plastic additives, such a method may be used to quantify sorbed
394 content. Applying the concept of double-shot Py-GCMS from Okoffo, *et al.* [66] to isolate the
395 sorbed material from the sample, but for subsequent quantification rather than disposal.
396 This could provide a method to address the aforementioned questions relating to
397 microplastic sorption behaviour in more detail.

398



399 Figure 2 - Simplified illustrated flow diagram of a proposed method based on the Py-GCMS
 400 technique of Okoffo, *et al.* [66].
 401
 402

403 It is possible that this method could be used to expand examination of accumulated
 404 biological factors; Py-GCMS has been used to this end previously. Zhu, *et al.* [67] used Py-
 405 GCMS to quantify microbial biomass through the detection of specific “microbial signals”
 406 (including benzyl nitrile, pyrrole and indole). The study used five pyrolysis products
 407 (including those mentioned above) as a “fingerprint” of microbial presence to measure the
 408 biomass in marine sediment samples [67]. Using the proposed double-shot Py-GCMS
 409 method to examine the relationship between biofilm formation and microplastic
 410 characteristics, could facilitate further developing our understanding of microplastic
 411 ecocoronaes.
 412

413 Various plastic additives are commonly used to manipulate the properties of plastics.
 414 Pigments are added for colour, antioxidants are added for age resistance and UV stabilisers
 415 are added for light resistance [65]. As microplastics are weathered by the environment
 416 these additives are progressively lost through the process of leaching [68]. The loss of these
 417 additives results in significant changes to microplastic properties and their chemical
 418 composition [69]. Py-GCMS has been shown to be a suitable method of quantification for
 419 these additives, as Fries, *et al.* [65] quantified organic plastic additives (including
 420 diethylhexyl phthalate, dibutyl phthalate and dimethyl phthalate) with sequential Py-GCMS.
 421 Furthermore, the leaching of additives could influence sorption behaviour, and as shown in
 422 the previously mentioned study by Ho and Leung [27], where co-solutes had either
 423 antagonistic and enhancing effects on sorption behaviours depending on the primary solute
 424 and the sorbent material (see earlier in this section). As such, potentially an adapted double-
 425 shot Py-GCMS method could be used to quantify the relationship between the sorption rate
 426 of different sorbates and the successive leaching of different plastic additives.
 427

428 While there is significant potential in the use of double-shot Py-GCMS to explore the above
429 stated research avenues, it is of note Py-GCMS does also result in sample destruction [64].
430 Due to this, no further observations or measurements can be made on the sample after the
431 technique has been used. As Py-GCMS only produces data relating to the chemical
432 composition of the sample, other characteristics such as colour, shape and size are lost if
433 not measured before the process [2]. Despite this drawback, the potential for the double-
434 shot Py-GCMS concept to be applied to the sorbed content of microplastics shows
435 significant potential to facilitate our understanding of microplastic sorption behaviour in
436 greater detail. Such possible analyses are supported by the extensive review by Picó and
437 Barceló [70] regarding the use of Py-GCMS on microplastics and associated environmental
438 material.

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441 **4. Examining surface interactions with Whispering Gallery Mode optical nanosensors**

