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Degradation of nanoplastics in the environment: Reactivity and impact on atmospheric and surface waters

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1 Degradation of nanoplastics in the environment:
2 reactivity and impact on atmospheric and surface
3 waters

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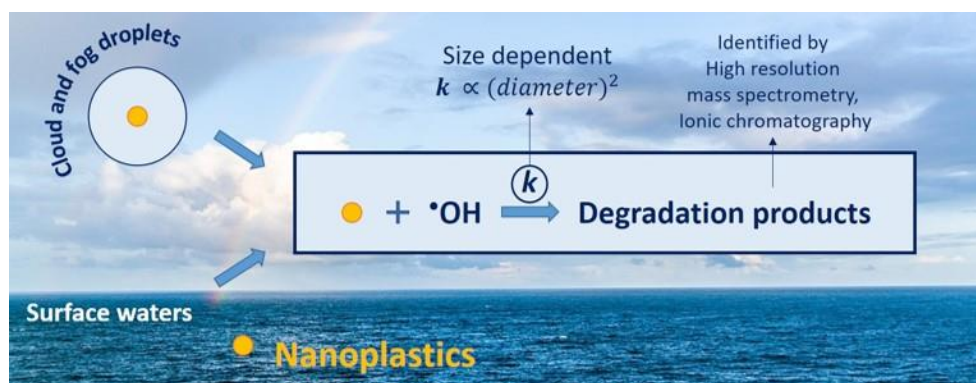
16 **HIGHLIGHTS**

- 17 • Smaller nanoplastics particles show higher reactivity with $\cdot\text{OH}$.
- 18 • Reactivity constants of polystyrene nanoparticles with $\cdot\text{OH}$ are measured.
- 19 • There is potential for nanoplastics to significantly scavenge $\cdot\text{OH}$ in the environment.
- 20 • Degradation of nanoplastics releases organic compounds in the aqueous phase.

21

22 GRAPHICAL ABSTRACT

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25

26

27 Abstract

28 Microplastics (MPs) and nanoplastics (NPs) are ubiquitous and contaminate soil, surface waters,
29 atmospheric aerosol, precipitations, indoor and outdoor environments. However, the occurrence,
30 transformation and fate of NPs in the environment are still unclear. In this work, polystyrene
31 nanoparticles (PS-NPs) are used as a proxy of NPs to study their reactivity and potential impact on
32 atmospheric and surface waters. In particular, the reactivity with hydroxyl radicals (•OH) in the
33 aqueous phase is investigated. For the first time, a reactivity constant for the reaction of NPs with
34 •OH is measured, strongly dependent on the exposed particle surface area of NPs. Degradation
35 products (short chain carboxylic acids and aromatic compounds), obtained by direct and •OH-
36 mediated photolysis of PS-NPs suspensions, are identified by mass spectrometry. Irradiation of a PS-
37 NPs suspension under natural sunlight for 1 year has shown the formation of formic acid and organic
38 compounds similar to those found in riverine and cloud dissolved organic matter, which could
39 contribute significantly to the dissolved organic matter in the aqueous phase.

40

41 **Keywords:** Nanoplastics; polystyrene; hydroxyl radical; dissolved organic matter; kinetic constant.

42

43 **1. Introduction**

44 The large production of plastic material (PlasticsEurope, 2019), together with the mishandling of
45 plastic waste, has resulted in ubiquitous plastic pollution, which now reaches even the most remote
46 areas of the Earth (Allen et al., 2019; Bergmann et al., 2019) and has dramatic consequences on flora
47 and fauna (Acampora et al., 2017; Todd et al., 2010). Plastics undergo a slow process of erosion in
48 the environment, which is defined as the mass loss of the polymer matrix and is due to the loss of
49 monomers, oligomers or even pieces of non-degraded polymer (Göpferich, 1996). This process
50 decreases the size of plastic debris down to microplastics (MPs) and nanoplastics (NPs), defined as
51 plastic debris with diameters between 1 μm and 5 mm and lower than 1 μm , respectively (Frias and
52 Nash, 2019). Other possible sources of MPs and NPs are landfills or waste incineration, as well as
53 synthetic fibers from clothes and houses (Dris et al., 2016; Liu et al., 2019).

54 Microplastics (MPs) contaminate soils, sediments and surface waters (both seawater and fresh
55 waters) (Besseling et al., 2014; Scheurer and Bigalke, 2018; Yonkos et al., 2014); for example they
56 represent 94% (in number) of collected plastic debris in the Great Pacific Garbage Patch (Lebreton
57 et al., 2018). Recent studies have shown that MPs occur also in atmospheric aerosol and precipitations
58 (Allen et al., 2019; Bergmann et al., 2019; Klein and Fischer, 2019), and their presence has also been
59 documented in indoor and outdoor environments in Paris and Dongguan (Cai et al., 2017; Dris et al.,
60 2017; Gasperi et al., 2018). In the last decades there has been a growing interest on MPs occurrence
61 in the environment and on their potential toxicity (Anbumani and Kakkar, 2018; Dris et al., 2018;
62 Koelmans et al., 2019), even though their environmental impact is still under debate (Backhaus and
63 Wagner, 2019). While MPs have been measured in several environmental matrices (Chen et al., 2020;
64 Han et al., 2019; Li et al., 2019; Xu et al., 2020), the occurrence of NPs in the environment is almost
65 unknown (Lehner et al., 2019), mainly due to sampling and instrumental limitations (Mintenić et al.,
66 2018; Schwaferts et al., 2019; Ter Halle et al., 2017). Up to now the occurrence, transformation,
67 transport and fate of NPs in the environment have still been unclear. Moreover, MPs and NPs are not

68 inert and they can react and interact with chemical species that occur in the surrounding environment
69 (Jeong et al., 2018; Lee et al., 2019).

70 Erosion of MPs and NPs is the result of mechanical abrasion, oxidation, UV radiation or
71 microbiological activity (da Costa et al., 2016; Dawson et al., 2018; Lambert et al., 2013; Mattsson
72 et al., 2018). When a plastic piece degrades down to parts with sizes in the nanometre scale, the
73 exposed area increases drastically and so does the surface reactivity (Mattsson et al., 2018). However,
74 the dependence of plastics degradation kinetics upon their particle size is almost unknown, because
75 most of the degradation studies are carried out on large plastics pieces or on polymeric films (Gewert
76 et al., 2015; O’Brine and Thompson, 2010).

77 The main abiotic degradation process of plastics is photo-initiated oxidation (Gomiero, 2019),
78 which leads to polymer chain scission, branching and formation of polymer fragments as well as of
79 volatile compounds (Gewert et al., 2015). Photochemistry plays a key role in these transformation
80 processes, by direct photodegradation or by indirect photolysis, through the photogeneration of
81 reactive transient species such as the hydroxyl radical, $\cdot\text{OH}$ (Calza and Vione, 2016; Faust, 1994).

82 MPs and NPs in the atmosphere and in surface waters are exposed to sunlight and oxidants (e.g.,
83 $\cdot\text{OH}$). Bubble bursting and wind action can suspend MPs and NPs in air, where they could be present
84 as dry or deliquescent (in-droplet) particles. In atmospheric waters, like cloud and fog droplets, MPs
85 and NPs are even more exposed to gas and aqueous phase oxidants: for instance, the $\cdot\text{OH}$ steady-state
86 concentration in cloud water is 2 orders of magnitude higher than in sea water (Lallement et al., 2018;
87 Olasehinde, 2012). Therefore, the degradation pathway(s) of MPs and NPs in atmospheric and surface
88 waters can be similar, considering that in both cases they are exposed to sunlight, gas-phase and
89 liquid-phase oxidants.

90 The objective of this work is to better understand the reactivity of an aqueous suspension of
91 polystyrene NPs (PS-NPs) in the presence of sunlight (direct photolysis) and hydroxyl radical
92 (indirect photolysis) that is a relevant oxidant in surface waters and atmospheric liquid particles. To

93 develop this new approach to study the reactivity of NPs in the environment, we decided to use well-
94 defined polymeric NPs. PS standards with different monodisperse particle sizes are commercially
95 available, and are very suitable for studying the correlation between the reactivity and the exposed
96 surface. For the first time, a reactivity constant with $\cdot\text{OH}$ is determined, which can be implemented
97 into atmospheric and surface waters chemistry models (Bodrato and Vione, 2014) to understand the
98 environmental impact of NPs degradation. Moreover, the identification of degradation products
99 allows for the estimation of the contribution of NPs degradation to the natural dissolved organic
100 matter occurring in the aqueous phase. This work can significantly contribute to assess the impact of
101 NPs abiotic degradation in the atmospheric aqueous phase, like cloud and fog droplets, and surface
102 waters.