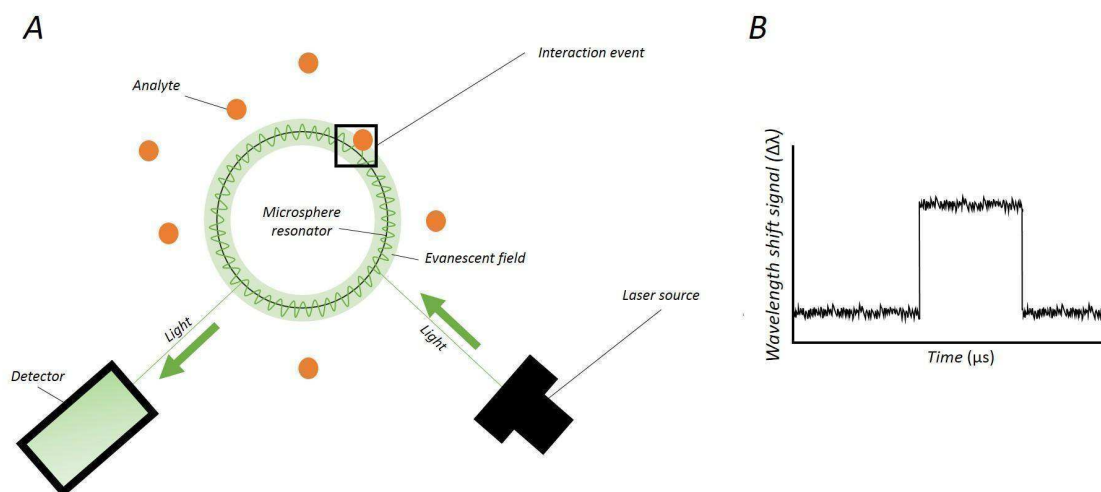
442

443 Understanding sorption kinetics of microplastics in greater detail is of fundamental
444 importance for interpreting studies of their interactions in the aquatic environment. More
445 detailed data collection on sorption kinetics will facilitate the development of more accurate
446 sorption kinetics models to mass balance models [59, 71]. This will in turn result in more
447 accurate estimation of the effects of microplastics on the fate, transport and bioavailability
448 of sorbed chemicals [59, 71]. Sorption kinetics have been measured using ICP-MS, liquid and
449 gas-chromatography MS to good effect [18, 19, 72]. Here, we describe a novel technique,
450 with potential to contribute to examining sorption kinetics in greater detail.

451

452 Whispering Gallery Mode (WGM) optical nanosensors utilise the “whispering gallery mode”
453 recirculation of photons involving the internal reflection of light within microcavities [73]
454 (Figure 3). This accumulation of photons generates an evanescent field which enables
455 significantly sensitive nanosensors [73] (Figure 3). The “Whispering gallery mode” name
456 comes from the phenomenon described by Lord Rayleigh in 1910 in which a whisper can be
457 heard from one end of the gallery of St Paul’s Cathedral, London, UK to the other (32m
458 apart) [74, 75]. This is caused by the acoustic waves being guided along the walls of the
459 circular room [75]. These WGM optical nanosensors harness a similar movement of waves
460 but that of light rather than sound [75]. Light is accumulated inside a resonator (which can
461 be formed of various materials and shapes, glass to silica, spheres to toroids) through the
462 internal reflection of light [73] (Figure 3). The longer the light is able to circulate within the
463 specific resonator, the higher the sensitivity of the measurement (Q factor) [73]. As such,
464 the Q factor is important when considering what materials are suitable for constructing the
465 microsphere resonator component.

466



467
 468 Figure 3 - Simplified illustrated diagram of the main components to a WGM nanosensor (A)
 469 and its ability to detect interactions on the surface of the resonator through measured
 470 changes in the light signal detected (B).
 471

472 To date the application of WGM to environmentally relevant micro/nanoplastics has not
 473 been reported. However, previous experiments have provided potential insights into how
 474 WGM may be applied to the study of nanoscale surface interactions on microplastic
 475 surfaces. Constructing a microsphere resonator with plastic would be of interest. This has
 476 been found to be possible with plastic materials using entirely plastic structures and silica
 477 microspheres coated in plastic material [76, 77]. In a paper by Dong, *et al.* [16], researchers
 478 coated silica microspheres with polymethyl methacrylate (PMMA) using a dip coating
 479 technique. The study found that the coating improved the Q factor of the microsphere
 480 resonator for WGM [76]. Furthermore, Lutti, *et al.* [77] demonstrated the suitability of
 481 polystyrene microspheres as WGM resonators thanks to a satisfactory Q factor when
 482 prepared in the described manner.
 483

484 The advantage of analysing microplastic surface structures using WGM optical nanosensors
 485 is that it would allow for the measurement of the number and duration of interactions with
 486 the resonator surface within a specific time resolution [73]. Simplified, an interaction
 487 between a resonating WGM evanescent field and a single molecule is detected by the
 488 resonance shift the molecule causes at the surface of the resonator [73]. Looking at a plastic
 489 surface, this could provide a wealth of information about the dynamism of interactions
 490 between single chemical factors and microplastics.
 491

492 The sorption of chemical factors is a dynamic process of sorption and desorption which
 493 reaches a state of equilibrium once concentrations in the solid phase (microplastic) and the
 494 liquid phase remain constant [59]. The detailed information WGM could produce from
 495 examining these interactions would provide more accurate data to improve sorption
 496 kinetics models and mass balance models [59, 71]. Ultimately, this would result in a more

497 accurate examination of the effects of microplastic sorption behaviour on chemical
498 transport in the context of the environment.

499

500 Limitations in using WGM come from method development. One example would be the
501 time resolution of measurements, being dependent on the “cavity lifetime” (τ) ($\tau = Q/\omega$,
502 where Q = Q factor and ω = the light’s angular frequency) [78]. This limits the time
503 resolution of WGM measurements to durations in the order of nanoseconds, potentially
504 missing more transient interactions [78]. While improvements to WGM sensors are planned
505 to surpass this threshold time resolution, currently they are limited by this “cavity lifetime”.
506 Another example relating to method development would be the considerations needed for
507 more complex samples such as may be generated in complex aquatic environments [79].
508 The more complex a sample is, the more likely non-specific interaction events are to occur,
509 creating signal noise [79]. For example, if a sample was being analysed for interaction with a
510 specific UV filter but included two more co-solute molecules, which readily interact with the
511 resonator surface, these co-solutes would generate non-specific interaction events. These
512 non-relevant signals can be mitigated in various ways, from quantifying the difference in
513 signal between all the sample constituents, to using labels to amplify the desired signal
514 (enzymes and antibodies have been previously used in WGM biosensing) [79]. These noise
515 mitigation methods, while effective, take time to develop, and as such can be seen as a
516 limitation to the method.

517

518

519 **5. Summary and recommendations**

520

521 The continued progress of microplastic chemical and physical characterisation is important
522 to develop more accurate and in depth understanding of their impacts on the environment.
523 We know microplastics are found throughout the environment, we now need to understand
524 in what form and how they interact. The physical characteristics of microplastics can have
525 implications for their reactivity and so their behaviour in the environment [19]. As such,
526 examining the relationship between physical characteristics (such as surface roughness) and
527 sorption behaviour of different sorbates is important to understand microplastic behaviour.

528

529 High resolution imaging of a sample surface can be provided by AFM while producing
530 quantified information about surface roughness [44, 47]. AFM could be applied to
531 microplastics research in studies investigating sorption, UV degradation and characterisation
532 of surface roughness. This would facilitate more in depth examination of the relationship
533 between physical characteristics and sorption, and help expand microplastic
534 characterisation in the literature.

535

536 Recent advances in double-shot Py-GCMS show potential to provide a novel method to
537 quantify sorbed microplastic content [66]. The technique could be used to examine sorption

538 rates of multi-solute media through analysis of accumulated surface layers. This would
539 provide more in depth data concerning microplastic sorption behaviour and so their
540 potential for environmental impact.

541
542 Furthermore, more detailed data collection on microplastic sorption kinetics would facilitate
543 the development of accurate models to estimate the environmental impact of microplastic
544 pollution [59, 71]. This is in terms of the transport and bioavailability of sorbed chemical
545 factors [59]. Therefore, it would be beneficial to develop methods which measure
546 microplastic surface interactions with greater precision.

547
548 The WGM technique shows significant potential to reveal more about how microplastics
549 interact with chemicals in the environment. Based on the knowledge that WGM techniques
550 enable the measurement of interactions between a chemical factor and the surface of a
551 microsphere resonator, that WGM resonators have been formed of plastic, and that WGM
552 can be coated in plastic; it is possible WGM could be used to examine microplastic surfaces
553 interactions [73, 76, 77].

554
555 Quantifying these interactions will lead to a more detailed grasp of the environmental
556 impact of microplastic pollution. This could go some way to addressing the concerns of
557 Connors, *et al.* [80] that greater physical and chemical characterisation is a necessary
558 development to microplastic research.