103

104 **2. Material and Methods**

105 *2.1. Materials and procedures*

106 Suspensions (1% solids content w/w) of PS-NPs in water were purchased from Thermo Fischer
107 Scientific (diameter of 102 ± 1 nm, 203 ± 5 nm, 400 ± 9 nm, and 600 ± 9 nm). The suspensions for
108 irradiation were prepared daily by mixing the stock suspension of PS-NPs, previously sonicated, with
109 MilliQ water. After irradiation and before analysis, all the suspensions were filtered on $0.22 \mu\text{m}$ nylon
110 filters from Sigma-Aldrich. Blank experiments were carried out to verify that no organic material was
111 released from the filter. Additional information on chemicals used are available in the Supporting
112 Information (SI), paragraph SI-S1.

113 *2.2. Analysis of product formation - UVA Irradiation*

114 Aliquots of 15 mL of PS-NPs suspensions in Milli-Q water (0.05% solid) were irradiated in a
115 photoreactor placed horizontally in a custom-built wood container covered with aluminium foil. The
116 photoreactor consisted of a closed quartz tube (diameter 2.5 cm). Two UVA fluorescent lamps (Narva
117 LT 18W/009), with emission spectrum ranging mainly from 300 to 440 nm, were placed on top of

118 the photoreactor (distance 6 cm), as reported in Figures S1-S2. UVA radiation was chosen because it
119 represents the main UV fraction of solar light. PS-NPs with diameter of 400 ± 9 nm were chosen for
120 this series of experiments, because they can be easily filtered and analysed by means of SMPS
121 (scanning mobility particle sizer, SI-S2), in order to determine the size and concentration of the
122 suspension and to investigate eventual formation of aggregates. All the experiments were carried out
123 at 293 ± 2 K using a continuous flow of compressed air to cool the system. An aliquot of the
124 suspension (3 mL) was withdrawn from the reactor and used for the analysis of degradation products
125 at fixed times. Filtered solutions were analysed using an ElectroSpray Ionization-Differential
126 Mobility Analyser (ESI-DMA) coupled with Atmospheric Pressure interface Time Of Flight Mass
127 Spectrometer (Tofwerk) (ESI-DMA-API-TOF) (Kangasluoma et al., 2016; Passananti et al., 2019).
128 Acetate and formate anions were determined by ion chromatography. More details on the analytical
129 methods and instrumentation are available in SI-S2. The size and the concentration of PS-NPs were
130 measured by SMPS before and after irradiation. No difference was found: PS-NPs keep the same
131 diameter (no aggregation) and the same concentration.

132 2.3. Competition method for the measurement of the reactivity constant between PS and $\cdot\text{OH}$.

133 The reaction rate constants between $\cdot\text{OH}$ and PS-NPs were measured using the competition method
134 described by Zhou and Mopper (1990), employing benzoic acid (hereafter BZ) as a probe.
135 Suspensions containing 0.05% PS-NPs, 50 mM H_2O_2 and BZ with different concentrations, varying
136 from 0.18 mM to 1.2 mM, were irradiated under UVA light for 60 minutes. In these experiments the
137 loading of PS-NPs was kept constant, to avoid interference of varying NPs loadings on the light field
138 and irradiance in the suspensions. In such a way, the light scattering of the suspension would not
139 change among different experiments and would thus not affect the measured rate constants. To carry
140 out kinetic competition, BZ concentration was thus varied. The time evolution of BZ was monitored
141 by High-Performance Liquid Chromatography coupled with Diode Array Detection (HPLC–DAD),

142 using conditions detailed in SI-S3. Blank experiments excluded the degradation of BZ under UVA
143 irradiation alone (direct photolysis).

144 *2.4. Experiment under real sunlight irradiation*

145 A suspension of PS 100 nm in MilliQ water (0.2% v/v) was exposed for 14 months (August 1st, 2018-
146 October, 1st, 2019) on the rooftop of the Physicum building in Kumpula Campus in Helsinki
147 (Finland). The irradiation set-up is shown in Figure S3. The average temperature during this period
148 was 8.5°C, with a minimum on January 22nd (2019) of -18.9°C and a maximum on July 28th (2019)
149 of 32.1°C. The suspension froze during wintertime, but the large amount of air inside the reactor
150 prevented breaking of the glass. Filters with mesh size lower than 0.2 µm were not available, thus we
151 filtered the 100 nm PS-NPs suspension on 0.2 µm filters by gravity, without application of pressure.
152 The resulting solution was limpid and the particles that might have passed through the filter did not
153 affect the following spectroscopic and spectrometric analysis. Solar radiation was measured by
154 SMEARIII station with a time resolution of one minute, and the relevant data are available online at
155 SMEAR website (<https://avaa.tdata.fi/web/smart/smear>).

156

157 **3. Results and Discussion**

158 *3.1 Interaction with hydroxyl radicals*

159 Surface modification due to polymers aging by light and gas-phase oxidants, such as O₃, is well
160 known (Singh and Sharma, 2008; Yousif and Haddad, 2013). However, experiments are usually
161 performed on films and with high concentration of O₃, which are non-representative of environmental
162 conditions. Concerning PS, attention has been focused on the functionalisation of the polymer chain
163 and on surface changes, using ATR/FTIR spectroscopy and microscopy techniques (SEM, AFM)
164 (Yang et al., 2018; Zhang et al., 2000).

165 PS particles occurring in surface waters and in cloud/fog waters can also react with aqueous-phase
166 oxidants, such as most notably the hydroxyl radicals (·OH) (Arakaki et al., 2013; Faust and Allen,

167 1993; Mopper and Zhou, 1990; Vione et al., 2010). A previous study of oxidation in dichloromethane
168 reveals that $\cdot\text{OH}$ addition to PS occurs at the phenyl groups, and that mucondialdehydes are produced
169 by chain scission (Weir, 1978). Surface modifications and functionalisation of MPs and NPs lead to
170 increased hydrophilicity, which could have an effect on ice nucleating properties (Ganguly and Ariya,
171 2019). However, to our knowledge, no study on PS reactivity with $\cdot\text{OH}$ has been carried out in the
172 aqueous phase. As first approach, we investigated the potential reactivity between PS-NPs and
173 photogenerated $\cdot\text{OH}$ in aqueous solution. Figure 1 reports a preliminary test of UVA-irradiation of
174 PS-NPs in the presence of H_2O_2 and benzoic acid (BZ) in water, using the experimental conditions
175 detailed in SI-S4. The plot reports the BZ concentration as a function of time. The degradation rate
176 of BZ decreases in the presence of PS-NPs, suggesting that PS-NPs may be able to significantly
177 scavenge $\cdot\text{OH}$.

178 3.2 Reactivity of PS-NPs: measurement of the reactivity constant with hydroxyl radical

179 PS-NPs react with $\cdot\text{OH}$, but no information on the reactivity rate constants is reported in previous
180 works. Reactivity constants are essential for modelling studies, with the aim of assessing PS-NPs
181 degradation in different environmental scenarios as well as their ability to scavenge $\cdot\text{OH}$ and to affect
182 photo-oxidation cycles in natural waters. For the first time, the rate constant of PS-NPs with $\cdot\text{OH}$ is
183 determined with the competition method described in Section 2.3, using BZ as reference compound.
184 Three different sizes of PS-NPs are used, namely 200 nm, 400 nm and 600 nm. As discussed in detail
185 in SI-S6, the second-order kinetic constants between PS and $\cdot\text{OH}$ are calculated with the following
186 equation:

$$187 \quad k_{\text{OH,PS}} = \frac{a}{b} \times k_{\text{OH,BZ}} - [\text{H}_2\text{O}_2] \times k_{\text{OH,H}_2\text{O}_2} \quad (1)$$

188 where a/b is the ratio between the slope and the intercept of the linear correlation reported in the plot
189 ($x = \text{inverse of BZ concentration}$, $y = \text{inverse of BZ degradation rate}$), $k_{\text{OH,BZ}}$ is the second-order
190 reaction rate constant between BZ and $\cdot\text{OH}$ ($5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988), $[\text{H}_2\text{O}_2]$ is the
191 hydrogen peroxide concentration, and $k_{\text{OH,H}_2\text{O}_2}$ is the second-order reaction rate constant between

192 $\cdot\text{OH}$ and H_2O_2 ($2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) (Buxton et al., 1988). Figure S4 shows the plot used to determine
193 the kinetic constant. BZ is also a degradation product of PS-NPs (*see below*); however, due to the
194 short time of the kinetic experiments and the large concentration difference between initially added
195 and photogenerated BZ, there is no interference due to the formation of degradation products. This
196 applies both to the monitoring of the BZ time trend, and to the ability of the products (including BZ)
197 to scavenge $\cdot\text{OH}$ on their own. Indeed, less than 0.1% of $\cdot\text{OH}$ would react with BZ produced during
198 PS degradation in one hour.