559
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561

562 **Competing interest**

563 The authors declare no conflict of interest.

564

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619 **References**

620

- 621 [1] Hartmann, N. B., Hüffer, T., Thompson, R. C., Hassellöv, M., Verschoor, A., Daugaard,
622 A. E., & Wagner, M. (2019). Are We Speaking the Same Language?
623 Recommendations for a Definition and Categorization Framework for Plastic Debris.
624 *Environmental Science and Technology*, 53(3), 1039–1047.
- 625 [2] Silva, A. B., Bastos, A. S., Justino, C. I. L., da Costa, J. P., Duarte, A. C., & Rocha-Santos,
626 T. A. P. (2018, August 9). Microplastics in the environment: Challenges in analytical
627 chemistry - A review. *Analytica Chimica Acta*, Vol. 1017, pp. 1–19.
- 628 [3] Kanhai, L. D. K., Gårdfeldt, K., Lyashevskaya, O., Hassellöv, M., Thompson, R. C., &
629 O'Connor, I. (2018). Microplastics in sub-surface waters of the Arctic Central Basin.
630 *Marine Pollution Bulletin*, 130, 8–18.
- 631 [4] Peng, X., Chen, M., Chen, S., Dasgupta, S., Xu, H., Ta, K., & Bai, S. (2018).
632 Microplastics contaminate the deepest part of the world's ocean. *Geochemical
633 Perspectives Letters*, 1–5.
- 634 [5] Waller, C. L., Griffiths, H. J., Waluda, C. M., Thorpe, S. E., Loaiza, I., Moreno, B., &
635 Hughes, K. A. (2017, November 15). Microplastics in the Antarctic marine system: An
636 emerging area of research. *Science of the Total Environment*, Vol. 598, pp. 220–227.
- 637 [6] Horton, A. A., & Dixon, S. J. (2018). Microplastics: An introduction to environmental
638 transport processes. *Wiley Interdisciplinary Reviews: Water*, 5(2), e1268.
- 639 [7] Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics
640 ever made. *Science Advances*, 3(7), e1700782.
- 641 [8] PlasticsEurope. (2019). *Plastics- The Facts*.
- 642 [9] PlasticsEurope. (2012). *Plastics - The Facts*.
- 643 [10] Haram, L. E., Carlton, J. T., Ruiz, G. M., & Maximenko, N. A. (2020). A
644 Plasticene Lexicon. *Marine Pollution Bulletin*, 150.
- 645 [11] Galloway, T. S., Cole, M., & Lewis, C. (2017). Interactions of microplastic
646 debris throughout the marine ecosystem. *Nature Ecology and Evolution*, Vol. 1.
- 647 [12] Ryberg, M., Laurent, A., & Hauschild, M. Z. (2018). Mapping of global plastics
648 value chain and plastics losses to the environment. *United Nations Environment
649 Programme*.
- 650 [13] Schnurr, R. E. J., Alboiu, V., Chaudhary, M., Corbett, R. A., Quanz, M. E.,
651 Sankar, K., & Walker, T. R. (2018). Reducing marine pollution from single-use plastics
652 (SUPs): A review. *Marine Pollution Bulletin*, 137, 157–171.
- 653 [14] Rochman, C. M., Brookson, C., Bikker, J., Djuric, N., Earn, A., Bucci, K., & Hung,
654 C. (2019, April 1). Rethinking microplastics as a diverse contaminant suite.
655 *Environmental Toxicology and Chemistry*, Vol. 38, pp. 703–711.
- 656 [15] Ateia, M., Zheng, T., Calace, S., Tharayil, N., Pilla, S., & Karanfil, T. (2020).
657 Sorption behavior of real microplastics (MPs): Insights for organic micropollutants

- 658 adsorption on a large set of well-characterized MPs. *Science of the Total*
659 *Environment*, 720.
- 660 [16] Lohmann, R. (2017). Microplastics are not important for the cycling and
661 bioaccumulation of organic pollutants in the oceans—but should microplastics be
662 considered POPs themselves? *Integrated Environmental Assessment and*
663 *Management*, Vol. 13, pp. 460–465.
- 664 [17] Xu, P., Ge, W., Chai, C., Zhang, Y., Jiang, T., & Xia, B. (2019). Sorption of
665 polybrominated diphenyl ethers by microplastics. *Marine Pollution Bulletin*, 145,
666 260–269.
- 667 [18] Müller, A., Becker, R., Dorgerloh, U., Simon, F. G., & Braun, U. (2018). The
668 effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics.
669 *Environmental Pollution*, 240, 639–646.
- 670 [19] Wang, Z., Chen, M., Zhang, L., Wang, K., Yu, X., Zheng, Z., & Zheng, R. (2018).
671 Sorption behaviors of phenanthrene on the microplastics identified in a mariculture
672 farm in Xiangshan Bay, southeastern China. *Science of the Total Environment*, 628–
673 629, 1617–1626.
- 674 [20] Guo, X., Wang, X., Zhou, X., Kong, X., Tao, S., & Xing, B. (2012). Sorption of
675 four hydrophobic organic compounds by three chemically distinct polymers: Role of
676 chemical and physical composition. *Environmental Science and Technology*, 46(13),
677 7252–7259.
- 678 [21] Farrow, M. R., Camp, P. J., Dowding, P. J., & Lewtas, K. (2013). The effects of
679 surface curvature on the adsorption of surfactants at the solid-liquid interface.
680 *Physical Chemistry Chemical Physics*, 15(28), 11653–11660.
- 681 [22] Müller, Y. K., Wernicke, T., Pittroff, M., Witzig, C. S., Storck, F. R., Klinger, J., &
682 Zumbülte, N. (2020). Microplastic analysis—are we measuring the same? Results on
683 the first global comparative study for microplastic analysis in a water sample.
684 *Analytical and Bioanalytical Chemistry*, 412(3), 555–560.
- 685 [23] Weis, J. S. (2019). Improving microplastic research. *AIMS Environmental*
686 *Science*, 6(5), 326–340.
- 687 [24] Teuten, E. L., Saquing, J. M., Knappe, D. R. U., Barlaz, M. A., Jonsson, S., Björn,
688 A., & Takada, H. (2009). Transport and release of chemicals from plastics to the
689 environment and to wildlife. *Philosophical Transactions of the Royal Society B:*
690 *Biological Sciences*, 364(1526), 2027–2045.
- 691 [25] Scopetani, C., Cincinelli, A., Martellini, T., Lombardini, E., Ciofini, A., Fortunati,
692 A., & Ugolini, A. (2018). Ingested microplastic as a two-way transporter for PBDEs in
693 *Talitrus saltator*. *Environmental Research*, 167, 411–417.
- 694 [26] Procter, J., Hopkins, F. E., Fileman, E. S., & Lindeque, P. K. (2019). Smells good
695 enough to eat: Dimethyl sulfide (DMS) enhances copepod ingestion of microplastics.
696 *Marine Pollution Bulletin*, 138, 1–6.