199 The kinetic constants between $\cdot\text{OH}$ and PS-NPs ($k_{\text{OH,PS}}$) are reported in Table 1. Because the
200 concentration of PS-NPs used for the rate-constant calculation was expressed in #particles mL^{-1} (see
201 SI-S6), the measure unit of $k_{\text{OH,PS}}$ is $\text{mL s}^{-1} \text{ #particles}^{-1}$. We observed that the size of the particles
202 (*i.e.*, their surface area) plays a role in particles reactivity, and that the values of $k_{\text{OH,PS}}$ are different
203 for each PS particle size. The kinetic constant is higher for PS 600 nm, which exposes a larger surface
204 area, and smaller for PS 200 nm, which exposes a surface area of $0.126 \mu\text{m}^2$ per particle (see Table
205 1). This result can be explained by the fact that $\cdot\text{OH}$ would react with the PS surface sites (most likely,
206 the aromatic rings) and it has no access to the polymer bulk. The measured kinetic constants are
207 proportional to the square of the diameter d of the particles ($k_{\text{OH,PS}} \propto d^2$, see Figure S5); therefore,
208 the reactivity constant of PS-NPs can be expressed as a function of their diameter, allowing for the
209 extrapolation of kinetic constants at different diameters (see Table 1). We decided to express the
210 kinetic constants as a function of the diameter, in order to employ them in kinetic models in
211 combination with environmental data. Indeed, environmental data about NPs and MPs provide
212 information on their concentration (#particles/volume) and size (generally a range), without
213 specifying the surface area or the specific shape of the collected debris. Therefore, a kinetic constant
214 expressed as a function of the diameter would be more useful compared to a surface-area-normalized
215 rate constant. Further studies are needed to obtain data on the surface area of NPs in the environment,
216 in order to overcome this spherical-approximation. It is important to notice that the reactivity is higher

217 for single particles with larger diameters and higher surface area; however, at equal mass
218 concentration, PS-NPs with lower particle size (200 nm) expose a higher surface area than PS-NPs
219 with larger particle size (600 nm) and thus show higher reactivity, as reported in Figure S6 and Table
220 S3.

221 3.3 Impact of environmental stressing agents on PS-NPs: degradation products

222 We have demonstrated that $\cdot\text{OH}$ reacts with PS-NPs and determined the reaction rate constants, but
223 little is known about the impact of degraded plastics on the environment, in particular concerning the
224 release of organic compounds. Vicente et al (2009) studied in detail the effect of O_3 and UVA
225 radiation on aerosolised PS-NPs. Davidson et al. (2005) investigated the surface modification after
226 O_3 and light exposure, and analysed the photodegradation products with GC-MS after washing with
227 methanol or water. They found that benzaldehyde, acetophenone, BZ, carboxylic acids, aromatic
228 ketones and esters are produced during PS exposure to O_3 and light. However, limited information is
229 available concerning the photodegradation products formed by $\cdot\text{OH}$ reactions with PS-NPs.
230 Therefore, we investigated how plastic degradation by $\cdot\text{OH}$ affects dissolved organic matter chemical
231 composition. Suspensions of PS-NPs were exposed to 4 experimental conditions described in Table
232 S1 under the irradiation set-up presented in Figure S2. This set-up allowed for estimating the impact
233 of: (1) direct photodegradation + photogenerated $\cdot\text{OH}$ (indirect photolysis); (2) direct
234 photodegradation alone; (3) reactivity with H_2O_2 in dark conditions; and (4) possible
235 hydrolysis/degradation in dark conditions. Suspensions were sampled at fixed times, then filtered on
236 nylon filters and analysed by ESI-DMA-APiToF. High-resolution mass spectrometry allows for the
237 attribution of molecular formulas to degradation products. Trends of the main products formed by
238 indirect and direct photodegradation are reported in Figure S7a and S7b, respectively, while
239 degradation products formed by reactivity with and without H_2O_2 in dark conditions are reported in
240 Figure S8. The $\cdot\text{OH}$ reactivity induces the formation of carboxylic compounds such as formic (also

241 detected as formic acid dimer), acetic, lactic acids, and aromatic acids like BZ, as well as aliphatic
242 and aromatic aldehydes like muconaldehyde and benzaldehyde.

243 Among the products of PS-NPs photodegradation, benzoquinone, dibenzoyl methane and benzoic
244 anhydride are also observed. The benzene signal increases by more than 350% of the initial value,
245 while the phenol signal increases by 40% during the first 24h and later on decreases, as shown in
246 Figure 2. The formation of degradation products could be explained through the $\cdot\text{OH}$ addition to π -
247 systems or hydrogen abstraction. A possible reaction mechanism, detailing the reactivity of
248 polystyrene and the formation of degradation products, is reported in Figure 3. We considered the
249 reactions induced by photogenerated $\cdot\text{OH}$ (light + H_2O_2), but the mechanism is probably the same
250 with light only. The tertiary polystyryl radicals, generated by hydrogen abstraction or $\cdot\text{OH}$ addition,
251 can efficiently react with molecular oxygen to form peroxy radicals, $\text{ROO}\cdot$. The latter can recombine
252 or give sequential reactions, leading to the formation of hydroxyl, carbonyl or carboxylic functions.
253 The carboxylic group RCOOH can react with $\cdot\text{OH}$ to give $\text{RCOO}\cdot$, which decomposes to form $\text{R}\cdot$ and
254 CO_2 (Gardette et al., 1995). Tertiary polystyryl radicals can be generated by absorption of light with
255 wavelength longer than 300 nm (Gardette et al., 1995), explaining why formation of BZ,
256 benzaldehyde, benzoic anhydride, dibenzoyl methane, benzene, acetic and formic acids are also
257 observed in the case of direct photodegradation (Figure 2). However, the formation of the tertiary
258 polystyryl radicals seems to be enhanced in the presence of $\cdot\text{OH}$, as suggested by the much higher
259 concentration values of photodegradation products in the H_2O_2 + light experiments compared to light
260 alone. A previous study on the irradiation of PS films in both humid and dry conditions revealed the
261 formation of acetophenone (Gardette et al., 1995). This degradation product is not detected under our
262 experimental conditions in the presence of $\cdot\text{OH}$, while its signal increases during the direct photolysis
263 process (200% of the initial value). The rationale for the lack of acetophenone in the $\cdot\text{OH}$ experiments
264 could be that this compound reacts rapidly with $\cdot\text{OH}$, with a second-order reaction rate constant of
265 $6.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (Neta and Dorfman, 1968), thereby disappearing immediately after formation. Dark

266 experiments yield degradation products in limited amount, as reported in Figure S8 that shows the
267 trends observed with PS-NPs and (when relevant) H₂O₂.

268 ESI-DMA-APiToF allows for clearly identifying the degradation products, but does not provide
269 reliable quantification: the complexity of the matrix makes it difficult to perform signal calibration,
270 even with standard additions. For this reason, PS-NPs suspensions subjected to experimental
271 condition (1) (H₂O₂ + light) were analysed with ion chromatography to quantify acetic and formic
272 acids, while benzoic acid (BZ) concentration was measured with the same HPLC method described
273 previously. Trends and comparison with mass signals are reported in Figure S9. During the first 24h
274 of irradiation, the concentration of acetic and formic acids increases rapidly. It then reaches 0.38 mM
275 and 0.25 mM respectively, after 4 days of irradiation. BZ concentration increases to around 63 μM
276 after 4 days of irradiation. The formation of these degradation products contributes to the dissolved
277 organic carbon (DOC): acetic acid is responsible for an increase of 9.1 mgC L⁻¹, formic acid of 3.0
278 mgC L⁻¹, and BZ of 5.3 mgC L⁻¹. These values are of the same order of magnitude as the DOC in
279 atmospheric hydrometeors (Bianco et al., 2015; Herckes et al., 2013, 2002; van Pinxteren et al., 2016)
280 and in surface waters, except for the high-DOC aquatic systems (Bittar et al., 2016; Chen et al., 2004;
281 Del Castillo et al., 1999; Galgani and Engel, 2016; Massicotte et al., 2017; Stedmon and Cory, 2014).
282 Therefore, PS-NPs degradation could potentially impact the composition of the aqueous phase in both
283 atmospheric and surface waters.