- 697 [27] Ho, W. K., & Leung, K. S. Y. (2019). Sorption and desorption of organic UV
698 filters onto microplastics in single and multi-solute systems. *Environmental Pollution*,
699 254.
- 700 [28] Fu, W., Min, J., Jiang, W., Li, Y., & Zhang, W. (2020). Separation,
701 characterization and identification of microplastics and nanoplastics in the
702 environment. *Science of the Total Environment*, 721.
- 703 [29] Primpke, S., Christiansen, S. H., Cowger, W., De Frond, H., Deshpande, A.,
704 Fischer, M., & Wiggin, K. (2020). Critical Assessment of Analytical Methods for the
705 Harmonized and Cost Efficient Analysis of Microplastics. *Applied Spectroscopy*,
706 000370282092146.
- 707 [30] Gong, M., Yang, G., Zhuang, L., & Zeng, E. Y. (2019). Microbial biofilm
708 formation and community structure on low-density polyethylene microparticles in
709 lake water microcosms. *Environmental Pollution*, 252, 94–102.
- 710 [31] Harrison, J. P., Hoellein, T. J., Sapp, M., Tagg, A. S., Ju-Nam, Y., & Ojeda, J. J.
711 (2018). Microplastic-Associated Biofilms: A Comparison of Freshwater and Marine
712 Environments. In M. Wagner & S. Lambert (Eds.), *Freshwater Microplastics: The
713 Handbook of Environmental Chemistry* 58 (pp. 181–201).
- 714 [32] Miao, L., Wang, P., Hou, J., Yao, Y., Liu, Z., Liu, S., & Li, T. (2019). Distinct
715 community structure and microbial functions of biofilms colonizing microplastics.
716 *Science of the Total Environment*, 650, 2395–2402.
- 717 [33] Oberbeckmann, S., & Labrenz, M. (2019). Marine Microbial Assemblages on
718 Microplastics: Diversity, Adaptation, and Role in Degradation.
- 719 [34] Ballent, A., Purser, A., de Jesus Mendes, P., Pando, S., & Thomsen, L. (2012).
720 Physical transport properties of marine microplastic pollution. *Biogeosciences
721 Discussions*, 9(12), 18755–18798.
- 722 [35] Gardette, J. L., Bussière, P. O., & Therias, S. (2018). Recent progress in the
723 field of polymer photodegradation. *AIP Conference Proceedings*, 1981.
- 724 [36] Mao, R., Lang, M., Yu, X., Wu, R., Yang, X., & Guo, X. (2020). Aging mechanism
725 of microplastics with UV irradiation and its effects on the adsorption of heavy
726 metals. *Journal of Hazardous Materials*, 393.
- 727 [37] Auras, R. (2007). Solubility of gases and vapors in polylactide polymers. In
728 *Thermodynamics, solubility and environmental issues* (pp. 343–368).
- 729 [38] Artioli, Y. (2008). Adsorption. In S. E. Jørgensen & B. D. Fath (Eds.),
730 *Encyclopedia of Ecology* (pp. 60–65).
- 731 [39] Akkas, T., Citak, C., Sirkecioglu, A., & Güner, F. S. (2013). Which is more
732 effective for protein adsorption: Surface roughness, surface wettability or swelling?
733 Case study of polyurethane films prepared from castor oil and poly(ethylene glycol).
734 *Polymer International*, 62(8), 1202–1209.
- 735 [40] Hüffer, T., & Hofmann, T. (2016). Sorption of non-polar organic compounds
736 by micro-sized plastic particles in aqueous solution. *Environmental Pollution*, 214,
737 194–201.

- 738 [41] Nonoyama, T., Lee, Y. W., Ota, K., Fujioka, K., Hong, W., & Gong, J. P. (2020).
739 Instant Thermal Switching from Soft Hydrogel to Rigid Plastics Inspired by
740 Thermophile Proteins. *Advanced Materials*, 32(4).
- 741 [42] Hartmann, N. B., Rist, S., Bodin, J., Jensen, L. H. S., Schmidt, S. N., Mayer, P., &
742 Baun, A. (2017). Microplastics as vectors for environmental contaminants: Exploring
743 sorption, desorption, and transfer to biota. *Integrated Environmental Assessment
744 and Management*, Vol. 13, pp. 488–493.
- 745 [43] Murrell, K. A., Ghetu, C. C., & Dorman, F. L. (2018). The combination of
746 spectroscopy, microscopy, and profilometry methods for the physical and chemical
747 characterization of environmentally relevant microplastics. *Analytical Methods*,
748 10(40), 4909–4916.
- 749 [44] De Oliveira, R. R. L., Albuquerque, D. A. C., Cruz, T. G. S., Yamaji, F. M., &
750 Leite, F. L. (2012). Measurement of the Nanoscale Roughness by Atomic Force
751 Microscopy: Basic Principles and Applications.
- 752 [45] Giessibl, F. J. (2003). Advances in atomic force microscopy. *Reviews of
753 Modern Physics*, 75(3), 949.
- 754 [46] Morita, S., Giessibl, F., Meyer, E., & Wiesendanger, R. (2015). Noncontact
755 Atomic Force Microscopy, Volume 3.
- 756 [47] Cai, L., Wu, D., Xia, J., Shi, H., & Kim, H. (2019). Influence of physicochemical
757 surface properties on the adhesion of bacteria onto four types of plastics. *Science of
758 the Total Environment*, 671, 1101–1107.
- 759 [48] Bergström, J. (2015). Experimental Characterization Techniques. In J.
760 Bergström (Ed.), *Mechanics of Solid Polymers: Theory and Computational Modeling*
761 (pp. 19–114).
- 762 [49] Dufrêne, Y. F., Ando, T., Garcia, R., Alsteens, D., Martinez-Martin, D., Engel,
763 A., & Müller, D. J. (2017, May 1). Imaging modes of atomic force microscopy for
764 application in molecular and cell biology. *Nature Nanotechnology*, Vol. 12, pp. 295–
765 307.
- 766 [50] Dunlap, M., & Adaskaveg, J. E. (1997). Introduction to the Scanning Electron
767 Microscope: Theory, practice, & procedures. *Facility for Advanced Instrumentation*
768 (52).
- 769 [51] Fu, W., & Zhang, W. (2018). Measurement of the surface hydrophobicity of
770 engineered nanoparticles using an atomic force microscope. *Physical Chemistry
771 Chemical Physics*, 20(37), 24434–24443.
- 772 [52] Zhang, W., Stack, A. G., & Chen, Y. (2011). Interaction force measurement
773 between *E. coli* cells and nanoparticles immobilized surfaces by using AFM. *Colloids
774 and Surfaces B: Biointerfaces*, 82(2), 316–324.
- 775 [53] Cho, H., Felts, J. R., Yu, M. F., Bergman, L. A., Vakakis, A. F., & King, W. P.
776 (2013). Improved atomic force microscope infrared spectroscopy for rapid
777 nanometer-scale chemical identification. *Nanotechnology*, 24(44).

- 778 [54] Yeo, B. S., Amstad, E., Schmid, T., Stadler, J., & Zenobi, R. (2009). Nanoscale
779 probing of a polymer-blend thin film with Tip-enhanced Raman spectroscopy. *Small*,
780 5(8), 952–960.
- 781 [55] Dazzi, A., & Prater, C. B. (2017). AFM-IR: Technology and applications in
782 nanoscale infrared spectroscopy and chemical imaging. *Chemical Reviews*, Vol. 117,
783 pp. 5146–5173.
- 784 [56] Baykara, M. Z., & Schwarz, U. D. (2016). Atomic Force Microscopy: Methods
785 and Applications. In *Encyclopedia of Spectroscopy and Spectrometry* (pp. 70–75).
- 786 [57] Mwema, F. M., Akinlabi, E. T., & Oladijo, O. P. (2020). Dependence of fractal
787 characteristics on the scan size of atomic force microscopy (AFM) phase imaging of
788 aluminum thin films. *Materials Today: Proceedings*.
- 789 [58] Reimonn, G., Lu, T., Gandhi, N., & Chen, W. T. (2019). Review of microplastic
790 pollution in the environment and emerging recycling solutions. *Journal of Renewable*
791 *Materials*, Vol. 7, pp. 1251–1268.
- 792 [59] Tourinho, P. S., Kočí, V., Loureiro, S., & van Gestel, C. A. M. (2019, September
793 1). Partitioning of chemical contaminants to microplastics: Sorption mechanisms,
794 environmental distribution and effects on toxicity and bioaccumulation.
795 *Environmental Pollution*, Vol. 252, pp. 1246–1256.
- 796 [60] Wang, Q., Zhang, Y., Wangjin, X., Wang, Y., Meng, G., & Chen, Y. (2020). The
797 adsorption behavior of metals in aqueous solution by microplastics effected by UV
798 radiation. *Journal of Environmental Sciences (China)*, 87, 272–280.
- 799 [61] Bakir, A., Rowland, S. J., & Thompson, R. C. (2012). Competitive sorption of
800 persistent organic pollutants onto microplastics in the marine environment. *Marine*
801 *Pollution Bulletin*, 64(12), 2782–2789.
- 802 [62] Hüffer, T., Weniger, A. K., & Hofmann, T. (2018). Sorption of organic
803 compounds by aged polystyrene microplastic particles. *Environmental Pollution*, 236,
804 218–225.
- 805 [63] Käßler, A., Fischer, M., Scholz-Böttcher, B. M., Oberbeckmann, S., Labrenz,
806 M., Fischer, D., & Voit, B. (2018). Comparison of μ -ATR-FTIR spectroscopy and py-
807 GCMS as identification tools for microplastic particles and fibers isolated from river
808 sediments. *Analytical and Bioanalytical Chemistry*, 410(21), 5313–5327.
- 809 [64] Kusch, P. (2012). Pyrolysis-Gas Chromatography/Mass Spectrometry of
810 Polymeric Materials. In *Advanced Gas Chromatography - Progress in Agricultural,*
811 *Biomedical and Industrial Applications*.
- 812 [65] Fries, E., Dekiff, J. H., Willmeyer, J., Nuelle, M. T., Ebert, M., & Remy, D.
813 (2013). Identification of polymer types and additives in marine microplastic particles
814 using pyrolysis-GC/MS and scanning electron microscopy. *Environmental Sciences:*
815 *Processes and Impacts*, 15(10), 1949–1956.
- 816 [66] Okoffo, E. D., Ribeiro, F., O'Brien, J. W., O'Brien, S., Tschärke, B. J., Gallen, M.,
817 & Thomas, K. V. (2020). Identification and quantification of selected plastics in