284 3.4 *Environmental conditions: PS-NPs exposed for 14 months to sunlight and temperature changes*
285 *(direct photolysis)*

286 Laboratory irradiations give a first rapid estimate of the degradation of PS-NPs in the aqueous phase.
287 However, longer irradiations in real environmental conditions are more suitable to investigate the
288 release of organic compounds during PS-NPs degradation. A suspension of PS 100 nm in MilliQ
289 water was exposed to sunlight from August 1st, 2018 to October, 1st, 2019. Figure S10 reports
290 temperature and radiation averaged on hourly measurements for the considered period. PS-NPs were

291 degraded, they agglomerated in clusters and the aqueous system became yellowish (visual control).
292 An UV-vis spectrum after filtration was recorded showing the formation of chromophoric organic
293 compounds that absorb in the UV region up to 400 nm (Figure S11). The suspension was analysed
294 before and after solar exposure, using the same methods described for the laboratory irradiation
295 (Section 2.2). Figure S12a reports the variation in MS signals of selected compounds, while Figure
296 S12b reports the full mass spectrum obtained for the irradiated suspension. Mass spectrometric
297 analysis shows the formation of formic, benzoic and lactic acids and of benzaldehyde, while the
298 formation of other compounds is negligible. Probably, during 1-year irradiation, the degradation
299 products of PS that absorb in the near UV (see Figure S11) are transformed into small organic
300 compounds by photochemical reactions. However, Figure S12b reveals the presence of many
301 unidentified compounds, with a spectrum shape similar to those obtained for riverine and cloud
302 dissolved organic matter.(Bianco et al., 2018; Dubinenkov et al., 2015) This similarity is probably
303 due to the presence of a large variety of organic compounds, with hydroxyl, carboxylic and carbonyl
304 functions, which might be similar to the composition of natural dissolved organic matter. This
305 hypothesis is supported by the Excitation Emission Matrix (EEM) fluorescence spectrum of the liquid
306 phase (Figure S13). The presence of an emission signal around 410 nm induced by excitation around
307 300 nm recalls one of the characteristic peaks of humic substances, namely peak C (Coble, 1996) that
308 is routinely observed in surface waters (Holbrook et al., 2006). A similar peak was also observed for
309 HULIS in the atmosphere (Muller et al., 2008), and it could be due to highly oxygenated small
310 compounds (Ghigo et al., 2019) that could derive from several oxidation steps during many months
311 of sunlight exposure. Formic, acetic and benzoic acid quantification reveals concentration values of
312 7.83 mM, 4.98 mM and 0.13 mM, respectively (see Table S2), and the detected concentration of
313 formic acid corresponds to 94.0 mgC L⁻¹. Formate represents the last step of the degradation of
314 organic matter in the aqueous phase, as described in many environmental aqueous phase chemistry
315 models (Ervens, 2015; Herrmann et al., 2000; Li et al., 2017; Mouchel-Vallon et al., 2017).

316 4. Conclusions

317 This work aims at evaluating the abiotic degradation of PS-NPs in the aqueous phase, as a proxy of
318 nanoplastics to study the reactivity with hydroxyl radicals. The results obtained can be useful for both
319 surface and atmospheric waters, like cloud and fog droplets.

320 To get insight into the environmental significance of the present findings we have compared the
321 potential effect of PS-NPs and DOC as $\cdot\text{OH}$ scavengers. The DOC is, indeed, the main scavenger of
322 $\cdot\text{OH}$ radicals occurring in freshwater and cloud-water (Arakaki et al., 2013; Gligorovski et al., 2015).
323 Figure 4 reports an estimate of $k_{\text{scavenger}}$ (s^{-1}) of $\cdot\text{OH}$, which is the sum of the contributions of $\cdot\text{OH}$
324 reaction with DOC and NPs, as a function of the DOC ($k_{\text{DOC}} = 2 \times 10^4 \text{ (L s}^{-1} \text{ mgC}^{-1}) \times \text{DOC}$) and NPs
325 (Gligorovski et al., 2015). The typical DOC interval in cloud water (0-10 mgC L^{-1}) (Deguillaume et
326 al., 2014; van Pinxteren et al., 2016) is highlighted in light blue in the figure, and that in surface
327 freshwaters ($> 1 \text{ mgC L}^{-1}$) in violet (Wetzel, 2001). Concentrations of DOC higher than 30 mgC L^{-1}
328 are measured in surface water in specific cases only (Wetzel, 2001) but they are not considered in
329 this work, because in such cases DOC is obviously the main scavenger of $\cdot\text{OH}$ radicals.

330 The concentration of PS-NPs in the environment is difficult to predict considering the lack of data.
331 For this reason, we varied the PS-NPs concentration from 10^{10} #particles mL^{-1} , one order of
332 magnitude higher than the concentration of NPs in polluted environments (10^9 #particles mL^{-1} , as per
333 Gallego-Urrea et al., (2010)) down to 10^6 #particles mL^{-1} , a reasonable concentration for lesser
334 polluted aqueous media (Gallego-Urrea et al., 2010). We considered a reactivity constant between
335 $\cdot\text{OH}$ and NPs of $1.93 \times 10^{-4} \text{ mL s}^{-1} \text{ #particles}^{-1}$, the one determined for PS-NPs 600 nm in this work.
336 Figure 4 shows that when the DOC concentration is low, like in DOC-poor surface freshwater and
337 atmospheric cloud-water, there is potential for NPs to significantly scavenge $\cdot\text{OH}$. In particular, at
338 10^9 particles mL^{-1} NPs could even become the main $\cdot\text{OH}$ scavenger if $\text{DOC} < 9 \text{ mgC L}^{-1}$. Moreover,
339 at very low DOC values (1 mgC L^{-1} or below) the organic compounds released by NPs

340 photodegradation, especially if the latter takes place over a long time period, could give a non-
341 negligible contribution to both the water DOC and the $\cdot\text{OH}$ scavenging ability.

342 The comparison in the reactivity of NPs and DOC suggests three main issues:

343 (i) The ability of NPs to scavenge $\cdot\text{OH}$ should be taken into account in models aimed at describing
344 the role of $\cdot\text{OH}$ in environmental waters. To do so, however, additional data are needed on the $\cdot\text{OH}$
345 reactivity of other plastic types (e.g., polyethylene and polypropylene), on the correlation between
346 size of particles and reactivity, and on the concentration of NPs in a wide variety of aquatic
347 environments.

348 (ii) Due to their scavenging ability, it is very important to assess the fate of NPs upon $\cdot\text{OH}$ reaction,
349 including the potential to release dissolved organic compounds.

350 (iii) There is also the need to compare the $\cdot\text{OH}$ scavenging ability of NPs themselves with that of the
351 compounds that are released by their photodegradation, especially over long irradiation times.

352 In aquatic environments with higher concentration of DOC (or other $\cdot\text{OH}$ scavengers, such as bromide
353 in seawater) (Buxton et al., 1988; Gligorovski et al., 2015), PS-NPs can react with sunlight as shown
354 through direct photolysis experiments, leading to the formation of very similar degradation products
355 as those obtained under $\cdot\text{OH}$ -mediated degradation. The identification of degradation products of PS-
356 NPs suspensions subjected to direct photolysis and $\cdot\text{OH}$ -induced degradation highlights the formation
357 of several compounds, mainly small carboxylic acids and some toxic compounds like benzene and
358 phenol. These compounds could have an effect on the ecosystems by increasing the dissolved organic
359 matter amount. Moreover, the production of light-absorbing species (Figure S11) could interfere with
360 the natural photochemical equilibrium in environmental waters.

361 Our results can be implemented in models, allowing for the estimation of the amount of organic matter
362 produced by NPs abiotic degradation and, therefore, of the impact of NPs on environmental equilibria.

363

364 **Declaration of Competing Interest**

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

367

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371

372 **Author contribution**

373 A.B. formal analysis and writing-original draft, F.S. formal analysis and writing-review and editing,
374 M.E. supervision and writing-review and editing, D.V. software, supervision and writing-review and
375 editing, M.P. conceptualization, funding, formal analysis, writing-original draft and review.

376

377 **Appendix A. Supplementary data**

378 Supplementary data to this article can be found online.

379

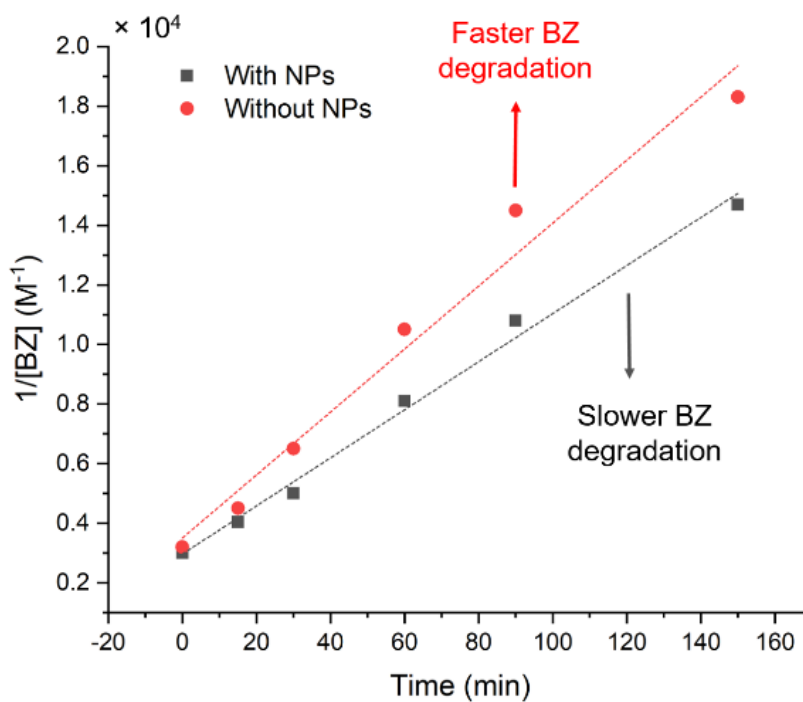
380 TABLES

Diameter of PS-NPs (μm)	Particle surface area (μm^2)	$k_{OH,PS}$ ($\text{mL s}^{-1} \text{\#particles}^{-1}$)
0.20	0.126	$(6.50 \pm 0.38) \times 10^{-5}$
0.40	0.502	$(8.64 \pm 1.30) \times 10^{-5}$
0.60	1.130	$(1.93 \pm 0.22) \times 10^{-4}$
Correlation between $k_{OH,PS}$ ($\text{mL s}^{-1} \text{\#particles}^{-1}$) and diameter of PS-NPs		
$k_{OH,PS} = (5.47 \pm 0.78) \times 10^{-4} d^2$		
d = diameter (μm)		

381 **Table 1:** Kinetic constants between $\cdot\text{OH}$ and PS-NPs ($k_{OH,PS}$) as a function of the particle surface area for each PS-NPs
382 size (200 nm, 400 nm and 600 nm). Correlation between $k_{OH,PS}$ and the diameter of PS-NPs. The error bounds represent
383 the sigma-level variability derived from data fit, which was used to obtain the relevant rate constant values.

384

385 FIGURES



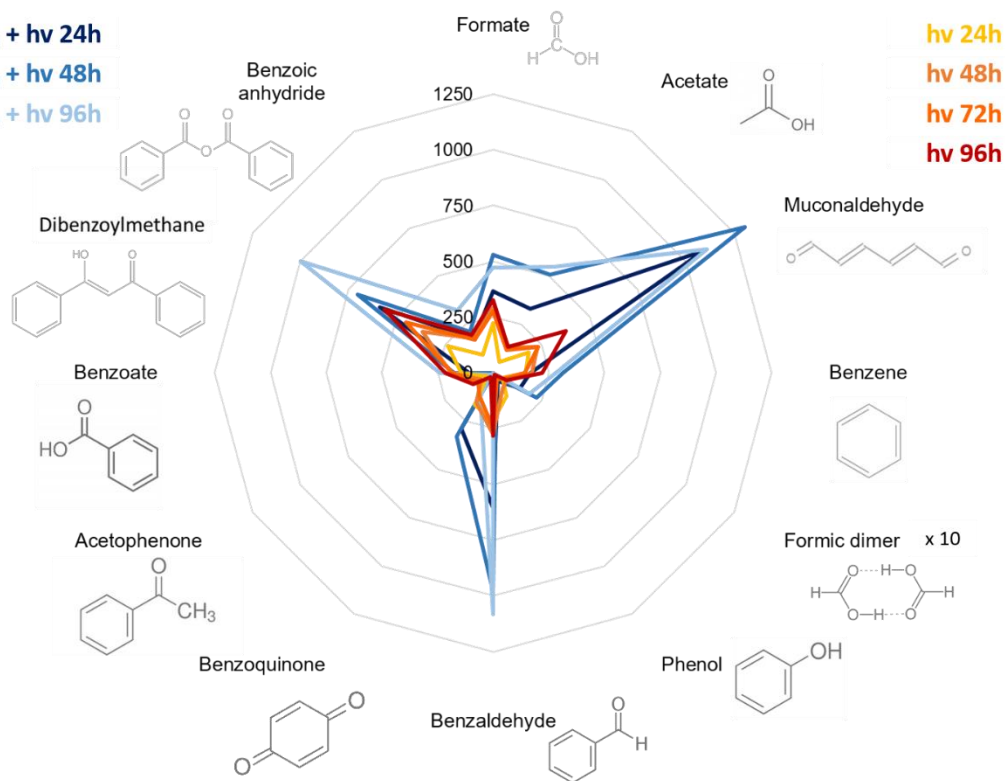
386

387 **Figure 1:** Degradation of BZ (expressed as $1/[\text{BZ}]$) as function of time with and without NPs in the presence of 50 mM
388 of H_2O_2 under UVA irradiation in water.

$H_2O_2 + hv$ 24h

$H_2O_2 + hv$ 48h

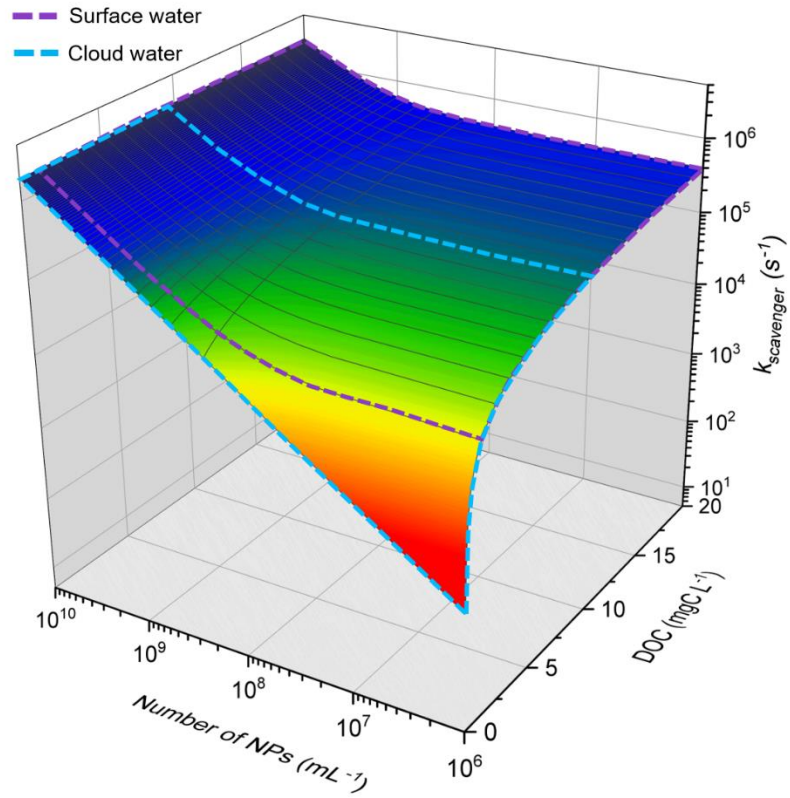
$H_2O_2 + hv$ 96h



389

390 **Figure 2:** Signal increase (%) of degradation products over time under: direct photolysis + hydroxyl radical mediated
391 oxidation ($H_2O_2 + hv$) (in shade of blue) and b) direct photolysis (hv) (in shade of red).

392



397

398 **Figure 4:** Estimated rate constants (k_{scav}) for the scavenging of $\cdot\text{OH}$ by PS-NPs and DOC. DOC concentration is
 399 representative of surface waters (higher than 1 mgC L^{-1}), depicted in the violet interval, and of cloud water (0-10 mgC
 400 L^{-1}), in light blue.

401

402 **References**

- 403 Acampora, H., Berrow, S., Newton, S., O'Connor, I., 2017. Presence of plastic litter in pellets from
404 Great Cormorant (*Phalacrocorax carbo*) in Ireland. *Mar. Pollut. Bull.* 117, 512–514.
405 <https://doi.org/10.1016/j.marpolbul.2017.02.015>
- 406 Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S.,
407 Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain
408 catchment. *Nat. Geosci.* 12, 339–344. <https://doi.org/10.1038/s41561-019-0335-5>
- 409 Anbumani, S., Kakkar, P., 2018. Ecotoxicological effects of microplastics on biota: a review.
410 *Environ. Sci. Pollut. R.* 25, 14373–14396. <https://doi.org/10.1007/s11356-018-1999-x>
- 411 Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S.,
412 Kimura, T., Tsuhako, A., Miyagi, Y., 2013. A general scavenging rate constant for reaction of
413 hydroxyl radical with organic carbon in atmospheric waters. *Environ. Sci. Tech.* 47, 8196–8203.
414 <https://doi.org/10.1021/es401927b>
- 415 Backhaus, T., Wagner, M., 2019. Microplastics in the Environment: Much Ado about Nothing? A
416 Debate. *Global Challenges* 1900022. <https://doi.org/10.1002/gch2.201900022>
- 417 Bergmann, M., Mützel, S., Primpke, S., Tekman, M.B., Trachsel, J., Gerdt, G., 2019. White and
418 wonderful? Microplastics prevail in snow from the Alps to the Arctic. *Sci. Adv.* 5, eaax1157.
419 <https://doi.org/10.1126/sciadv.aax1157>
- 420 Besseling, E., Wang, B., Lüring, M., Koelmans, A.A., 2014. Nanoplastic affects growth of *S.*
421 *obliquus* and reproduction of *D. magna*. *Environ. Sci. Technol.* 48, 12336–12343.
422 <https://doi.org/10.1021/es503001d>
- 423 Bianco, A., Deguillaume, L., Vaïtilingom, M., Nicol, E., Baray, J.-L., Chaumerliac, N., Bridoux,
424 M.C., 2018. Molecular characterization of cloud water samples collected at the puy de Dôme (France)
425 by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Environ. Sci. Tech.*
426 <https://doi.org/10.1021/acs.est.8b01964>
- 427 Bianco, A., Passananti, M., Perroux, H., Vyard, G., Mouchel-Vallon, C., Chaumerliac, N., Mailhot,
428 G., Deguillaume, L., Brigante, M., 2015. A better understanding of hydroxyl radical photochemical
429 sources in cloud waters collected at the puy de Dôme station – experimental versus modelled
430 formation rates. *Atmos. Chem. Phys.* 15, 9191–9202. <https://doi.org/10.5194/acp-15-9191-2015>
- 431 Bittar, T.B., Berger, S.A., Birsa, L.M., Walters, T.L., Thompson, M.E., Spencer, R.G., Mann, E.L.,
432 Stubbins, A., Frischer, M.E., Brandes, J.A., 2016. Seasonal dynamics of dissolved, particulate and
433 microbial components of a tidal saltmarsh-dominated estuary under contrasting levels of freshwater
434 discharge. *Estuar. Coast. Shelf. S.* 182, 72–85. <https://doi.org/10.1016/j.ecss.2016.08.046>
- 435 Bodrato, M., Vione, D., 2014. APEX (Aqueous Photochemistry of Environmentally occurring
436 Xenobiotics): a free software tool to predict the kinetics of photochemical processes in surface waters.
437 *Environ. Sci.: Processes Impacts* 16, 732–740. <https://doi.org/10.1039/C3EM00541K>
- 438 Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants
439 for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}\text{OH}/\text{O}^{\bullet-}$ in aqueous
440 solution. *J. Phys. Chem. Ref. Data* 17, 513–886. <https://doi.org/10.1063/1.555805>

- 441 Cai, L., Wang, J., Peng, J., Tan, Z., Zhan, Z., Tan, X., Chen, Q., 2017. Characteristic of microplastics
442 in the atmospheric fallout from Dongguan city, China: preliminary research and first evidence.
443 *Environ. Sci. Pollut. R.* 24, 24928–24935. <https://doi.org/10.1007/s11356-017-0116-x>
- 444 Calza, P., Vione, D., 2016. *Surface Water Photochemistry, Comprehensive Series in Photochemical*
445 *& Photobiological Sciences.* The Royal Society of Chemistry.
446 <https://doi.org/10.1039/9781782622154>
- 447 Chen, G., Feng, Q., Wang, J., 2020. Mini-review of microplastics in the atmosphere and their risks
448 to humans. *Sci. Total Environ.* 703, 135504. <https://doi.org/10.1016/j.scitotenv.2019.135504>
- 449 Chen, R.F., Bissett, P., Coble, P., Conmy, R., Gardner, G.B., Moran, M.A., Wang, X., Wells, M.L.,
450 Whelan, P., Zepp, R.G., 2004. Chromophoric dissolved organic matter (CDOM) source
451 characterization in the Louisiana Bight. *Mar. Chem.* 89, 257–272.
452 <https://doi.org/10.1016/j.marchem.2004.03.017>
- 453 Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation-
454 emission matrix spectroscopy. *Mar. Chem.* 51, 325–346. [https://doi.org/10.1016/0304-](https://doi.org/10.1016/0304-4203(95)00062-3)
455 [4203\(95\)00062-3](https://doi.org/10.1016/0304-4203(95)00062-3)
- 456 da Costa, J.P., Santos, P.S., Duarte, A.C., Rocha-Santos, T., 2016. (Nano) plastics in the
457 environment—sources, fates and effects. *Sci. Total Environ.* 566, 15–26.
458 <https://doi.org/10.1016/j.scitotenv.2016.05.041>
- 459 Davidson, M.R., Mitchell, S.A., Bradley, R.H., 2005. Surface studies of low molecular weight
460 photolysis products from UV-ozone oxidised polystyrene. *Surf. Sci.* 581, 169–177.
461 <https://doi.org/10.1016/j.susc.2005.02.049>
- 462 Dawson, A.L., Kawaguchi, S., King, C.K., Townsend, K.A., King, R., Huston, W.M., Nash, S.M.B.,
463 2018. Turning microplastics into nanoplastics through digestive fragmentation by Antarctic krill. *Nat.*
464 *Commun.* 9, 1001. <https://doi.org/10.1038/s41467-018-03465-9>
- 465 Deguillaume, L., Charbouillot, T., Joly, M., Vaïtilingom, M., Parazols, M., Marinoni, A., Amato, P.,
466 Delort, A.-M., Vinatier, V., Flossmann, A., Chaumerliac, N., Pichon, J.M., Houdier, S., Laj, P.,
467 Sellegri, K., Colomb, A., Brigante, M., Mailhot, G., 2014. Classification of clouds sampled at the puy
468 de Dôme (France) based on 10 yr of monitoring of their physicochemical properties. *Atmos. Chem.*
469 *Phys.* 14, 1485–1506. <https://doi.org/10.5194/acp-14-1485-2014>
- 470 Del Castillo, C.E., Coble, P.G., Morell, J.M., Lopez, J.M., Corredor, J.E., 1999. Analysis of the
471 optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy. *Mar.*
472 *Chem.* 66, 35–51. [https://doi.org/10.1016/S0304-4203\(99\)00023-7](https://doi.org/10.1016/S0304-4203(99)00023-7)
- 473 Dris, R., Gasperi, J., Mirande, C., Mandin, C., Guerrouache, M., Langlois, V., Tassin, B., 2017. A
474 first overview of textile fibers, including microplastics, in indoor and outdoor environments. *Environ.*
475 *Pollut.* 221, 453–458. <https://doi.org/10.1016/j.envpol.2016.12.013>
- 476 Dris, R., Gasperi, J., Rocher, V., Tassin, B., 2018. Synthetic and non-synthetic anthropogenic fibers
477 in a river under the impact of Paris Megacity: Sampling methodological aspects and flux estimations.
478 *Sci. Total Environ.* 618, 157–164. <https://doi.org/10.1016/j.scitotenv.2017.11.009>
- 479 Dris, R., Gasperi, J., Saad, M., Mirande, C., Tassin, B., 2016. Synthetic fibers in atmospheric fallout:
480 a source of microplastics in the environment? *Mar. Pollut. Bull.* 104, 290–293.
481 <https://doi.org/10.1016/j.marpolbul.2016.01.006>

482 Dubinenkov, I., Flerus, R., Schmitt-Kopplin, P., Kattner, G., Koch, B.P., 2015. Origin-specific
483 molecular signatures of dissolved organic matter in the Lena Delta. *Biogeochemistry* 123, 1–14.
484 <https://doi.org/10.1007/s10533-014-0049-0>

485 Ervens, B., 2015. Modeling the processing of aerosol and trace gases in clouds and fogs. *Chem. Rev.*
486 115, 4157–4198. <https://doi.org/10.1021/cr5005887>

487 Faust, B.C., 1994. Photochemistry of clouds, fogs, and aerosols. *Environ. Sci. Tech.* 28, 216A-222A.
488 <https://doi.org/10.1021/es00054a001>

489 Faust, B.C., Allen, J.M., 1993. Aqueous-phase photochemical formation of hydroxyl radical in
490 authentic cloudwaters and fogwaters. *Environ. Sci. Tech.* 27, 1221–1224.
491 <https://doi.org/10.1021/es00043a024>

492 Frias, J., Nash, R., 2019. Microplastics: Finding a consensus on the definition. *Mar. Pollut. Bull.* 138,
493 145–147. <https://doi.org/10.1016/j.marpolbul.2018.11.022>

494 Galgani, L., Engel, A., 2016. Changes in optical characteristics of surface microlayers hint to
495 photochemically and microbially mediated DOM turnover in the upwelling region off the coast of
496 Peru. *Biogeosciences* 13, 2453–2473. <https://doi.org/10.5194/bg-13-2453-2016>

497 Gallego-Urrea, J.A., Tuoriniemi, J., Pallander, T., Hassellöv, M., 2010. Measurements of
498 nanoparticle number concentrations and size distributions in contrasting aquatic environments using
499 nanoparticle tracking analysis. *Environ. Chem.* 7, 67. <https://doi.org/10.1071/EN09114>

500 Ganguly, M., Ariya, P.A., 2019. Ice nucleation of model nanoplastics and microplastics: a novel
501 synthetic protocol and the influence of particle capping at diverse atmospheric environments. *ACS*
502 *Earth Space Chem.* 3, 1729–1739. <https://doi.org/10.1021/acsearthspacechem.9b00132>

503 Gardette, J.-L., Mailhot, B., Lemaire, J., 1995. Photooxidation mechanisms of styrenic polymers.
504 *Polym. Degrad. Stabil.*, 48(3), 457–470. [https://doi.org/10.1016/0141-3910\(95\)00113-Z](https://doi.org/10.1016/0141-3910(95)00113-Z)

505 Gasperi, J., Wright, S.L., Dris, R., Collard, F., Mandin, C., Guerrouache, M., Langlois, V., Kelly,
506 F.J., Tassin, B., 2018. Microplastics in air: are we breathing it in? *Current Opinion in Environmental*
507 *Science & Health* 1, 1–5. <https://doi.org/10.1016/j.coesh.2017.10.002>

508 Gewert, B., Plassmann, M.M., MacLeod, M., 2015. Pathways for degradation of plastic polymers
509 floating in the marine environment. *Environ. Sci.: Processes Impacts* 17, 1513–1521.
510 <https://doi.org/10.1039/C5EM00207A>

511 Ghigo, G., Vione, D., Berto, S., 2019. Experimental and theoretical study of the fluorescence
512 emission of ferulic acid: Possible insights into the fluorescence properties of humic substances.
513 *Spectrochim. Acta A* 117587. <https://doi.org/10.1016/j.saa.2019.117587>

514 Gligorovski, S., Strekowski, R., Barbati, S., Vione, D., 2015. Environmental Implications of
515 Hydroxyl Radicals ($\cdot\text{OH}$). *Chem. Rev.* 115, 13051–13092. <https://doi.org/10.1021/cr500310b>

516 Gomiero, A. (Ed.), 2019. *Plastics in the Environment*. IntechOpen.
517 <https://doi.org/10.5772/intechopen.75849>

518 Göpferich, A., 1996. Mechanisms of polymer degradation and erosion. *Biomaterials* 17, 103–114.
519 [https://doi.org/10.1016/0142-9612\(96\)85755-3](https://doi.org/10.1016/0142-9612(96)85755-3)

- 520 Han, M., Niu, X., Tang, M., Zhang, B.-T., Wang, G., Yue, W., Kong, X., Zhu, J., 2019. Distribution
521 of microplastics in surface water of the lower Yellow River near estuary. *Sci. Total Environ.* 135601.
522 <https://doi.org/10.1016/j.scitotenv.2019.135601>
- 523 Herckes, P., Lee, T., Trenary, L., Kang, G., Chang, H., Collett, J.L., 2002. Organic matter in central
524 California radiation fogs. *Environ. Sci. Tech.* 36, 4777–4782. <https://doi.org/10.1021/es025889t>
- 525 Herckes, P., Valsaraj, K.T., Collett, J.L., 2013. A review of observations of organic matter in fogs
526 and clouds: Origin, processing and fate. *Atmos. Res.* 132–133, 434–449.
527 <https://doi.org/10.1016/j.atmosres.2013.06.005>
- 528 Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., Zellner, R., 2000. CAPRAM2.3:
529 A chemical aqueous phase radical mechanism for tropospheric chemistry. *J. Atmos. Chem.* 36, 231–
530 284. <https://doi.org/10.1023/A:1006318622743>
- 531 Holbrook, R.D., Yen, J.H., Grizzard, T.J., 2006. Characterizing natural organic material from the
532 Occoquan Watershed (Northern Virginia, US) using fluorescence spectroscopy and PARAFAC. *Sci.*
533 *Total Environ.* 361, 249–266. <https://doi.org/10.1016/j.scitotenv.2005.11.020>
- 534 Jeong, C.-B., Kang, H.-M., Lee, Y.H., Kim, M.-S., Lee, Jin-Sol, Seo, J.S., Wang, M., Lee, Jae-Seong,
535 2018. Nanoplastic ingestion enhances toxicity of persistent organic pollutants (POPs) in the
536 Monogonont Rotifer *Brachionus koreanus* via multixenobiotic resistance (MXR) disruption. *Environ.*
537 *Sci. Technol.* 52, 11411–11418. <https://doi.org/10.1021/acs.est.8b03211>
- 538 Kangasluoma, J., Attoui, M., Korhonen, F., Ahonen, L., Siivola, E., Petäjä, T., 2016. Characterization
539 of a Herrmann-type high-resolution differential mobility analyzer. *Aerosol Sci. Tech.* 50, 222–229.
540 <https://doi.org/10.1080/02786826.2016.1142065>
- 541 Klein, M., Fischer, E.K., 2019. Microplastic abundance in atmospheric deposition within the
542 Metropolitan area of Hamburg, Germany. *Sci. Total Environ.* 685, 96–103.
543 <https://doi.org/10.1016/j.scitotenv.2019.05.405>
- 544 Koelmans, A.A., Mohamed Nor, N.H., Hermsen, E., Kooi, M., Mintenig, S.M., De France, J., 2019.
545 Microplastics in freshwaters and drinking water: Critical review and assessment of data quality.
546 *Water Res.* 155, 410–422. <https://doi.org/10.1016/j.watres.2019.02.054>
- 547 Lallement, A., Vinatier, V., Brigante, M., Deguillaume, L., Delort, A.M., Mailhot, G., 2018. First
548 evaluation of the effect of microorganisms on steady state hydroxyl radical concentrations in
549 atmospheric waters. *Chemosphere* 212, 715–722.
550 <https://doi.org/10.1016/j.chemosphere.2018.08.128>
- 551 Lambert, S., Sinclair, C.J., Bradley, E.L., Boxall, A.B., 2013. Effects of environmental conditions on
552 latex degradation in aquatic systems. *Sci. Total Environ.* 447, 225–234.
553 <https://doi.org/10.1016/j.scitotenv.2012.12.067>
- 554 Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo,
555 S., Schwarz, A., Levivier, A., 2018. Evidence that the Great Pacific Garbage Patch is rapidly
556 accumulating plastic. *Sci. Rep.* 8, 4666. <https://doi.org/10.1038/s41598-018-22939-w>
- 557 Lee, W.S., Cho, H.-J., Kim, E., Huh, Y.H., Kim, H.-J., Kim, B., Kang, T., Lee, J.-S., Jeong, J., 2019.
558 Bioaccumulation of polystyrene nanoplastics and their effect on the toxicity of Au ions in zebrafish
559 embryos. *Nanoscale* 11, 3173–3185. <https://doi.org/10.1039/C8NR09321K>

- 560 Lehner, R., Weder, C., Petri-Fink, A., Rothen-Rutishauser, B., 2019. Emergence of nanoplastic in the
561 environment and possible impact on human health. *Environ. Sci. Technol.* 53, 1748–1765.
562 <https://doi.org/10.1021/acs.est.8b05512>
- 563 Li, C., Busquets, R., Campos, L.C., 2019. Assessment of microplastics in freshwater systems: A
564 review. *Sci. Total Environ.* 135578. <https://doi.org/10.1016/j.scitotenv.2019.135578>
- 565 Li, Y., Barth, M.C., Patton, E.G., Steiner, A.L., 2017. Impact of In-Cloud Aqueous Processes on the
566 Chemistry and Transport of Biogenic Volatile Organic Compounds: Impact of In-Cloud Processes
567 on BVOC. *J. Geophys. Res. Atmos.* 122, 11,131–11,153. <https://doi.org/10.1002/2017JD026688>
- 568 Liu, K., Wu, T., Wang, X., Song, Z., Zong, C., Wei, N., Li, D., 2019. Consistent Transport of
569 Terrestrial Microplastics to the Ocean through Atmosphere. *Environ. Sci. Technol.* 53, 10612–10619.
570 <https://doi.org/10.1021/acs.est.9b03427>
- 571 Massicotte, P., Asmala, E., Stedmon, C., Markager, S., 2017. Global distribution of dissolved organic
572 matter along the aquatic continuum: Across rivers, lakes and oceans. *Sci. Total Environ.* 609, 180–
573 191. <https://doi.org/10.1016/j.scitotenv.2017.07.076>
- 574 Mattsson, K., Jovic, S., Doverbratt, I., Hansson, L.-A., 2018. Nanoplastics in the aquatic environment,
575 in: *Microplastic Contamination in Aquatic Environments*. Elsevier, pp. 379–399.
576 <https://doi.org/10.1016/B978-0-12-813747-5.00013-8>
- 577 Mintenig, S.M., Bäuerlein, P.S., Koelmans, A.A., Dekker, S.C., van Wezel, A.P., 2018. Closing the
578 gap between small and smaller: towards a framework to analyse nano- and microplastics in aqueous
579 environmental samples. *Environ. Sci.: Nano* 5, 1640–1649. <https://doi.org/10.1039/C8EN00186C>
- 580 Mopper, K., Zhou, X., 1990. Hydroxyl radical photoproduction in the sea and its potential impact on
581 marine processes. *Science* 250, 661–664. <https://doi.org/10.1126/science.250.4981.661>
- 582 Mouchel-Vallon, C., Deguillaume, L., Monod, A., Perroux, H., Rose, C., Ghigo, G., Long, Y.,
583 Leriche, M., Aumont, B., Patryl, L., Armand, P., Chaumerliac, N., 2017. CLEPS 1.0: A new protocol
584 for cloud aqueous phase oxidation of VOC mechanisms. *Geosci. Model Dev.* 10, 1339–1362.
585 <https://doi.org/10.5194/gmd-10-1339-2017>
- 586 Muller, C.L., Baker, A., Hutchinson, R., Fairchild, I.J., Kidd, C., 2008. Analysis of rainwater
587 dissolved organic carbon compounds using fluorescence spectrophotometry. *Atmos. Environ.* 42,
588 8036–8045. <https://doi.org/10.1016/j.atmosenv.2008.06.042>
- 589 Neta, P., Dorfman, L.M., 1968. Pulse radiolysis studies. XIII. Rate constants for the reaction of
590 hydroxyl radicals with aromatic compounds in aqueous solutions, *Radiation Chem.* 81, 222–230.
591 <https://doi.org/10.1021/ba-1968-0081.ch015>
- 592 O’Brine, T., Thompson, R.C., 2010. Degradation of plastic carrier bags in the marine environment.
593 *Mar. Pollut. Bull.* 60, 2279–2283. <https://doi.org/10.1016/j.marpolbul.2010.08.005>
- 594 Olasehinde, E.F., 2012. Determination of hydroxyl radical in Seto inland sea and its potential to
595 degrade irgarol. *IOSRJAC* 1, 07–14. <https://doi.org/10.9790/5736-0150714>
- 596 Passananti, M., Zapadinsky, E., Zanca, T., Kangasluoma, J., Myllys, N., Rissanen, M.P., Kurtén, T.,
597 Ehn, M., Attoui, M., Vehkamäki, H., 2019. How well can we predict cluster fragmentation inside a
598 mass spectrometer? *Chem. Commun.* 55, 5946–5949. <https://doi.org/10.1039/C9CC02896J>

- 599 PlasticsEurope, 2019. Plastics the facts - 2018. Retrieved from
600 <https://www.plasticseurope.org/en/resources/publications/619-plastics-facts-2018>
- 601 Scheurer, M., Bigalke, M., 2018. Microplastics in Swiss floodplain soils. *Environ. Sci. Technol.* 52,
602 3591–3598. <https://doi.org/10.1021/acs.est.7b06003>
- 603 Schwaferts, C., Niessner, R., Elsner, M., Ivleva, N.P., 2019. Methods for the analysis of
604 submicrometer- and nanoplastic particles in the environment. *TrAC Trend Anal. Chem.* 112, 52–65.
605 <https://doi.org/10.1016/j.trac.2018.12.014>
- 606 Singh, B., Sharma, N., 2008. Mechanistic implications of plastic degradation. *Polym. Degrad. Stabil.*
607 93, 561–584. <https://doi.org/10.1016/j.polymdegradstab.2007.11.008>
- 608 Stedmon, C.A., Cory, R.M., 2014. Biological origins and fate of fluorescent dissolved organic matter
609 in aquatic environments. *Aquatic organic matter fluorescence* 278–299.
610 <https://doi.org/10.1017/CBO9781139045452.013>
- 611 Ter Halle, A., Jeanneau, L., Martignac, M., Jardé, E., Pedrono, B., Brach, L., Gigault, J., 2017.
612 Nanoplastic in the North Atlantic Subtropical Gyre. *Environ. Sci. Technol.* 51, 23, 13689-13697.
- 613 Todd, P.A., Ong, X., Chou, L.M., 2010. Impacts of pollution on marine life in Southeast Asia.
614 *Biodivers. Conserv.* 19, 1063–1082. <https://doi.org/10.1007/s10531-010-9778-0>
- 615 van Pinxteren, D., Fomba, K.W., Mertes, S., Müller, K., Spindler, G., Schneider, J., Lee, T., Collett,
616 J.L., Herrmann, H., 2016. Cloud water composition during HCCT-2010: Scavenging efficiencies,
617 solute concentrations, and droplet size dependence of inorganic ions and dissolved organic carbon.
618 *Atmos. Chem. Phys.* 16, 3185–3205. <https://doi.org/10.5194/acp-16-3185-2016>
- 619 Vicente, J.S., Gejo, J.L., Rothenbacher, S., Sarojiniamma, S., Gogritchiani, E., Wörner, M., Kasper,
620 G., Braun, A.M., 2009. Oxidation of polystyrene aerosols by VUV-photolysis and/or ozone.
621 *Photochem. Photobiol. Sci.* 8, 944. <https://doi.org/10.1039/b902749a>
- 622 Vione, D., Bagnus, D., Maurino, V., Minero, C., 2010. Quantification of singlet oxygen and hydroxyl
623 radicals upon UV irradiation of surface water. *Environ. Chem. Lett.* 8, 193–198.
624 <https://doi.org/10.1007/s10311-009-0208-z>
- 625 Weir, N.A., 1978. Reactions of hydroxyl radicals with polystyrene. *Eur. Polym. J.* 14, 9–14.
626 [https://doi.org/10.1016/0014-3057\(78\)90144-1](https://doi.org/10.1016/0014-3057(78)90144-1)
- 627 Wetzel, R.G., 2001. *Limnology: lake and river ecosystems.* gulf professional publishing.
- 628 Xu, S., Ma, J., Ji, R., Pan, K., Miao, A.-J., 2020. Microplastics in aquatic environments: Occurrence,
629 accumulation, and biological effects. *Sci. Total Environ.* 703, 134699.
630 <https://doi.org/10.1016/j.scitotenv.2019.134699>
- 631 Yang, R., He, Q., Wang, C., Sun, S., 2018. Surface modification of polystyrene microsphere using
632 ozone treatment. *Ferroelectrics* 530, 130–135. <https://doi.org/10.1080/00150193.2018.1453200>
- 633 Yonkos, L.T., Friedel, E.A., Perez-Reyes, A.C., Ghosal, S., Arthur, C.D., 2014. Microplastics in four
634 estuarine rivers in the Chesapeake Bay, U.S.A. *Environ. Sci. Technol.* 48, 14195–14202.
635 <https://doi.org/10.1021/es5036317>
- 636 Yousif, E., Haddad, R., 2013. Photodegradation and photostabilization of polymers, especially
637 polystyrene: review. *SpringerPlus* 2, 398. <https://doi.org/10.1186/2193-1801-2-398>

- 638 Zhang, D., Dougal, S., Yeganeh, M., 2000. Effects of UV irradiation and plasma treatment on a
639 polystyrene surface studied by IR– visible sum frequency generation spectroscopy. *Langmuir* 16,
640 4528–4532. <https://doi.org/10.1021/la991353i>
- 641 Zhou, X., Mopper, K., 1990. Determination of photochemically produced hydroxyl radicals in
642 seawater and freshwater. *Mar. Chem.* 30, 71–88. [https://doi.org/10.1016/0304-4203\(90\)90062-H](https://doi.org/10.1016/0304-4203(90)90062-H)