- 818 biosolids by pressurized liquid extraction combined with double-shot pyrolysis gas
819 chromatography–mass spectrometry. *Science of the Total Environment*, 715.
- 820 [67] Zhu, R., Versteegh, G. J. M., & Hinrichs, K. U. (2016). Detection of microbial
821 biomass in subseafloor sediment by pyrolysis-GC/MS. *Journal of Analytical and*
822 *Applied Pyrolysis*, 118, 175–180.
- 823 [68] Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., &
824 Galloway, T. S. (2013). Microplastic ingestion by zooplankton. *Environmental Science*
825 *and Technology*, 47(12), 6646–6655.
- 826 [69] Lambert, S., Scherer, C., & Wagner, M. (2017, May 1). Ecotoxicity testing of
827 microplastics: Considering the heterogeneity of physicochemical properties.
828 *Integrated Environmental Assessment and Management*, Vol. 13, pp. 470–475.
- 829 [70] Picó, Y., & Barceló, D. (2020). Pyrolysis gas chromatography-mass
830 spectrometry in environmental analysis: focus on organic matter and microplastics.
831 *TrAC Trends in Analytical Chemistry*, 115964.
- 832 [71] Fred-Ahmadu, O. H., Bhagwat, G., Oluyoye, I., Benson, N. U., Ayejuyo, O. O.,
833 & Palanisami, T. (2020, March 1). Interaction of chemical contaminants with
834 microplastics: Principles and perspectives. *Science of the Total Environment*, Vol.
835 706.
- 836 [72] Turner, A., & Holmes, L. A. (2015). Adsorption of trace metals by microplastic
837 pellets in fresh water. *Environmental Chemistry*, 12(5), 600–610.
- 838 [73] Vollmer, F., & Arnold, S. (2008). Whispering-gallery-mode biosensing: Label-
839 free detection down to single molecules. *Nature Methods*, 5(7), 591–596.
- 840 [74] D’Aguanno, G., & Menyuk, C. R. (2016). Nonlinear mode coupling in
841 whispering-gallery-mode resonators. *Physical Review A*, 93(4).
- 842 [75] Subramanian, S., Wu, H. Y., Constant, T., Xavier, J., & Vollmer, F. (2018,
843 December 20). Label-Free Optical Single-Molecule Micro- and Nanosensors.
844 *Advanced Materials*, Vol. 30.
- 845 [76] Dong, C. H., Sun, F. W., Zou, C. L., Ren, X. F., Guo, G. C., & Han, Z. F. (2010).
846 High- Q silica microsphere by poly(methyl methacrylate) coating and modifying.
847 *Applied Physics Letters*, 96(6).
- 848 [77] Lutti, J., Langbein, W., & Borri, P. (2008). A monolithic optical sensor based on
849 whispering-gallery modes in polystyrene microspheres. *Applied Physics Letters*,
850 93(15).
- 851 [78] Frustaci, S., & Vollmer, F. (2019, August 1). Whispering-gallery mode (WGM)
852 sensors: review of established and WGM-based techniques to study protein
853 conformational dynamics. *Current Opinion in Chemical Biology*, Vol. 51, pp. 66–73.
- 854 [79] Foreman, M. R., Swaim, J. D., & Vollmer, F. (2015). Whispering gallery mode
855 sensors. *Advances in Optics and Photonics*, 7(2), 168.
- 856 [80] Connors, K. A., Dyer, S. D., & Belanger, S. E. (2017). Advancing the quality of
857 environmental microplastic research. *Environmental Toxicology and Chemistry*,
858 36(7), 1697–1703.

Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: