



HAL
open science

Photodegradation of disposable polypropylene face masks: Physicochemical properties of debris and implications for the toxicity of mask-carried river biofilms

Isabelle Bihannic, Renaud Gley, Lucas Gallo, Apolline Badura, Angelina Razafitianamaharavo, Maximilien Beuret, David Billet, Clément Bojic, Céline Caillet, Philippine Morlot, et al.

► To cite this version:

Isabelle Bihannic, Renaud Gley, Lucas Gallo, Apolline Badura, Angelina Razafitianamaharavo, et al.. Photodegradation of disposable polypropylene face masks: Physicochemical properties of debris and implications for the toxicity of mask-carried river biofilms. *Journal of Hazardous Materials*, 2024, 465, pp.133067. 10.1016/j.jhazmat.2023.133067 . hal-04693545

HAL Id: hal-04693545

<https://hal.univ-lorraine.fr/hal-04693545v1>

Submitted on 10 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1 **Photodegradation of disposable polypropylene face masks: physicochemical properties of**
2 **debris and implications for the toxicity of mask-carried river biofilms**

3
4 Isabelle Bihannic,^{a,*} Renaud Gley,^a Lucas Gallo,^a Apolline Badura,^a Angelina Razafitianamaharavo,^a
5 Maximilien Beuret,^b David Billet,^a Clément Bojic,^b Céline Caillet,^a Philippine Morlot,^b Marie Zaffino,^b
6 Fatina Jouni,^b Béatrice George,^c Pascal Boulet,^d Camille Noûs,^e Michael Danger,^b Vincent Felten,^b
7 Christophe Pagnout,^b Jérôme F.L. Duval^{a,*}
8

9 a. Université de Lorraine, CNRS, LIEC, F-54000 Nancy, France.

10 b. Université de Lorraine, CNRS, LIEC, F-57000 Metz, France.

11 c. Université de Lorraine, INRAE, LERMAB, F-54000 Nancy, France.

12 d. Université de Lorraine, CNRS, IJL, F-54000 Nancy, France.

13 e. Cogitamus Laboratory, Paris, France.

14 * Corresponding authors. Email: isabelle.bihannic@univ-lorraine.fr, jerome.duval@univ-lorraine.fr

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35 **Abstract.**

36 COVID-19 outbreak led to a massive dissemination of protective polypropylene (PP) face masks in the
37 environment, posing a new environmental risk amplified by mask photodegradation and
38 fragmentation. Masks are made up of a several kilometres long-network of fibres with diameter from
39 a few microns to around 20 microns. After photodegradation, these fibres disintegrate, producing
40 water dispersible debris. Electrokinetics and particle stability observations support that
41 photodegradation increases/decreases the charge/hydrophobicity of released colloidal fragments.
42 This change in hydrophobicity is related to the production of UV-induced carbonyl and hydroxyl
43 reactive groups detectable after a few days of exposure. Helical content, surface roughness and
44 specific surface area of mask fibres are not significantly impacted by photodegradation. Fragmentation
45 of fibres makes apparent, at the newly formed surfaces, otherwise-buried additives like TiO₂
46 nanoparticles and various organic components. Mortality of gammarids is found to increase
47 significantly over time when fed with 3 days-UV aged masks that carry biofilms grown in river, which
48 is due to a decreased abundance of microphyte therein. In contrast, bacteria abundance and microbial
49 community composition remain unchanged regardless of mask degradation. Overall, this work reports
50 physicochemical properties of pristine and photodegraded masks, and ecosystemic functions and
51 ecotoxicity of freshwater biofilms they can carry.

52

53 **Keywords.** Polypropylene, Micro/nanoplastics, Freshwater biofilms, Algae, Gammarids mortality.

54 **Environmental Implication.**

55 As a legacy of COVID-19 pandemic, environments inherited new hazardous materials: polypropylene-
56 based face masks and their secondary products generated by degradation. Scrutiny of their eco-
57 impacts requires addressing how photodegradation -a dominant mask alteration process- mediates
58 the interplay between physicochemical properties of masks (structure, composition and colloidal
59 features of released debris) and their reactivity towards biota, in particular their colonization by
60 freshwater biofilms and ensuing effects on consumers. Following a multiscale physicochemical
61 approach in combination with ecotoxicity assays and onsite biofilm monitoring, this work sheds light
62 on the photodegradation-induced properties and reactivity of masks under environmentally relevant
63 conditions.

64

65

66

67

68

69

70

71

72

73

74

75 **1. Introduction.**

76 At a time when governments are legislating against the consumption of single-use plastic items,
77 measures adopted to counteract the spread of COVID-19 pandemic led to a dramatic surge of plastic
78 materials in our everyday life, in the form of packaging for protection purpose and personal protective
79 equipment (PPE) like gloves and masks (Benson et al., 2021; Prata et al., 2020). As a result, the global
80 daily production of masks - 90% of which are composed of polypropylene - was marked by a
81 spectacular 30-fold increase from 2019 to 2020-2021, with 1 billion units per day (Prata et al., 2020;
82 STATISTA, 2022). This massive production is not only explained by the needs to protect healthcare
83 workers, but also by the recommendations and obligations formulated towards the society to wear
84 masks in public places, medical centres and transports (Patrício Silva et al., 2020; WHO, 2021). The
85 large use of personal protective equipment by the population is a new societal phenomenon, and it
86 has now become a source of concern to treat and manage masks-related wastes beyond the
87 specialized channels of the medical sector. The heavy constraints on waste collection channels, the
88 overflow of treatment facilities and the behaviour of some consumers are all components of
89 mismanagement of wastes and of their ensuing dispersion in e.g. rainwater, sewage networks, and
90 natural environments (Ammendolia et al., 2021; Aragaw, 2020; Benson et al., 2021; Parashar and Hait,
91 2021; Prata et al., 2020). Realizing that most of the wastes ending up in oceans originates from a poor
92 management, it is estimated that between 0.15 and 0.39 million tons of mask debris could end up in
93 the global oceans on a yearly basis (Chowdhury et al., 2021). Noteworthy, whereas people were
94 encouraged to wear face masks to avoid COVID-19 dissemination, a study highlighted recently the
95 need to study long-term human-health risks associated with use of such protective equipment because
96 face masks were evidenced to release fine particles and various (semi)volatile organic compounds (Guo
97 et al., 2023).

98 The question then arises as whether the presence of masks in the environment can be assimilated
99 to that of other 'conventional' plastic wastes. The answer is probably no, and masks along with their
100 degradation products require a special attention for several reasons. Firstly, the general public in its
101 majority does not necessarily know that masks and other disposable wet wipes do not degrade in the
102 environment as easily as other cellulose-based materials would (Hu et al., 2022). Secondly, masks
103 consist of fibres that are a few microns in diameter, which makes easier their breaking and
104 fragmentation into micron-sized debris compared to other massive plastic objects. Another defining
105 characteristic of masks is their large surface area, with strong implications in terms of e.g. adsorption
106 of pollutants like metals or organics. Ma et al. (2022) reported that the surface area of a single mask is
107 of the order of 1.4 m², which is 14 times larger than that of a 500 mL plastic bottle. In addition, based
108 on mask fibre nature and size (cf. Ma et al. (2022)), PP density characteristics and considering a typical
109 mass of a few grams for a mask (Saliu et al., 2021), it is easily estimated that the overall length of the
110 fibres contained in the inner and outer layers of 3-ply masks can exceed a few kilometres and that it
111 may even reach several hundred kilometres for the middle layer. Another important issue to consider
112 when addressing the impact of masks dispersion and debris is the large spectrum of contaminants they
113 can accumulate depending on places where degradation is operative, e.g. landfills, urban surfaces
114 (sidewalks, gutters, parking lots) or road areas (Men et al., 2018).

115 Degradation of masks in the environment proceeds according to common plastic weathering
116 processes, i.e. mechanical abrasion caused by wind and/or wave actions, UV radiation, oxidation in
117 humid environments, or sea salinity-induced effects (Andrady, 2017; Gigault et al., 2018; Lambert and
118 Wagner, 2016). For polyolefins (polyethylene and polypropylene), the most abundant polymers in

119 oceanic and freshwater environments, it is the action of solar UV that initiates photodegradation
120 (Andrady, 2017), leading to material oxidation and breaking of polymer chains preferentially in
121 amorphous areas. In turn, defects and cracks are produced, which favours fragmentation and the
122 production of daughter particles. The generated fragments are qualified as secondary microplastics or
123 nanoplastics if their size is below the micron scale (Gigault et al., 2018; Lambert and Wagner, 2016).
124 Chemical modifications associated with photodegradation are accompanied by changes of the physical
125 material properties, which includes size, porosity, density, crystallinity rate, surface charge or
126 hydrophobicity. These properties further govern the reactivity of neo-formed colloidal particles (e.g.
127 aggregation, buoyancy, etc.) and their interactions with aquatic organisms (Lambert et al., 2017). In
128 literature, analyses of masks degradation consist generally in counting and characterizing debris
129 spread by masks that were subjected to different ageing protocols intended to mimic environmental
130 conditions, e.g. mechanical abrasion under dry conditions (Morgana et al., 2021), in fresh or salt water
131 (Rathinamoorthy and Balasaraswathi, 2022), in the presence or not of sediments (Wang et al., 2021;
132 Wu et al., 2022), following a first natural (Rathinamoorthy and Balasaraswathi, 2022) or artificial (Liu
133 et al., 2022; Saliu et al., 2021) photodegradation step. All studies evidence the production of fibres and
134 micro-fragments, in line with mask structure and literature results on polyolefin. Literature further
135 suggests that photodegradation is the process that impacts most significantly the integrity of masks,
136 with severe changes of their mechanical properties, modifications of their chemical groups (Liu et al.,
137 2022) and increase of their hydrophilicity (Wang et al., 2021). We emphasize that, in literature, the
138 signatures of chemical alterations of masks following photodegradation were found similar under
139 natural and artificial conditions (Saliu et al., 2021).

140 Due to their size, nano- and microplastics - regardless of their origin (conventional wastes or
141 masks) - can be easily ingested by many living species. The adhesion of nanoparticles on the surface of
142 primary producers like microalgae has also been evidenced (Wright et al., 2020), together with their
143 entry in the food chain (Chae et al., 2018). Whereas excretion processes may mitigate the extent to
144 which some invertebrates accumulate plastics (Mateos-Cárdenas et al., 2020), impacts on their health
145 have been reported, e.g. loss of mass, decreased growth and fertility, decreased mobility and/or
146 increased mortality (Wright et al., 2013). The reasons for such adverse effects of plastics remain poorly
147 understood, and various hypotheses have been formulated, i.e. false feeling of satiety, decreased
148 ability to assimilate food due to dilution of available nutrients, or presence of lesions on- and
149 inflammation of- the walls of digestive systems (Au et al., 2015; Blarer and Burkhardt-Holm, 2016). The
150 response of organisms to plastics and residues thereof is most significant for fibrous shaped-particles
151 due to the longer residence of these plastic fragments in the intestinal tract (Ogonowski et al., 2016),
152 which disrupts severely cell metabolism and affects organism ability to process food (Au et al., 2015;
153 Blarer and Burkhardt-Holm, 2016; Qiao et al., 2019). Toxicity of ingested microplastics may result from
154 the action of their constitutive contaminants or the chemicals they carry, i.e. additives, catalysis
155 residues, fillers (Oehlmann et al., 2009), or adsorbed pollutants (Felten et al., 2020).

156 To the best of our knowledge, most reports on nanoplastics have focused so far on polystyrene
157 (PS) (Ferreira et al., 2019), whereas polypropylene (PP)-based materials like face masks received less
158 attention despite of their abundance in the field (de Sá et al., 2018). This lack of studies on PP effects
159 is partly explained by the large hydrophobicity of PP particles, which renders difficult their dispersion
160 in aqueous medium, an issue that is often solved with the recourse to stabilizing surfactant agents of
161 poor environmental relevance. There is however a strong connection between hydrophobicity of PP
162 particles and their affinity to apolar contaminants, as illustrated by Rochman et al. (2013) who

163 evidenced large accumulation of polyaromatic hydrocarbons (PAH) et polychlorinated biphenyls (PCB)
164 on PP particles under marine conditions. These elements advocate for further studies on PP plastic
165 type, like surgical masks of central interest in this work. In addition, whereas studies have documented
166 processes driving the degradation and release of PP masks debris, few of them comprehensively
167 reported (i) the colloidal properties of these debris in terms of electrostatic charge, size and stability,
168 (ii) how these properties are connected to conventional physicochemical descriptors of microplastic
169 degradation evaluated by common microscopy and spectroscopy techniques, and (iii) whether or not
170 ageing increases masks reactivity towards biota (toxicity issue). The assessment of surface features of
171 released mask debris is also of particular interest not only because these debris develop a reactive
172 surface area larger than that of conventional plastic waste, but also because they impact significantly
173 on the fate, bioavailability and toxicity of aquatic contaminants like metals and organics and may act
174 themselves as pollutants.

175 Accordingly, we report here a thorough characterization of the three layers composing disposable
176 face masks using a suite of dedicated physicochemical techniques, from the molecular, colloidal to
177 macroscopic scale. The physical, chemical and morphological information collected as a function of
178 photodegradation treatment (mimicking solar degradation) are then discussed and compared with
179 measured colloidal properties of released debris. A striking result inferred from this multi-technique
180 assessment of mask degradation is that charged masks debris feature a moderate dependence of their
181 colloidal features on duration of mask photodegradation. This contrasts with the marked macroscopic
182 alteration of masks when exposed to UV radiation. Results therefore contradict the intuition according
183 to which reactivity of debris generated by mask photodegradation is all the more important as UV
184 exposure and macroscopic modification of mask properties are significant. We further address and
185 discuss the extent to which physicochemical properties of aged masks, evaluated here across spatial
186 and time scales, are relevant for defining (i) their capacity to host biofilm in freshwaters (Moselle River,
187 Lorraine) and (ii) hazardous effects on the opportunist detritivore *Gammarus roeselii*. In detail, the
188 objectives of this work are:

- 189 • **(a)** to address the physical-chemical properties of photodegraded masks - from the macroscopic
190 down to the molecular scale and from the massive material to the generated colloidal debris - using a
191 large spectrum of techniques (FTIR, AFM, DRX, elemental analysis, WAXS, SEM-EDS, electrokinetics,
192 confocal imaging, gas adsorption, granulometry) detailed below. The analysis is performed for each
193 constitutive polypropylene mask layer as a function of UV-exposure duration.
- 194 • **(b)** to analyze whether or not UV-mediated degradation of masks (and of their constitutive layers) -
195 as specifically analysed in **(a)** - impacts the composition of biofilms grown on these masks once
196 immersed in freshwater (here The Moselle River, France). The analysis is performed via examining the
197 abundance and diversity of organisms found in river-biofilms grown on pristine, 1 day- and 3 days-aged
198 masks, with the UV-aging process being realized prior to the immersion of masks in the river (cf. **(a)**).
- 199 • **(c)** to evaluate the toxicity of biofilms grown on undegraded and degraded masks (those biofilms are
200 specifically generated and analysed in **(b)**) towards the opportunist detritivore gammarids *Gammarus*
201 *roeselii*. The purpose is here to figure out the extent to which the river-biofilms (serving as food for
202 gammarids) carried by the pristine and aged masks impact the survival of gammarids, i.e. whether or
203 not mask aging process (and related biofilm composition, cf. **(b)**) leads/contributes to gammarids
204 mortality.
205

206

207 **2. Materials and methods.**

208 **2.1. Materials and photodegradation.**

209 Disposable 3-ply surgical blue masks of the brand TD® Tidy Professional were made available by
210 the French Ministry of Research and Education. These masks of type II (according to the EN14683
211 standard) are composed of three polypropylene (PP) layers. The white inner and blue outer layers
212 (hereafter denoted as IL and OL, respectively) consist of spun-bound non-woven fabric, with 25 g/m²
213 and 18 g/m² weights, respectively. The intermediate or middle PP layer (ML in short) is made of white
214 meltblown fabric (20 g/m²).

215 Samples were subjected to ageing for 0, 1, 2, 3 and 28 days in a QUV tester (Q-Lab, USA) equipped
216 with UV-A 340 lamps delivering an irradiation of 0.68 W/m²/nm. In this work, we selected the 'Standard
217 practice for fluorescent UV exposure of plastics' (ASTM-D4329) to perform mask aging following Cycle
218 A of that standard. Each Cycle A of 12 hours consisted in a first UV exposure period of 8 hours at 60°C,
219 followed by a 4 hours condensation period in dark at 50°C. Prior to exposure, mask ties and nose
220 bridges were removed, and test specimen were cut into 14 cm×8 cm pieces. Exposed surface of the
221 layers was 6 cm×9 cm. After the UV-exposure period, masks were disassembled and layers were sorted
222 according to their IL, OL and ML origin. Subsequently, layers were stored in dark at 15°C prior to further
223 analysis. The nomenclature adopted to name analysed samples was defined according to: name of the
224 layer (IL, OL or ML) followed by UV exposure duration, e.g. IL28d stands for inner mask layer exposed
225 to UV for 28 days. Pristine samples, i.e. samples that were not subjected to UV treatment, were named
226 ILp, OLp or MLp.

227

228 **2.2. Physicochemical methods for characterization of mask material.**

229 **Chemical elemental analysis.** Pristine samples were characterized in terms of their elemental
230 composition of inorganics by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Pristine masks
231 were analysed by the SARM laboratory (Service d'Analyse des Roches et des Minéraux, Nancy, France)
232 using an ICP-MS iCapQ instrument. Samples were prepared by microwave-assisted acid digestion in
233 quartz vessels using HNO₃-H₂O₂ solutions, following a procedure adapted from Muller et al. (2016) and
234 Pereira et al. (2016). We placed 80 to 100 mg of mask layer material in a quartz vessel containing 1 mL
235 (30% concentrated) H₂O₂-2 ml (65% or 14 M) HNO₃ mixture. This mixture was then positioned in a
236 microwave digestion chamber (UltraWAVE ECR by Milestone). Digestion was conducted under
237 maximal N₂-pressure of 60 bars at 240 °C temperature.

238 **Wide Angle X-ray Scattering (WAXS).** In order to derive information on phase composition and degree
239 of masks crystallinity depending on photodegradation level, WAXS data were collected on a Bruker
240 Kappa Apex II diffractometer equipped with a mirror monochromator and a Cu K α microsource
241 ($\lambda=1.5406$ Å). Measurements were recorded in transmission mode on a two-dimensional detector
242 placed at a 0.065 m distance from the samples. The reader is referred to **Appendix A** for details on
243 data acquisition, evaluation and analysis of WAXS diffractions curves. Following a procedure available
244 elsewhere (Goikhman et al., 1984; Isasi et al., 1999; Kotek et al., 2004; Lima et al., 2002), for each
245 analysed sample we estimated a crystalline index (denoted as Cl_x) defined by the ratio between area
246 under the peaks corresponding to all crystalline phases and total area under the entire WAXS curve.

247 **Fourier Transform Infrared spectroscopy (FTIR).** To get insight into chemical composition of pristine
248 and photodegraded mask materials, FTIR spectra were collected using a BRUKER VECTOR 22
249 spectrophotometer operated in transmission mode between 400 and 4000 cm⁻¹ with 4 cm⁻¹ resolution.
250 Fifty scans were averaged per spectrum. The reader is referred to **Appendix A** for details on samples
251 preparation. Effects of sample oxidation due to UV treatment were monitored according to the
252 procedure by Almond et al. (2020). Namely, we evaluated a carbonyl index, denoted as Cal_{IR} and
253 defined by the ratio between band areas corresponding to C=O carbonyl group (1850 to 1650 cm⁻¹)

254 and methylene group (1500 to 1420 cm^{-1}). Prior to signal integration, linear baseline was subtracted
255 from the signal in the 2000 to 740 cm^{-1} range. The helical content, denoted as HC_{IR} , was further derived
256 from FTIR data after proper baseline correction (Hughes, 1969). HC_{IR} corresponds to the ratio between
257 absorbances measured at 998 cm^{-1} and 973 cm^{-1} and it reflects the extent of polymer ordering, i.e. the
258 amount of chains with helical conformation found in the isotactic domains (Blais et al., 1972; Luongo,
259 1960).

260 **Scanning electron microscopy (SEM).** Pieces of masks were imaged on a TESCAN VEGA scanning
261 electron microscope (SEM) operating at 10 kV voltage. SEM set up was coupled to a Bruker XFlash6®
262 30 mm^2 EDS detector for energy dispersive X-ray spectroscopy (EDS) measurements. Square pieces
263 were cut from materials with sufficient mechanical cohesion (relevant to pristine mask layers, to IL3d
264 and OL3d samples). These pieces were then fixed with double-sided carbon tape on metallic sample
265 holders. For most degraded samples, tape covered pads were dipped into powder of mask debris and
266 cleaned gently with pressurized air to remove non-adhered materials.

267 **Gas adsorption.** The specific surface areas (SSA) of the pristine and 28 days-exposed masks were
268 determined from krypton adsorption-desorption isotherms measured at 77K on a BELSORP-max II
269 instrument (MicrotracBEL Corp.) following a step-by-step point acquisition method. The reader is
270 referred to **Appendix A** for details on measurement procedure and evaluation of SSA using Brunauer-
271 Emmet-Teller (BET) equation (Brunauer et al., 1938).

272 **Atomic Force Microscopy (AFM).** To address surface topography of mask samples, AFM experiments
273 were performed on a FastScan Dimension Icon equipped with a Nanoscope V controller (Bruker). AFM
274 imaging was carried out using contact mode at ambient temperature in air. The reader is referred to
275 **Appendix A** for details on samples preparation and adopted AFM probes. Surface roughness of fibres
276 was estimated on XY images using Bruker NanoScope Analysis software (version 1.9). Roughness
277 calculations were based on the entire images of the upper surface of cylinders laid lengthwise on the
278 support. As fibres featured curved surfaces, flattening procedure was applied before roughness
279 estimation. The entire images we considered for roughness evaluation consisted of 5-micron squares
280 for the inner and outer layers and 2-micron squares for the middle one. All squares were 256 by 256
281 pixels. Two parameters defining roughness were computed: R_a and R_q that correspond to the
282 arithmetic average of profile height deviations from mean surface, and the root mean square of these
283 deviations, respectively. For the inner pristine layer, R_a and R_q were calculated on the basis of a single
284 image. For the other layers analysed and conditions investigated, R_a and R_q calculations correspond to
285 an average over two or three images.

286 **Electrokinetics (electrophoresis).** To address electrostatic properties of masks debris, their
287 electrophoretic mobility (μ) was measured by micro-electrophoresis instrument (Zetaphoremeter IV,
288 CAD Instrumentations, Les Essarts le Roi, France) in a quartz cell at 24°C as a function of salinity and
289 pH of electrolyte solution, cf. details in **Appendix A**. The technique consists in measuring the velocity
290 of charged particles suspended in an electrolyte solution under applied electric field condition (800 V
291 m^{-1}). Displacements were converted into electrophoretic mobility with CAD image analysis software.
292 Mask debris were dispersed in a 'very soft' water (cf. details in **Appendix A**) at final 0.225 g L^{-1}
293 concentration. Conversion of μ into zeta-potential value requires application of available theories
294 whose validity domains strongly depend on particle size and charge, particle nature (i.e. permeable or
295 not to ions and/or electroosmotic flow developed under electrophoresis measuring conditions) and
296 electrolyte concentration (cf. recent review by Gopmandal et al. (2022)). Accordingly, we did not
297 proceed here to such a conversion.

298

299 **Granulometry.** After measurement of electrokinetic properties, particle size distributions were
300 evaluated by laser diffraction granulometry (Malvern Panalytical Mastersizer 3000 instrument). For
301 that purpose, 80 mL of the suspensions used for electrophoresis were dispersed in the very soft water
302 medium described in **Appendix A** to reach a final volume of 400 mL. Size distributions were then
303 evaluated from average of 3 measurements of ten seconds duration each. As investigated particles
304 were anisometric, number- rather than volume-distributions were reported.

305 **Confocal scanning laser microscopy.** To visualize fibres of pristine and photodegraded masks in three
306 dimensions on the basis of their defining fluorescence properties, we used confocal scanning laser
307 microscopy (CLSM). CLSM images were recorded on a ZEISS Axio observer 7 microscope, equipped with
308 a scanning head LSM 880. Pristine samples and 28 days UV exposed samples were placed in glass
309 bottom dishes for visualization. Images of autofluorescence were recorded using a 561-nm diode laser
310 for excitation. Emitted fluorescence was detected in the 570 to 694 nm wavelength range.

311 **2.3. Formation of river-biofilms on pristine and photodegraded masks.**

312 **Experimental setup and sample collection.** Pristine masks and masks photodegraded for 1 or 3 days
313 (termed 1d and 3d masks, respectively) were placed in the Moselle River (49.282881 N 6.187556 E -
314 Lorraine, France) for biofilm colonization. To that end, masks were maintained between two
315 transparent polymethyl methacrylate sheets with an opening in the upper sheet to allow mask
316 colonization by microorganisms. The experimental device was weighted and immersed horizontally at
317 the edge of the river at a depth of ca. 1 m (**Appendix B, Figure B.1**). Masks were collected on May 19th,
318 2021 after 4 weeks immersion. They were gently rinsed with sterilized water to remove non-adherent
319 microorganisms and transferred to laboratory for analyses. Depending on planned experiments,
320 samples were either used freshly or stored at -20°C. On the same experimental site, alder leaves
321 (*Aulus Glutinosa* (L.)) were also conditioned by microorganisms for 10 days and served as controls of
322 the experiments involving gammarids (cf. details below). A period of 4 weeks was selected for the
323 immersion of masks for two main reasons: (i) the low microbial density typical of water column in
324 Moselle River at the spring season, and (ii) the need to have a sufficient microbial biomass on masks
325 so as to support toxicological experiments involving gammarids.

326 **DNA extraction.** Frozen masks were cut according to 1 cm diameter discs with a cork borer. Discs were
327 then placed in a 2 mL tube and cut with scissors into small pieces for DNA extraction. DNA was
328 extracted using the PowerSoil DNA Isolation Kit (MOBIO Laboratories, Carlsbad, CA) according to
329 manufacturer's recommendations. The total amount and purity of DNA were determined by
330 spectrometry at 260 nm and 230 nm using a NanoDrop spectrophotometer.

331 **16S rRNA gene quantification.** The abundance of bacterial 16S rRNA genes was estimated by qPCR
332 using primers 968f and 1401r (Felske et al., 1998), and the reader is referred to **Appendix A** for related
333 experimental details. For quantification, samples and standard plasmid dilutions were run in triplicate
334 on the same plates. Quantitative PCR used a Step One Plus Real Time PCR system (Applied Biosystem).

335 **Library construction, sequencing and data processing.** Extracted DNA samples (4 replicates) were sent
336 to Microsynth AG (Balgach, Switzerland) for sequencing. This company provides sample quality control
337 and Nextera two-step PCR amplification using primer set 515f/806r targeting the V4 region of 16S
338 rDNA (Klindworth et al., 2013), PCR product purification, quantification and equimolar pooling. Then,
339 PCR libraries were sequenced on an Illumina MiSeq platform using a v2 500 cycles kit. Downstream
340 processing including demultiplexing, merging, primer removal, quality filtering, trimming of Illumina
341 adaptor residuals, chimera removal, operational taxonomic unit (OTU) clustering and OTU assignments
342 were performed by Microsynth. Raw sequence files are available on the NCBI Short Read Archive (SRA)
343 database under BioProject ID: PRJNA997609 and accession numbers: SAMN36684029 to 36684040.

344 **Taxonomic identification of phytoplankton.** Algal counting and identification analyses were
345 performed with an inverted microscope (ZEISS Axiovert A1) following the Utermöhl method (Lund et
346 al., 1958) at 400× magnification. For each sample, at least 400 individuals (filaments, colonies, and
347 single-cell organisms) were enumerated and results were expressed in term of abundance of coenobes
348 (coenobes mL⁻¹).

349 **Confocal scanning laser microscopy (CSLM on colonized masks).** After their immersion in Moselle
350 River, mask samples were observed with a confocal scanning laser microscope (ZEISS LSM 880) in order
351 to visualize deposited materials. Autofluorescence of the different masks' components was recorded
352 using three different channels in a line sequential acquisition mode. Channels were set using the
353 following parameters. Channel 1: Excitation at 488 nm – Emission from 499 to 570 for Channel 1.
354 Channel 2: Excitation at 561 nm – Emission from 570 to 632 for Channel 2 (this channel corresponds
355 to the mask fibers autofluorescence, cf. *Confocal scanning laser microscopy in §2.2*). Channel 3
356 corresponded to chlorophyll autofluorescence with an excitation at 633 nm and an emission recorded
357 between 641 and 694 nm. The colour code adopted for the images of each channel corresponds to the
358 median detection wavelength in that channel.

359 **2.4. Assessment of pristine and photodegraded masks toxicity.**

360 **Biological material collection.** *Gammarus roeselii* were collected with a hand net in La Nied River
361 (Remilly, north-eastern France, 49°00'N and 6°23'E). The animals were placed in plastic coolers and
362 transported within 30 min to the laboratory, where they were unfed and acclimated for 3 days (14 °C,
363 darkness, aerated La Nied water).

364 **Toxicity assay.** The assay was designed to evaluate the effects of mask ageing on *Gammarus roeselii*
365 survival and growth. Four food resources were tested: Leaf litter used as control food (alder, *Aulus*
366 *Glutinosa*; L, cf. §2.3), pristine masks and 1d or 3d photodegraded masks immersed in the Moselle
367 River for 4 weeks. Each condition was replicated 18 times. Each microcosm consisted of a 60 mL glass
368 tank containing 30 mL of La Nied-filtered (GF/F Whatman filter, nominal cut off 0.7µm) stream water,
369 one *G. roeselii*, and two 8 mm diameter-discs of chosen food resource. The reader is referred to
370 **Appendix A** for details on the conditioning of food resource disks and on the *G. roeselii* organisms. The
371 assay was conducted for 14 days in a temperature-controlled chamber (14±1°C) under dark condition.
372 Gammarids were allowed to feed *ad libitum*. To limit chemical variations, La Nied River water in each
373 tank and resources were renewed every week. For each replicate, water and discs remaining prior to
374 resource renewal were frozen at -20 °C for assessment of plastic fibre dispersion and feeding rate,
375 respectively.

376
377 **Endpoints.** The number of dead gammarids was recorded daily: death date was recorded and dead
378 gammarids were removed. After 14 days exposure, gammarid individuals were rapidly photographed
379 for size assessment (see above; (final - initial size)/(initial size x time); in days⁻¹), transferred in 1.5 mL
380 Eppendorf tubes containing 1 mL of ethanol at 70% and finally stored at 4°C until gut content analysis.

381 **Gut content analysis.** Diet composition of (living) *G. roeselii* at the end of the experiment was
382 determined by gut content analyses according to Felten et al. (2008). Briefly, dissected foregut
383 contents were placed into a drop of water on microscope slides, homogenized, then examined at
384 different magnifications from x40 to x400 (Epifluorescence microscope Olympus BX41) to assess the
385 approximate percentage (by area) of seven recorded items: (i) animal material, (ii) FPOM (fine
386 particulate organic matter corresponding to amorphous detritus lacking well-defined cellular
387 structure), (iii) diatoms, (iv) filamentous algae, (v) CPOM (coarse particulate organic matter: mainly
388 leaf detritus with brownish palisade cell layers), (vi) small mineral particles, and (vii) plastic fibers.

389 **Fibres in gut and water analysis.** Plastic fibres were visually counted using Olympus BX41 microscope
390 and sized using the VHX-6000_950F associated software (Keyence Corporation).

391 **Statistical analysis.** Time-to-event data analysis was used to investigate the direct or indirect (i.e. mask
392 as a support of food resource) effects of mask and its ageing on *G. roesellii* survival. This approach
393 allowed to (i) consider events occurring during the whole study period (not only at the final time point)
394 and (ii) account for right-censored values, i.e. organisms whose death was not observed within the
395 study period. Kaplan-Meier curves were used for time-to-event data representation. Log-rank tests
396 were performed to compare survival curves between pairwise treatments. Bonferroni correction was
397 applied for multiple comparisons (n=3 ad hoc planned pairwise comparisons). To test differences
398 between treatments, one-way ANOVAs were performed when assumptions concerning normality of
399 data distribution (Shapiro-Wilk test) and homoscedasticity (Bartlett test) were met, followed by post-
400 hoc Tukey tests. When ANOVA assumptions were not met, Kruskal-Wallis tests were used followed by
401 Mann Whitney test with Bonferroni correction for pairwise comparisons. Data analyses were
402 implemented in R statistical environment (R Core Team, 2019). A significant level of $p \leq 0.05$ was
403 considered.

404

405 **3. Results and discussion**

406 The first step of our work consisted in exposing masks to UV-radiation. After 28 days exposure, the
407 3 different mask layers (IL, OL and ML) were completely shredded (**Appendix C, Figure C.1**) and their
408 manipulation was impaired by their easy disintegration into powder. Despite of this difficulty, it was
409 possible to separate properly the different layers with tweezers. For masks subjected to shorter UV
410 exposure, degradation was less pronounced even though signs of alteration were clearly visible by eyes
411 after 3 days exposure with the appearance of tears at the folding zones of the intermediate layer. We
412 further observed that ML, IL and OL became brittle after 24, 48 and 72 hours of UV exposure,
413 respectively.

414

415 **3.1. Bulk material characterization of pristine and photodegraded mask layers.**

416 Elemental compositions of pristine mask layers are reported in **Figure 1A**. Overall, the chemical
417 composition reflects the nature of the inorganic additives used as pigments in masks or employed as
418 fillers to reduce costs and improve mechanical properties. In particular, the identified elements Na,
419 Mg, Al, Si, P, S, K and Ca probably originate from mineral phases like talc, mica, kaolinite, calcium and
420 magnesium carbonate or barium sulphate, all commonly added to reinforce polymers (Ren et al., 2002;
421 Shrivastava, 2018). The analysis further reveals the presence of Ti, Zn, S and Ba that enter the
422 composition of white pigments like titanium oxide or lithopone (co-precipitate of zinc sulphide and
423 barium), the former being the most frequently adopted pigment (Al-Malaika et al., 2017). Differences
424 in composition are observed depending on the layer type considered. Indeed, the amount of titanium
425 is lowest in ML, barium is mainly detected in IL and the only OL contains copper. The presence of
426 copper may be connected to the blue colour of OL since this metal is one of the components of the
427 blue pigment copper phtalocyanine (Gooch, 2002).

428

429 X-ray diffractograms are shown in **Figures 1B(a)-(c)**. Regardless of UV exposure, Bragg's reflections
430 pertaining to OL and IL (**Figures 1B(a),(c)**, respectively) reveal the presence of the α -monoclinic phase
431 of polypropylene (PP) (Machado et al., 2005) with an additional halo corresponding to the amorphous
432 phase. Values of the crystallinity index Cl_x obtained from diffraction data are reported in **Table 1** for IL,
433 OL and ML depending on UV exposure duration. For IL and OL, Cl_x ranges from 0.42 to 0.78, in

434 agreement with 0.5 value given by Machado et al. (2005) and Kotek et al. (2004), and with the 0.5-0.77
 435 range in Isasi et al. (1999). In addition, there is no obvious correlation between Cl_x and ageing time.

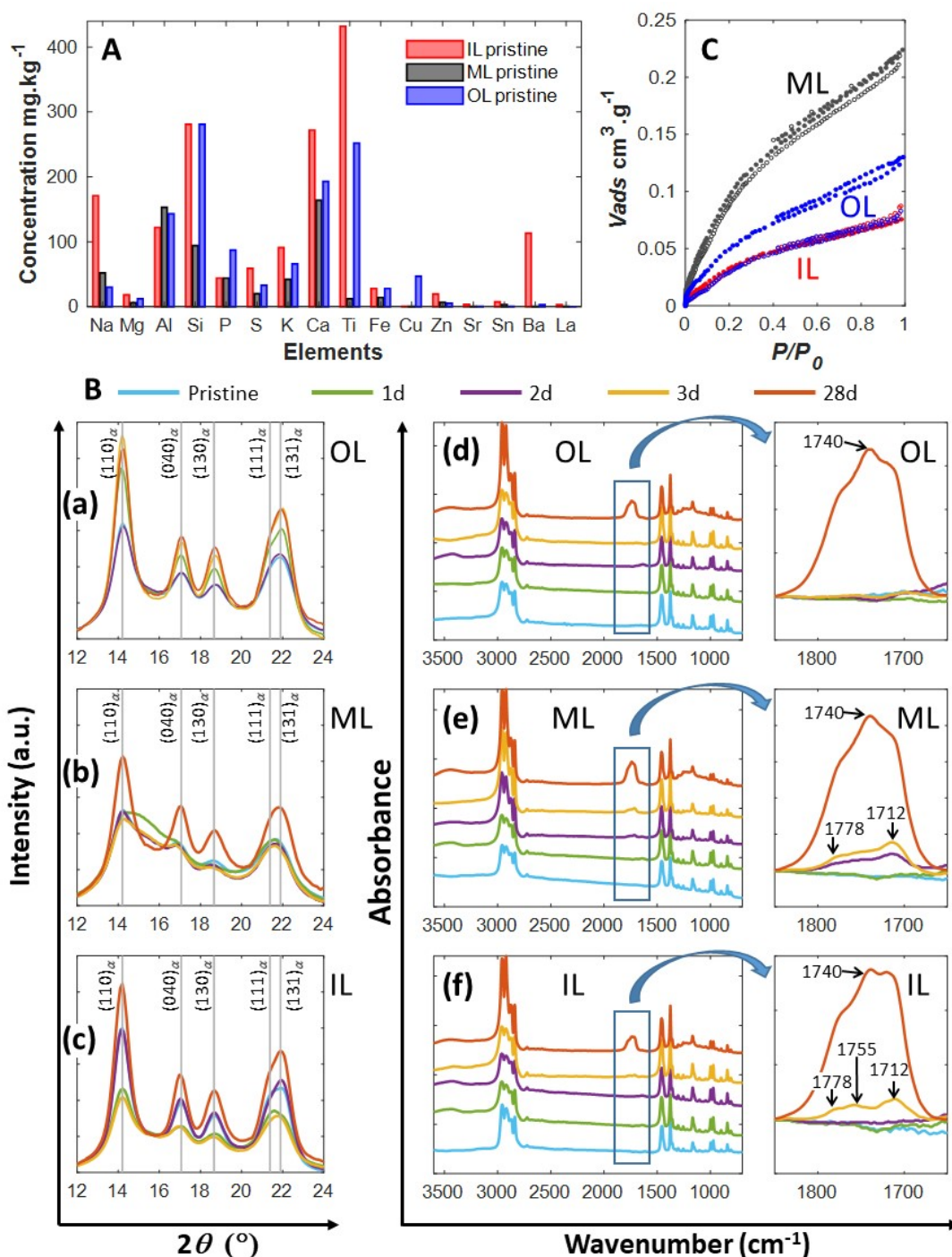


Figure 1. (A) Elemental chemical composition determined by ICP-MS for the three different layers prior to exposure (pristine). IL: inner layer, ML: middle layer, OL: outer layer (indicated). Only elements with concentrations larger than 3 mg/kg are reported for the sake of clarity. (B) panels (a)-(c): Wide Angle X-ray Scattering (WAXS) curves expressed in intensity versus diffraction angle 2θ (in degrees), recorded with Cu $K\alpha$ microsource. OL: outer layer (a), ML: middle layer (b), IL: inner layer (c). (B) panels (d)-(f): Fourier Transform Infrared spectra (FTIR) recorded in transmission mode and expressed as a function of the wavenumber, with a zoom on the spectral region corresponding to carbonyl groups (right column). OL: outer layer (d), ML: middle layer (e) and IL: inner layer (f). In (B) panels (a) to (f), Pristine: no exposure; 1d, 2d, 3d, 28d: samples after 1 day, 2 days, 3 days and 28 days UV-exposure, respectively. (C) Krypton adsorption isotherms collected on OL, ML and IL

(indicated), before UV-exposure (pristine, open circles) and after 28 days under UV radiation (full circles). The volume of adsorbed gas is plotted as a function of the relative pressure P/P_0 .

436
437
438
439
440
441
442
443
444

Table 1. Parameters derived from material characterization methods. Cl_x : crystallinity index calculated from WAXS. $H_{C_{IR}}$: helical content derived from FTIR spectra. Ca_{IR} : carbonyl index estimated from FTIR spectra. R_a and R_q : roughness parameters obtained from AFM maps representing surface height variations, with R_a and R_q the arithmetic average and root mean square of these deviations, respectively. Results derived from krypton adsorption experiments: SSA (specific surface area), C (surface energy constant) and E_1 (enthalpy of adsorption for the first gas layer). OL, ML, IL: outer, middle and inner layer, respectively. p: pristine (no UV exposure). 1d-28d: duration of UV-exposure in days. For the inner pristine layer, R_a and R_q were calculated on the basis of a single image.

	Cl_x (no unit)	$H_{C_{IR}}$ (no unit)	Ca_{IR} (no unit)	AFM		Kr adsorption		
				R_a (nm)	R_q (nm)	SSA ($m^2 g^{-1}$)	C constant (no unit)	E_1 ($J mol^{-1}$)
OLp	0.50	0.84	0.20	4.4±1.5	5.9±2.3	0.26	4.07	9979
OL1d	0.67	0.88	0.21					
OL2d	0.48	0.88	0.16					
OL3d	0.78	0.95	0.16					
OL28d	0.70	0.93	1.48	4.9±3.2	6.6±4.6	0.30	10.92	10610
MLp	0.27	0.85	0.24	4.8±1.4	6.0±1.5	0.60	7.67	10384
ML1d	0.17	0.88	0.16					
ML2d	0.29	0.95	0.33					
ML3d	0.24	0.90	0.40					
ML28d	0.72	0.88	1.83	4.8±2.0	6.2±2.5	0.60	9.94	10550
ILp	0.69	0.90	0.15	3.2	4.4	0.25	4.60	10057
IL1d	0.42	0.88	0.18					
IL2d	0.70	0.89	0.19					
IL3d	0.42	0.85	0.28					
IL28d	0.74	0.92	1.21	4.2±0.8	5.4±1.1	0.21	8.96	10484

445
446
447
448
449
450
451
452
453
454
455

The dispersion of Cl_x values may be attributed to intrinsic spatial heterogeneities of mask samples. Indeed, the size of X-ray beam (diameter < 300 μm) did not make it possible to analyse a volume representative of the whole sample where heterogeneities effects would be averaged. This dispersion of Cl_x -data between samples is further consistent with results by Celina et al. (1993) who evidenced that oxidation kinetics of PP powder could differ from one particle to another due to differentiated presence of catalytic residues or impurities. Then, constitutive differences in composition of mask specimen likely overrule the effects of oxidation treatment on Cl_x value, effects that are probably very limited or absent as judged from data by Kotek et al. (2004) and Aslanzadeh and Haghghat Kish (2010), respectively.

456
457
458
459
460
461
462

WAXS curves for ML (**Figure 1B(b)**) differ from those for IL and OL, except after 28 days degradation time. Peaks assigned to ML α -monoclinic phase are barely discernible for all samples except 28 days exposed ones: they all take the form of weak intensity modulations of the amorphous halo. The shape of the signals obtained on ML under such conditions typically correspond to that expected for the mesophase, which is a conformationally disordered phase closely related to the α -monoclinic form (Androsch et al., 2010; Natta and Corradini, 1960; Nishida et al., 2012). The structure of the mesophase is intermediate between that for amorphous and crystalline state: it is characterized by two broad

463 peaks at 2θ -angles of 15 and 21.6°, which corresponds to 5.9 nm and 4.1 nm distances, respectively
464 (Androsch et al., 2010). For all samples except the one after 28 days degradation, it is necessary to
465 consider 2 split Gaussian functions to fit signal contributions from both mesophase and amorphous
466 component (**Appendix D, Figure D.1**). In turn, crystallinity index Cl_x does not fully reflect the
467 crystallinity level of the samples as contributions from mesophase and amorphous phase cannot be
468 differentiated. With this limitation in mind, Cl_x was estimated for 0 to 3 days-exposed ML layers in the
469 same way as it was for IL and OL samples, with resulting values that are significantly lower than those
470 for IL and OL and with a relative variability of Cl_x from one sample to another.

471
472 After 28 days UV exposure, the ML mesophase identified at shorter degradation times disappear
473 (**Figure 1B(b)**) and leaves place to the monoclinic α -phase with a resulting 0.72 crystallinity index,
474 which basically corresponds to maximal values estimated for IL and OL. As a support of this finding,
475 Androsch et al. (2010) evidenced that transformation of mesophase into α -monoclinic structure is
476 triggered by temperature. Interestingly, while these authors showed the mesophase/ α -state transition
477 above 60°C with ramp-experiments, the phase transition for our samples does not depend on
478 temperature (despite of alternated irradiating cycles between 50°C and 60°C, taken similar for all
479 samples) but on irradiation duration. This indicates that the phase transition in our case is probably
480 ruled by both thermodynamics and kinetics, and impacted over time by material damages.

481
482 To address possible changes of the chemical groups carried by IL, ML and OL samples depending on
483 degradation time, we measured the corresponding FTIR spectra (**Figures 1B(d)-(f)**). The wavenumber
484 domain from 3030 to 2760 cm^{-1} corresponds to stretching vibrations of methyl and methylene groups,
485 and associated bands are clearly saturated in most of investigated IL, ML and OL samples. It is only for
486 sufficiently degraded samples that these bands start to be well resolved, with joint apparition of
487 additional contributions from oxygen-containing products detected in the carbonyl domain (1850 to
488 1650 cm^{-1} , cf. zooms in **Figures 1B(d)-(f)**) corresponding to $>C=O$ groups (carboxylic acids, esters and
489 ketones, etc) (Lacoste et al., 1993; Luongo, 1960; Philippart et al., 1999). In the range 3600 to 3200 cm^{-1} ,
490 the band corresponding to $-OH$ groups (alcohol, hydroperoxides, acids, etc) increases with
491 degradation time, especially so at 28 days UV exposure. In addition, for 28 days-degraded IL, ML and
492 OL specimen, the curves feature a shallow bump in the 1400-1000 cm^{-1} range, which we attribute to
493 C-O-X species (Lacoste et al., 1993).

494
495 Using FTIR data, the helical content HC_{IR} was calculated as detailed in Materials and Method section.
496 Values are reported in **Table 1** and vary between 0.84 and 0.95, without clear dependence on the
497 duration of degradation. A stronger impact of UV exposure on HC_{IR} might have been expected after
498 inspection of data by Aslanzadeh and Haghghat Kish (2010) who reported helical content value as high
499 as 0.95 for melt-spun PP fibres after 200 hours ageing at 25°C under UV-C radiation exposure. On the
500 other hand, using attenuated total reflection (ATR) technique, Blais and co-workers (Blais et al., 1972)
501 evidenced a restructuring of the surface layer of PP samples with a continuous increase of the helical
502 content from 0.83 to 1 within UV-A exposure duration as short as 80 h. This effect was however
503 restricted to the outermost surface of their 22 μm -thick samples, as evidenced by measurements in
504 transmission mode that pinpointed the absence of variation of bulk material properties with changing
505 radiation duration. The latter result agrees with our conclusions obtained from FTIR data also collected
506 in transmission mode.

507 Beside the evaluation of the amount of helical structure at given radiation duration, FTIR unveils
508 useful information on the formation of degradation products over time. In the carbonyl domain (cf.
509 zooms in **Figures 1B(d)-(f)**), a broad ill-defined band can be observed after a delay corresponding to a
510 so-called induction time (Aslanzadeh and Haghghat Kish, 2010; Philippart et al., 1997; Rouillon et al.,
511 2016; Severini et al., 1988). This induction period depends on the layer type considered: 2 days for ML,
512 3 days for IL and >3 days for OL. The carbonyl index (Ca_{IR}) was computed from the area under the
513 carbonyl band following the procedure given by Almond et al. (2020), and values are summarized in
514 **Table 1**. For radiation durations shorter than the induction period, Ca_{IR} is in the range 0.15 to 0.24, in
515 agreement with the 0.18 value by Almond et al. for pristine PP samples. Maxima of Ca_{IR} are reached
516 at 28 days-degradation time (1.21, 1.83 and 1.48 for IL, ML and OL, respectively) but remain lower than
517 those by Almond et al. (2020) ($Ca_{IR}>2$ after 20 days irradiation) probably because sample irradiation
518 protocol adopted by these authors is different from ours.

519
520 A detailed examination of the carbonyl band (**Figures 1B(d)-(f)**) shows that its shape evolves with
521 UV exposure duration. For the shortest ageing time (IL3d, ML2d and ML3d), the band is broad with a
522 shallow maximum at 1712 cm^{-1} assigned to carboxylic acid in dimer form, and with a shoulder at 1778
523 cm^{-1} stemming from γ -lactone and/or esters (Lacoste et al., 1993; Philippart et al., 1999). Another
524 shoulder can be distinguished on IL3d at 1755 cm^{-1} , corresponding to free carboxylic acid (Philippart et
525 al., 1999). After 28 days exposure, the main component of the carbonyl band at 1740 cm^{-1} is attributed
526 to esters (Lacoste et al., 1993; Philippart et al., 1999), with the shoulders at 1712 and 1778 cm^{-1} invoked
527 above. This evolution of the carbonyl band with a shift of the maximum of absorption upon increasing
528 exposure duration is well documented in literature (Aslanzadeh and Haghghat Kish, 2010; Rouillon et
529 al., 2016). It is explained by the fact that acetic acid, a molecule of low weight, can migrate from the
530 polymer to the gas phase, unlike macromolecular photoproducts e.g. ester groups and acids that keep
531 on accumulating in the material during degradation (Rouillon et al., 2016).

532 **3.2. Surface properties of pristine and photodegraded mask layers.**

533 As evidenced by SEM (**Figures 2A,B**), the two pristine peripheral layers of the mask (IL and OL)
534 display similar organization, typical of that characterizing thermal bonded non-woven fabrics. Both
535 types of layer consist of a web of fibres with $20\text{ }\mu\text{m}$ average diameter, and the material structure is
536 reinforced with square-shaped bond points clearly observable in the micrographs. The size of the bond
537 differs between IL and OL, with ca. $500\text{ }\mu\text{m}$ and $700\text{ }\mu\text{m}$ dimensions, respectively, and this difference
538 may contribute to differences in IL and OL mechanical properties. Back scattered electrons (BSE)
539 pictures further reveal the presence of round-shaped grains with size lower than 500 nm on the surface
540 of all fibres (**Appendix E, Figure E.1(a)-(b)**). Energy Dispersive X-ray Spectroscopy (EDS) shows that
541 most brilliant grains are composed of titanium and oxygen (**Figure E.1(c)**), which explains their bright
542 appearance on BSE micrographs. In line with this finding, titanium dioxide particles have already been
543 identified on the surface of plastic debris extracted from sediments (Fries et al., 2013). The observation
544 of particles consisting of titanium further agrees with the chemical analysis in **Figure 1A**. The remaining
545 surface of the fragments has a composition reminiscent of minerals with aluminium and silicon
546 elements (**Figure E.1(d)**), it features crystallized salts (e.g. Na, Ca, Cl, S) (**Figure E.1(d)**) or consists of
547 only carbon (**Figure E.1(e)**). All these defining properties are common to pristine IL and OL samples.

548
549 After 3 days UV exposure, IL and OL fibres fragmented into rods, the length of which vary from a
550 few tens to several hundreds of microns (**Figures 2D-F** and **Figure E.2 in Appendix E**). There is no
551 splintered elements at the fibre surface and the observed fractures are rather sharp, even though burrs

552 appear at some places. **Figures 2D,E** make it clear that photodegradation leads to shorter fibers with
553 a fragmentation that proceeds in a section that is perpendicular to the main axis of the fibers, leading
554 to reduction of fiber length. A description of why such a fragmentation follows this pattern would
555 require a refined analysis of the mechanical features of the fibers and their microstructural properties
556 along the two main directions of the fiber geometry. In addition to fibres fragmentation, cavities are
557 formed on IL and OL after UV exposure (**Figure 2F**). The diameter of corresponding voids amounts to a
558 few hundreds of nanometres and some of them are filled with titanium dioxide nanoparticles (cf. zoom
559 in **Figure 2F**), thereby suggesting that cavity genesis proceeds according to photocatalytic degradation
560 mediated by TiO₂ (Lee and Li, 2021; Ohtani et al., 1989). Cavities are observed on both fibres surface
561 and sections newly generated by fragmentation (**Figures 2E,F**), therefore implying that titanium
562 particles were located in the core of fibres prior to degradation. After 28 days ageing (**Figures 2G-I** and
563 **Figure E.3 in Appendix E**), rods are still observed and are decorated by multiple micron-sized plastic
564 fragments (**Figure 2G**). The cavities are still visible on IL and OL fibres, some of them are filled with TiO₂
565 grains and others not (**Figures E.3(a),(b),(g),(h)**). For both IL and OL, some fibres appear extremely
566 cracked (**Figure 2I, Figure E.3(b),(c),(d),(f),(g),(h)**), which confers upon them a laminated and powdery
567 aspect. Some of the observed cracks seem to have grown from the cavities (cf. rectangles in **Figures**
568 **E.3(b),(h)**). Additional types of defects appear on IL and OL upon ageing, such as surface blister-like
569 structures of a few microns in size (**Figure 2H, Figure E.3(e)**). The main elemental component of these
570 structures is carbon. Overall, we find that fibres are either covered predominantly by the above blister-
571 defects or altered significantly with presence of numerous cracks, and few fibres exhibit both
572 properties (**Figure 2H and Figures E.3(d),(f)**). The resulting structural heterogeneity of degraded IL and
573 OL comforts the significant dispersion in Cl_X and Cal_{IR} indexes estimated from WAXS and FTIR,
574 respectively.

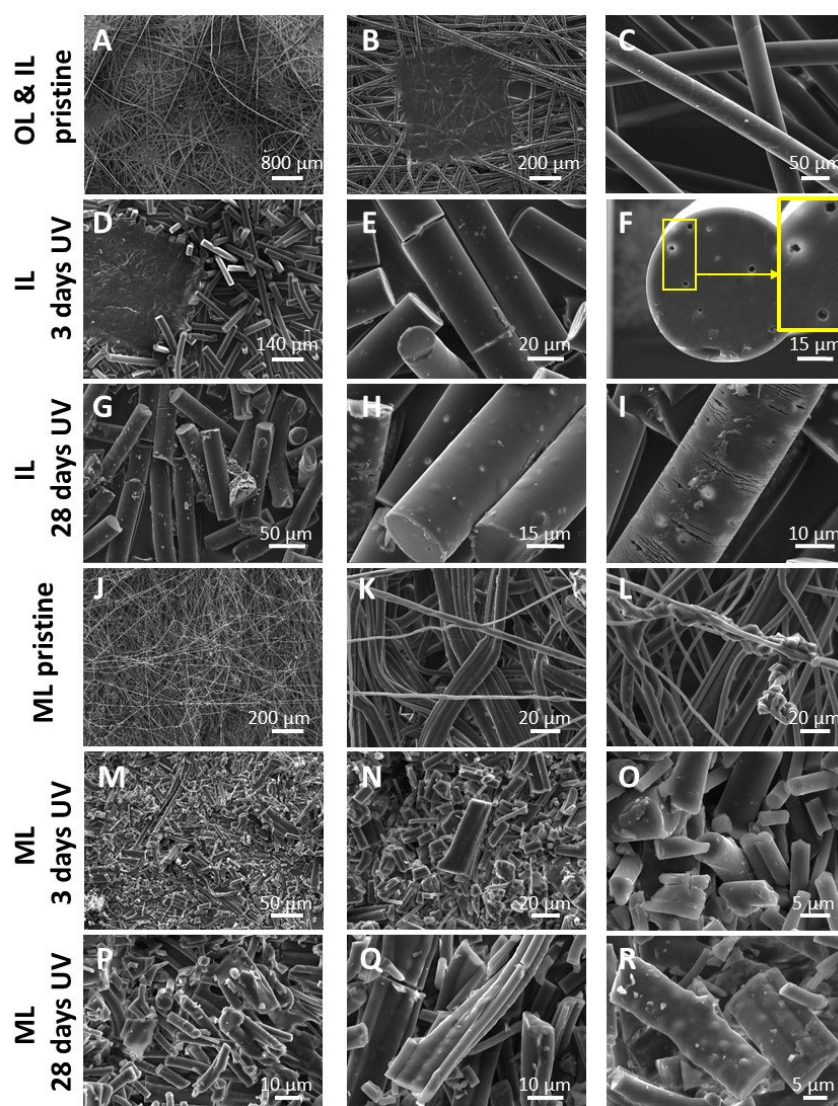


Figure 2. Scanning electron micrographs (secondary electron detection mode). **(A,C)**: pristine inner layer (IL). **(B)**: pristine outer layer (OL). **(D)-(F)**: IL after 3 days UV exposure. **(G)-(I)**: IL after 28 days UV exposure. **(J)-(L)**: pristine middle layer (ML). **(M)-(O)**: ML after 3 days UV exposure. **(P)-(R)**: ML after 28 days UV exposure. Zoom in **(F)** shows that some of the holes are filled with bright nanoparticles, probably TiO_2 according to literature and data of Figure 1A and Figure E.1 in Appendix E.

575

576 The structure of pristine ML takes the form of an entangled and heterogeneous network of fibres
 577 polydisperse in size (**Figures 2J-L**). In detail, isolated fibres with diameter in the 1.5 to 8 μm range
 578 coexist with flat bundles formed from fused fibres, the width of which is ca. 10-20 μm . The few
 579 fragments observed on ML fibres are composed of carbon, or they feature a chemical composition
 580 typical of salts with the presence of calcium, sodium chloride or sulphate. This finding suggests that
 581 these salt entities are not plastic additives but likely originate from exogenous deposits during mask
 582 life cycle. Unlike IL and OL, pristine ML are free of TiO_2 nanoparticles. Exposure to UV leads to the
 583 formation of elongated fragments, heterogeneous in size and shape (**Figures 2M-O**). In addition, no
 584 cavities nor cracks are observed, irrespectively of the exposure time, while some fragments display
 585 blisters after 28 days UV-treatment (**Figures 2P-R**).

586

587 As an intermediate conclusion, the above SEM results evidence that UV exposure leads to
588 fragmentation, cracks and cavities formation, and to occurrence of blisters on most degraded samples.
589 To further address the impacts of UV-mediated weathering of samples at the infra-micronic level, we
590 used AFM in contact mode. **Figure F.1** in **Appendix F** reports illustrative AFM images (256×256 pixels)
591 with 5 μm×5 μm dimensions for IL and OL, and 2 μm×2 μm for ML, all recorded on both pristine and
592 28 days degraded samples. At first sight, there is no change in surface topography with ageing, and all
593 scanned surfaces appear smooth and similar for the 3 fibre types. This qualitative observation is
594 confirmed by values taken by R_a and R_q surface roughness parameters, i.e. 3.2 nm-4.9 nm and 4.4 nm-
595 5.9 nm, respectively (**Table 1**). These data are consistent with those reported elsewhere for different
596 PP forms and radiation procedures (Ma et al., 2021; Rouillon et al., 2016; Slepíčka et al., 2010).

597
598 One drawback of microscopy techniques like SEM and AFM is that observations and related
599 conclusions are based on the analyses of selected objects with possible bias in terms of overall sample
600 representativeness. To circumvent this difficulty, we performed additional surface sample
601 characterization by gas adsorption technique, which has the merit to provide surface properties
602 statistically averaged over the whole sample body. The krypton adsorption isotherms recorded for
603 pristine and 28 days exposed samples are displayed in **Figure 1C** and corresponding BET results are
604 provided in **Table 1**. For all samples, the evaluated specific surface area (SSA) is low ($\leq 0.6 \text{ m}^2\text{g}^{-1}$) and
605 does not change noticeably with degradation. As expected, highest surface area is obtained for ML
606 samples that feature the fibers with lowest diameter. Quantitative geometric arguments are provided
607 in **Appendix G** to support the lack of change in SSA with increasing UV exposure and material
608 fragmentation (**Figure G.1** in **Appendix G**, and cf. associated comments). Following these arguments,
609 it is evidenced that the contribution of lateral surfaces in the overall SSA overwhelms that from basal
610 surfaces. In turn, cracks do not contribute much to the overall SSA. The polydispersity of the fibres (in
611 terms of both length and diameter) does not further ease detection of cracks from the only inspection
612 of specific surface area values.

613
614 Even if SSA does not change significantly with varying UV-exposure, gas adsorption remains a
615 valuable tool for monitoring effects caused by UV on surfaces. Indeed, BET application to experimental
616 data also allows derivation of the so-called C constant defined by $C = \exp[(E_1 - E_l)/R_g T]$ which
617 characterizes the interaction between atoms of krypton and surface (Brunauer et al., 1938), with E_1
618 the enthalpy of adsorption for the first gas layer, E_l is that for subsequent layers and it equates with
619 the enthalpy of liquefaction, R_g is the gas constant and T is the temperature. Values of C are collected
620 in **Table 1** together with E_1 evaluated by considering a Krypton heat of liquefaction of 9.08 kJ/mol. The
621 energy of adsorption of the first layer is found highest for all degraded samples, which reflects a
622 modification of the surface. This difference between initial and end (degraded) state is most
623 pronounced for the two external mask layers (IL and OL). Following arguments by Chow and Grant
624 (1988), difference in the surface energy of pristine and photodegraded PP may result from surface
625 diffusion phenomena mediated by temperature.

626
627 **3.3. Electrokinetic and stability features of colloidal debris from photodegraded mask layers.**

628 *Electrophoretic mobility measurements.* **Figure 3A** shows the measured dependence of electrophoretic
629 mobility (μ) of plastic debris suspended in solution *versus* KNO_3 concentration (denoted as C_{KNO_3}). These
630 debris originate from photodegraded masks and their constitutive layers once in powdery state.
631 Overall, μ is negative, in line with surface electronegativity of plastic materials (Jacobasch, 1984;

632 Zimmermann et al., 2001), and magnitude of μ is that of systems that are significantly charged.
 633 Remarkably, regardless of sample and UV treatment delay, μ varies with the logarithm of c_{KNO_3}
 634 according to a characteristic quadratic-like curve (termed hereafter ‘banana’ profile) with a marked
 635 minimum at ca. 10 mM. In addition, μ tends asymptotically toward a non-zero plateau value at
 636 sufficiently large c_{KNO_3} , as further evidenced by **Figure H.1 (Appendix H)**. This plateau-property is the
 637 signature of the electrokinetic behaviour of so called-soft particles, i.e. particles whose 3D surface
 638 structure is permeable to electroosmotic flow (Gopmandal and Duval, 2022). Similarly, hard
 639 (impermeable) particles featuring a surface roughness comparable to the Debye length can exhibit
 640 such an electrokinetic response as particle charges probed by the electroosmotic flow are then
 641 effectively distributed within a 3D region (Duval et al., 2004; Škvarla, 2007).
 642

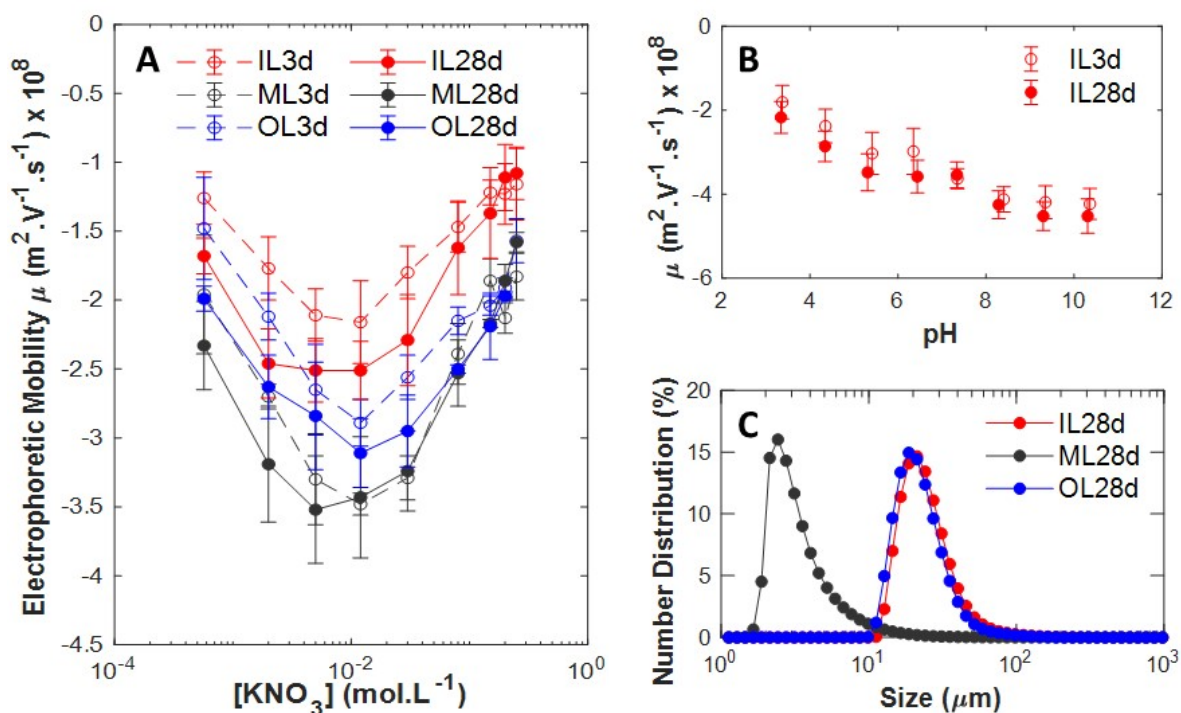


Figure 3. (A) Electrophoretic mobility (μ) measured on masks debris dispersed in KNO_3 electrolyte as a function of KNO_3 concentration at pH 7.35. IL: inner layer, ML: middle layer, OL: outer layer. 3d, 28d: debris after 3 days and 28 days UV-exposure, respectively. Dotted and solid lines: electrophoretic mobility for layers after 3 days and 28 days UV exposure, respectively. Errors bars correspond to triplicate measurements. (B) pH-dependence of the electrophoretic mobility of fragments of the inner layer after 3 days (IL3d) and 28 days (IL28d) UV-exposure. Measurements were performed in 1.2×10^{-2} mol/L KNO_3 electrolyte. (C) Size distributions measured by laser diffraction on 28 days UV-aged debris dispersed in water. The distributions are expressed in number percentage. IL: inner layer, ML: middle layer, OL: outer layer.

643 Obviously, the plastic debris of interest here are representatives of this second type of particles,
 644 recalling that the Debye length varies between ca. 10 nm and 1 nm with increasing salt concentration
 645 from 1 to 100 mM, to be compared with the obtained surface roughness $R_a \sim 3.2\text{-}4.9$ nm (**Table 1**). The
 646 decrease of μ (in absolute value) with increasing c_{KNO_3} above ca. 10 mM is a consequence of the
 647 increased screening of debris surface charge by ions from background electrolyte. The decrease of μ
 648 (in absolute value) with decreasing electrolyte concentration below 10 mM can originate from several
 649 processes already documented in literature for different particulate materials. In detail, Duval et al.
 650 (2013) reported such a non-monotonous electrokinetic behaviour for highly charged latex

651 nanoparticles and argued that it is caused by electric double layer polarization, in line with quantitative
652 predictions from soft surface electrokinetic theory. Interestingly, these latex particles exhibited an
653 outer fuzzy surface layer of ca. 1 nm in thickness, which is of the order of magnitude of the surface
654 roughness of our colloidal plastic debris. Given the nature of these debris (cf. SEM pictures in **Figure 2**)
655 and their characteristic surface roughness, it is likely that the minimum in μ is caused by electric double
656 layer polarization effects, similarly to that observed for latex particles.

657
658 When comparing the electrophoretic mobility- c_{KNO_3} patterns collected for all samples of interest,
659 we observe that the ‘banana’ profile associated with a given 28 days-degraded layer type is basically
660 shifted towards more negative μ values as compared to that for its 3 days exposure analogue. In
661 addition, regardless of the treatment delay, ‘banana’ profiles pertaining to colloidal residues from IL,
662 ML and OL are shifted one with respect to the other according to the sequence $|\mu(\text{IL})| < |\mu(\text{OL})| < |\mu(\text{ML})|$.
663 Qualitatively, the positioning of the banana profiles displayed in **Figure 3A** is likely explained by the
664 presence of additives of different nature (**Figure 1A**) depending on layer type considered, by the
665 possible generation of ionisable surface groups following UV treatment (cf. §3.1) and/or by the way in
666 which the particle surface roughness is affected by that treatment. Related to the latter point, whereas
667 AFM measurements (**Figure E.1**) do not evidence significant change in roughness of lateral surface of
668 fibres, it cannot be excluded that an increase in mean particle surface roughness (evidenced by SEM,
669 **Figure 2**) due to newly created basal surfaces (fractured areas) affects the electrophoretic mobility of
670 masks debris.

671
672 In **Figure 3B** we report the dependence of μ on pH at $c_{\text{KNO}_3}=12$ mM for IL3d and IL28d. Overall, μ
673 increases (in absolute value) with increasing pH from 3 to 5, it levels off from pH 5 to ca. 7-7.5, and it
674 increases with further increasing pH before reaching a plateau value at pH>8. Unlike electrokinetic
675 data on non-degraded PP surfaces measured (mostly) by streaming potential technique (Aranberri-
676 Askargorta et al., 2003; Ismail et al., 2021; Košíková et al., 1995), our measurements do not evidence
677 an isoelectric point in the pH range 3 to 10. They rather indicate that charge of debris originates from
678 two different types of acidic functional groups whose complete dissociations are marked by the two
679 aforementioned plateau regimes in the μ versus pH representation. Based on spectroscopic data given
680 in **Figure 1B(d)-(f)**, the deprotonable functional groups revealed by electrokinetics are likely of the
681 forms R-O-OH (e.g. hydroperoxide), R-OH (hydroxide) or R-COOH (carboxylic acid). It is remarkable that
682 the pH-dependence of μ identified in this work significantly deviates from the quasi-linearity expected
683 for hydrophobic polymer materials like PP (Ismail et al., 2021; Slepíčka et al., 2010), PE or PET
684 (Jacobasch, 1984) (Zimmermann et al., 2001). Accordingly, the samples investigated here most likely
685 exhibit a polar character that can be connected to the polar functional groups revealed by FTIR. Even
686 if these groups surely determine the hydrophilic properties of aged samples, the presence of
687 hydrophobic patches cannot be ruled out, as evidenced by Song et al. for UV-irradiated
688 poly(dimethylsiloxane) surfaces (Song et al., 2007). The overall hydrophobicity/hydrophilicity balance
689 of the colloidal mask fragments goes in the sense of a gain in hydrophilicity with increasing UV-
690 exposure as evidenced by electrokinetics *and* by the difficulty to properly disperse the fragments
691 released by 1-day UV-exposed masks. This conclusion agrees with the results by Alimi et al. (2023) on
692 the reduced sorption capacity of weathered microplastics to hydrophobic contaminants (triclosan).
693 Last, the nature of the adopted degradation treatment seems to be of utmost importance in defining
694 the electrostatic features of the surfaces, including sign of the charge. Indeed, whereas (Slepíčka et al.,
695 2010) reported an increase in μ towards positive values for PP surfaces subjected to argon-plasma
696 irradiation, our results display an opposite trend for PP materials exposed to UV for 3 and 28 days
697 (**Figure 3A**). Moreover, results provided in **Figure 3B** versus pH do not show significant change in debris

698 charge with increasing UV-exposure duration, which agrees with the similar slopes μ versus $\log(c_{\text{KNO}_3})$
699 at $c_{\text{KNO}_3} > 100$ mM in **Figure 3A**.

700

701 *Granulometry*. Granulometry results are given in **Figure 3C** for samples exposed to UV for 28 days. Data
702 acquired on 3 days UV-exposed samples were not considered for such measurements, as they were
703 not reproducible. The reason originates from the fact that 3 days-aged samples exhibited a more
704 pronounced hydrophobic character than 28 days exposed samples. Accordingly, they tended to stick
705 on vessel surfaces, and the granulometry stirring conditions further favoured the trapping of air
706 bubbles with plastic fragments. For all 3 samples tested, the size distributions are asymmetric and
707 present a mode that roughly corresponds to fibre diameters (2.4 μm , 18.7 μm and 21.2 μm for ML, OL
708 and IL, respectively). Small fragments possibly originating from the fibre fracture zones were possibly
709 present but they could not be detected due to their weak contribution compared to that of larger
710 debris. Interestingly, size distribution of ML sample is shifted significantly to lower sizes as compared
711 to the other two layer types. In contrast, the electrophoretic mobility collected for the three layers did
712 not differ much within experimental error, therefore suggesting that the electrophoretic response of
713 the layer debris is dominated by local modifications of layer structure - as argued in the preceding
714 section - rather than by changes in debris size. This absence of dependence of electrophoretic mobility
715 on particle size is in line with the fact that the particles dimensions well exceed the Debye layer
716 thickness and, therefore, that retardation effects and electric double layer polarization are not
717 significant (Duval and Ohshima, 2006).

718 **3.4. Effects of UV-treatment on the physicochemical properties of masks and their colloidal debris:** 719 **summary.**

720 The experimental data detailed in the previous sections make it possible to sketch an overview of
721 the impacts of photodegradation on the physicochemical properties of surgical face masks (**Figure 4**)
722 and their released debris in aquatic media. Although results were obtained here for a specific brand of
723 mask under artificial ageing conditions, they may be considered generic as literature evidences similar
724 fibre release irrespectively of mask brands (Wu et al., 2022) or similar spectral signature of degradation
725 for masks either aged artificially or collected on beaches (Saliu et al., 2021). Each horizontal bar in
726 **Figure 4** summarizes qualitatively the measured evolution of a given material property as a function
727 of UV-exposure delay, with the following colour nomenclature: white for unavailable data, blue for a
728 property that has not significantly changed, orange for one that has significantly evolved. It should be
729 pointed out that it was not possible to perform electrophoretic mobility measurements on pristine
730 masks. Indeed, even after cutting them into small pieces, it was impossible to prepare a proper
731 colloidal suspension of mask fragments as the latter were floating at the surface of the electrolyte
732 mainly because of their hydrophobic property.

733

734 The first striking feature revealed by **Figure 4** is that changes of macroscopic mask properties
735 inferred from sample manipulation systematically occur before bulk material properties start to evolve
736 significantly. Indeed, after three days of UV-exposure, the material becomes brittle and breaks up
737 easily. It then became less difficult to disperse it in water, therefore suggesting that neo-formed
738 fragments are less hydrophobic. Concerning PP bulk properties evaluated by WAXS, the main
739 modification is the change after 28 days of the crystal structure of ML from a conformationally
740 disordered phase (mesophase) to the α -monoclinic structure, with a companion increase in
741 crystallinity. This crystal transformation is the only change of material property revealed by X-rays
742 scattering analysis. Crystallinity for IL and OL varies from one sample to another, with no obvious

743 dependence on UV exposure time. The same conclusion holds for the helical content index evaluated
744 for IL, OL and ML by FTIR. The quantity of chains in helicoidal conformation, as reflected by this index,
745 does not depend on the duration of degradation. In addition, the helical content is surprisingly of the
746 same order of magnitude for both mesophase and α -monoclinic phase. Among all parameters that
747 define bulk plastic materials, it is the carbonyl index that most clearly changes with duration of
748 photodegradation. Significant changes of this index are identified only for conditions marking extreme
749 variations in macroscopic material properties. This finding is in agreement with literature results that
750 report a period of induction for the increase in the carbonyl band (Benítez et al., 2013; Philippart et al.,
751 1997; Rouillon et al., 2016; Severini et al., 1988). The loss of mechanical properties and the emission
752 of organic molecules (cf. below) could be detected prior to increase of the carbonyl index (Aslanzadeh
753 and Haghighat Kish, 2010; Rouillon et al., 2016). UV action leads to fragmentation of fibers into rods,
754 which proceeds by the generation of transverse fractures (Aslanzadeh and Haghighat Kish, 2010; Kotek
755 et al., 2004). There is no variation of the surface roughness of fibers that are further devoid of flakes
756 or peels. Instead, the surface of fibers only features craters, some of them formed around titanium
757 dioxide particles, which likely results from the photocatalytic properties of this mineral. Even though
758 most fragments produced by degradation have rod shape with a few tens of microns length, there is
759 also generation of submicronic particles deposited at the rods surface, as observed by SEM.

760 As shown in **Figures 3A,B** the electrophoretic properties of mask fragments feature particles with
761 significant electrostatic charge, and these properties are not characteristic of those expected for non-
762 polar materials. They further depend moderately on UV exposure duration and layer type. All
763 electrokinetic data follow a characteristic ‘banana curve’ marking the dependence of electrophoretic
764 mobility on salt concentration. Remarkably, this ‘banana curve’ is also measured for PP granulates
765 exposed to UV lamp (cf. details in **Appendix I** and **Figure I.1** therein), even though mask fragments are
766 2 to 3 orders of magnitude larger in size (**Figure I.2** in **Appendix I** and **Figure 3C**). This supports the idea
767 that the surface reactivity of plastic debris is not dominated by size.

768 As a last remark, SEM and EDS results reveal that the degradation of mask materials favours the
769 surface exposure (and possible release) of contaminants like TiO₂ nanoparticles which are otherwise
770 embedded in the bulk material, and these contaminants are further found at the surface of the fibres
771 after fragmentation. Obviously, this change in the location of TiO₂ nanoparticles may have important
772 implications in terms of ecotoxicological risk. As far as organic moieties are concerned, we measured
773 an overall release of acetate, citrate, formate and lactate from UV-exposed mask layers over a period
774 of 3 months with a slight increase of the released amount with increasing UV exposure duration,
775 especially so after 7 days monitoring (**Figure J.1** in **Appendix J**). Finally, we suggest that
776 photodegradation leads to the migration of some molecular compounds from bulk to surface, as
777 suggested by CSLM measurements that pinpoint a displacement of auto-fluorescent species with
778 increasing UV-mediated ageing of the materials (**Figure 5**). The fluorescence of UV-aged samples
779 (**Figures 5A(b),B(b),C(b)**) appears in the form of well-defined spots located on the surface of the fibres,
780 whereas that of pristine samples is distributed in the bulk of the fibres according to a pebbled pattern
781 (**Figures 5A(a),B(a),C(a)**). Regardless of the layer type, the blisters observed by SEM on fibres surface
782 (**Figures 5A(c),B(c),C(c)**) concentrate the fluorescence imaged by CSLM, which supports the idea of an
783 ageing-mediated diffusion of organics.

784
785
786
787

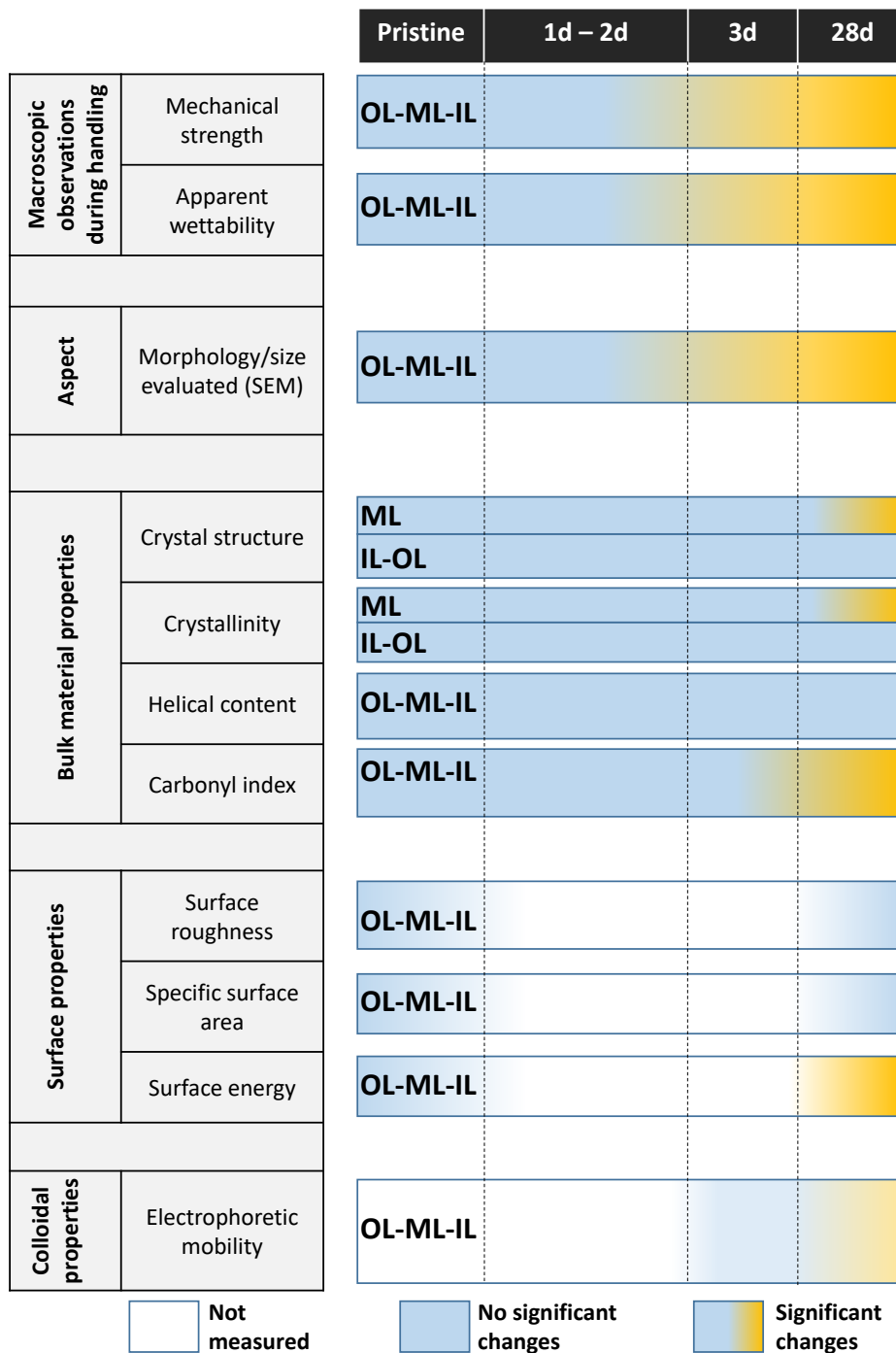


Figure 4. Scheme illustrating the evolution of material physicochemical properties (indicated) as a function of UV-exposure, relative to the pristine initial state. The colour blue means that properties do not change significantly, transition from blue to orange indicates major changes and white colour indicates that the property is not measured. The type of layer concerned with the depicted evolution is specified.

788

789

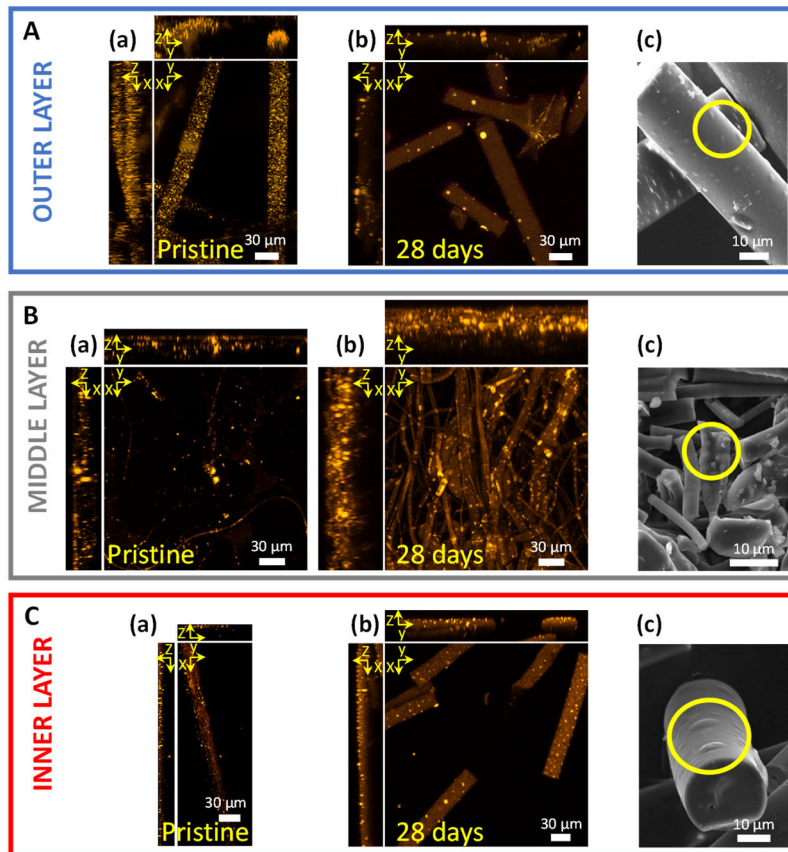


Figure 5. Orthogonal views of the Maximum Intensity Projections (MIP) derived from z-stacks by Confocal Laser Scanning Microscopy (CLSM) for OL (**A**), ML (**B**) and IL (**C**) in pristine state (**a**) and after 28 days UV-exposure (**b**). The results evidence changes in the fluorescence distribution due to photodegradation: the fluorescence of UV-aged samples is mainly located on the surface of the fibres whereas that of pristine samples is distributed in the bulk of the fibres according to a pebbled pattern. (**c**) SEM micrographs recorded on 28 days UV-exposed fragments (back scattered electron detection). Yellow circles highlight the blisters displaying fluorescence.

790 Following the multiscale physicochemical characterization of masks summarized in **Figure 4**, a
 791 question remains: do the observed modifications of masks following photodegradation impact on their
 792 reactivity towards aquatic biota? This issue is tackled in developments below where we analysed (i)
 793 the extent by which photodegradation of masks (prior to their 4 weeks-immersion in Moselle River)
 794 alters the composition of subsequently formed freshwater biofilms, and (ii) the mortality of *Gammarus*
 795 *roeselii* species fed in the laboratory with the biofilms grown on the masks.
 796

797 **3.5. Photodegradation of masks: implications for their reactivity towards aquatic biota.**

798 *3.5.1. Characterization of river-biofilm formed on masks.*

799 After 4 weeks incubation in Moselle River, pristine and 1 or 3 days UV-exposed mask samples were
 800 collected and brought back to the laboratory. DNA quantities obtained on 1-cm diameter discs are
 801 given in **Figure 6A**. With increasing the level of UV-mediated alteration, the data reveal a well-marked
 802 decrease of the mean total DNA concentration extracted from the masks and therewith a reduction of
 803 the overall biomass in the biofilms. However, this conclusion is tempered by ANOVA test that suggests
 804 a non-statistical significance of the observed trend ($p=0.113$). In addition, for the same amount of
 805 extracted DNA analysed, the number of 16S rRNA gene copies seems to be lower on photodegraded

806 masks, thus indicating a reduction in the number of bacteria within the biofilms (**Figure 6B**). Here again
807 these differences are poorly marked according to ANOVA test ($p=0.0885$). Bacteria and algae (mainly
808 diatoms) are found to be the main components of the biofilms formed on masks (**Figure 6C**). This
809 finding is commonly reported for the type of environment considered here (Cooksey and
810 Wigglesworth-Cooksey, 1995) as diatoms and bacteria are considered as pioneering species for the
811 development of photic biofilms (Rao et al., 1997), and they act as the major primary producers and
812 consumers of organic matter, respectively.

813 The ratio between bacteria and algae (mainly diatoms) is significantly affected by the level of
814 photodegradation (**Figure 6C**; ANOVA; $p=0.0369$), while the structure of the bacterial community
815 remains almost unchanged (**Figure 6D and Figure K.1 in Appendix K**). Diversity of bacteria on these
816 artificial supports is relatively large with 7 bacterial classes represented ($> 1\%$ of the total sequences
817 recovered). The most dominant phyla are *Proteobacteria*, *Bacteroidetes*, *Verrucomicrobia*,
818 *Planctomycetes*, and to a lower extent, *Acidobacteria*, *Cyanobacteria* and *Armatimonadetes* (**Figure**
819 **K.1(a)**). At a class-distribution level, 12 bacterial classes are identified, the most dominant being the
820 *Gamma*- and *Beta*-*proteobacteria* (**Figure K.1(b)**). Regarding microalgae, small pennate diatoms (10-
821 11 μm) like *Achnantheidium* dominate the communities (**Table L.1 in Appendix L**). Diatoms belonging
822 to the *Encyonema* and *Amphora* genera are also well represented, especially on altered masks.
823 Whereas masks were exposed under similar sunlight conditions in the river, we observe a strong
824 heterogeneity within biofilm planktonic communities with sometimes a high relative abundance of
825 Chlorophytes belonging to the *Characium* genus, or *Chaetophorales*, *Chlamydomonadales*,
826 *Ulotrichales* orders (**Table K.1**). Cyanobacteria from the *Synechococcales* order (*Leptolyngbya* and
827 *Heteroleibleinia* genera) are also widely represented in different biofilms we analysed.

828 CLSM observations confirm the high diversity of microorganisms adsorbed on masks and further
829 reveal that biofilm structure is mainly dominated by the spatial organization of the constitutive mask
830 fibres as microorganisms are preferentially located in their vicinity (**Figures 6E and 6F**). Additional
831 CLSM images displayed in **Figure M.1 (Appendix M)** illustrate the variety of solitary (e.g. **Figures**
832 **M.1(a)-(e)**) or in-groups (filaments or colonies, **Figures M.1(f)-(i)**) freshwater algae found on masks.
833 Some of these colonies also wrap the mask fibres (**Appendix M, Figures M.1(g),(h),(i)**). However, no
834 obvious relationship could be inferred between the degree of degradation of the UV-exposed PP fibres
835 and such occurrences. Most of the fluorescence from phytoplankton organisms is recorded in the red
836 channel (e.g. **Figures M.1(a),(f)**), corresponding to chlorophyll emission ($> 641\text{ nm}$), and for a few cells
837 in both the red and orange (570-632 nm) channels, resulting in white pixels (**Figure M.1(g),(h),(i)**). In
838 that latter case, it is likely that fluorescence recorded in the orange channel is emitted by some blue
839 pigments (e.g. phycobiliprotein) involved in microphytes photosynthesis. Most of the diatoms
840 observed are in motion outside the biofilm and located on the glass bottom of the dish used for
841 microscopy observations (**Figure M.1(a)**). CSLM pictures also show the occurrence of platy particles, a
842 few tens of microns in size, emitting fluorescence in the green channel (channel 1: 499-561 nm). The
843 shape of these objects suggests that they are of mineral composition, as confirmed by electron
844 microscopy observation with EDS analyses and loss on ignition measurements (**Figure N.1 and Figure**
845 **N.2 in Appendix N**). The micrographs evidence that these platy particles are aggregates of submicronic
846 entities consisting of carbonates and aluminosilicates (**Figure N.1**).

847 To summarize, results show that masks acting as inert supports for microorganism growth (i.e. they
848 are not a source of nutrients) can host high microbial diversity and abundance. CSLM data do not reveal
849 any preferential adhesion locations of microorganisms versus mask photodegradation, which suggests
850 an apparent lack of connection between bioadhesion and UV-mediated changes in physicochemical
851 properties of fibers. However, macroscopic observations (**Figure N.3 in Appendix N**) evidence that it is

852 the entangled organization of the fibers that acts as an efficient trap for phytoplankton and mineral
 853 particles, while locations corresponding to thermal bond points are by far lesser covered by biofilm.
 854 Overall, mask ageing primarily reduces the abundance of algae (mainly diatoms), as confirmed by
 855 independent *Nitzschia palea* diatoms colonization assays performed in laboratory as a function of mask
 856 UV-exposure duration (not shown). This decrease in mask colonization by diatoms with ageing may
 857 result from the decrease of mask hydrophobicity (diatoms would be sensitive to) observed for the
 858 colloidal fragments. Mask ageing further poorly affects both bacteria abundance and microbial
 859 community structure, which pinpoints that bacteria are less sensitive to changes in fibre surface
 860 properties (in particular hydrophobicity) than diatoms.

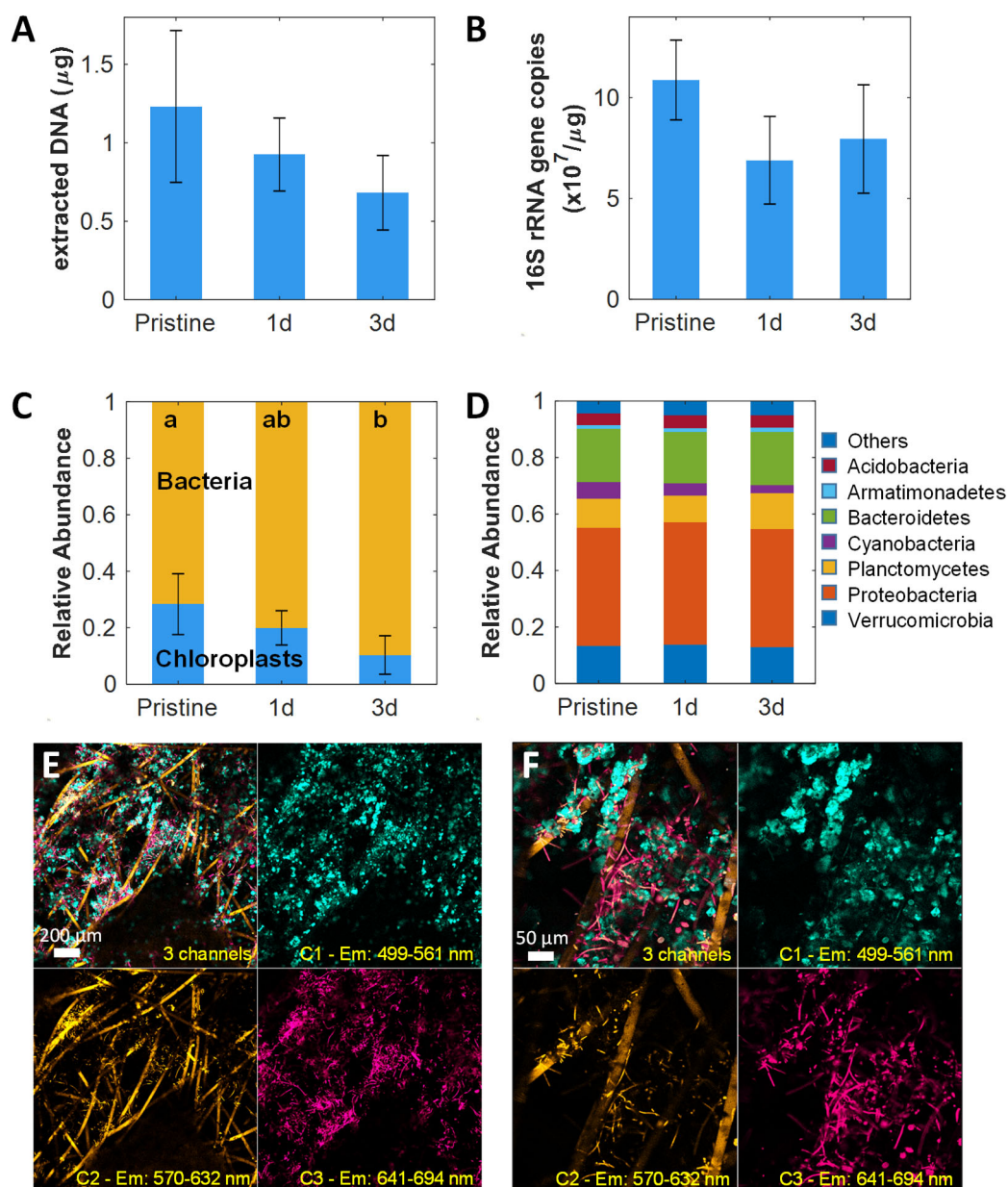


Figure 6. Microbial diversity analysis of biofilms on masks incubated 4 weeks in the Moselle River. Pristine: no exposure; 1d and 3d: masks after 1 day and 3 days of UV-exposure. For each condition, 4 replicates corresponding to 4 different masks were averaged. **(A)** Biomass determined by the total amount of DNA extracted. **(B)** Bacterial abundance, determined by the number of 16S rRNA gene copies. ANOVA p-values are 0.11 and 0.08 in Figure 6A and 6B, respectively. **(C)** Estimation of the bacteria/algae ratio within biofilms based on the ratio of 16S rRNA sequences from bacteria and chloroplasts. Lowercase letters a, ab and b in panel C indicate significant differences

($p < 0.05$). **(D)** Bacterial community structure analysis at the phylum-level. Others include phyla with $< 1\%$ average relative abundance and unaffiliated sequences. **(E),(F)** CLSM images showing the autofluorescence of the components of biofilms on pristine masks after incubation in the Moselle River at two different magnifications. Autofluorescence was recorded over three different spectral ranges (C1, C2, C3) specified in each panel. The colour adopted for each channel corresponds to the median detection wavelength in that channel. In (E) and (F), the upper left tile is the image after merging of the 3 channels.

861

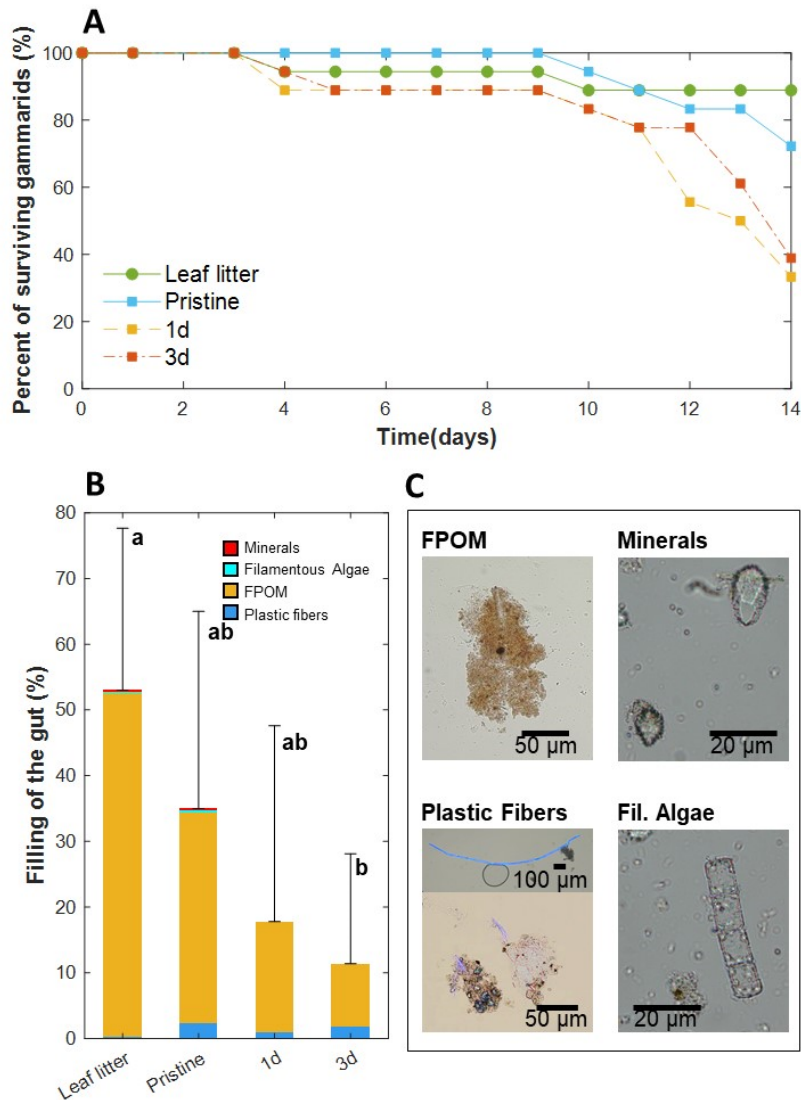
862 3.5.2. Ecotoxicity and gut content of *G. roeselii*.

863 High survival (ca. 90%) was recorded for gammarids fed on alder litter during 14 days. According to
864 Kaplan-Meier curves analyses, survival of *G. roeselii* is significantly affected by the type of resource
865 (Log rank test, $p = 0.005$; **Figure 7A**): the survival of gammarids fed on leaf litter is significantly higher
866 than that of organisms fed on mask (leaf vs masks: $p < 0.005$), whereas those fed on pristine masks show
867 a significantly higher survival (72%) compared to those fed on aged masks (pristine vs. aged masks: Log
868 rank test, $p = 0.014$; 1d: 33.3%; 3d: 38.9%). No effect of resource type is detected on the growth of *G.*
869 *roeselii* (ANOVA; $p = 0.705$; Mean \pm Sd: $0.0125 \pm 0.0044 \text{ day}^{-1}$) (data not shown). Three non-exclusive
870 hypotheses can explain the higher mortality of gammarids under aged mask conditions: (1) an impact
871 of microplastics fibres on gammarids as a result of material toxicity (direct effect) and/or obstruction
872 of consumers' digestive tracts (indirect effect), (2) a reduction in the quantity of biofilm present on
873 aged mask discs, leading to mortality due to underfeeding/starvation (quantitative deficiency), (3) a
874 decrease in the food quality of the biofilms developed on the aged substrates (qualitative deficiency).

875 Analyses of *G. roeselii* gut contents show significant influence of the resource type on gammarid
876 gut filling (ANOVA and post hoc tests; $p = 0.0155$; **Figure 7B**), with a significant 4.7 times-lower filling of
877 *G. roeselii* gut when fed on 3d treated masks (11.4%) compared to those fed on leaf litter (53%). Gut
878 filling of gammarids fed on pristine (35%) and 1d masks (17.8%) is intermediate between that
879 pertaining to organisms fed on leaf litter and 3d masks. Gammarid's gut contents are mainly composed
880 of FPOM and also plastic fibres *albeit* to a much lower proportion (see illustrative pictures in **Figure**
881 **7C**). The fractions of microplastic fibres evaluated with respect to the overall gut volume and the
882 effectively occupied gut volume are found *statistically* similar (pristine, 1d & 3d masks; Kruskal-Wallis
883 ANOVA: $p > 0.05$; global mean \pm Sd: $1.4 \pm 2.6 \%$; relative mean \pm Sd: $7 \pm 11.7\%$). Relative proportion of
884 other items were similar between treatments (Kruskal-Wallis ANOVA: $p > 0.05$).

885

886 The above results show that *G. roeselii* feeding on biofilm grown on masks can ingest plastic fibres.
887 As the quantity of plastic fibres ingested by gammarids is similar for the different mask treatments
888 tested, material toxicity (direct toxicity) or gut occlusion (indirect toxicity) by plastic fibre material
889 cannot explain alone the higher mortality of organisms with aged masks (hypothesis (1): toxicity
890 hypothesis rejected). In the current study, aged masks carry biofilms that are less colonized by diatoms
891 and are dominated by bacteria in comparison to pristine masks for which gammarids survival is highest.
892 These results are in agreement with data by Crenier et al. (2017) and Rollin et al. (2018) who reported
893 strong and positive influences of diatoms (a high quality resource) on gammarids survival, growth and
894 reproduction. In their *in situ* study, Labed-Veydert et al. (2022) also confirmed the influence of
895 diatoms-dominated biofilms on survival and growth of macroinvertebrates (including gammarids).
896 Therefore, if the qualitative deficiency hypothesis (hypothesis (3)) seems to be the most relevant one
897 for explaining higher mortality of *G. roeselii* fed with biofilm grown on aged masks, we cannot totally
898 exclude the concomitant influence of quantity deficiency (hypothesis (2)) as gut contents of gammarids
899 are reduced with ageing treatment. This latter point is supported by the fragile nature of the biofilms
900 that may inhibit efficient resource shredding by the gammarids. Finally, concerning the potential role
901 of gammarids as dispersers of plastic fibres, experiments do not show evidence significant differences among
902 the various resources considered in terms of number or size of plastic fibre transferred to water
903 (ANOVA: $p > 0.05$; Mean \pm Sd: $0.66 \pm 0.90 \text{ mm}$): plastic fibre transfer by gammarids in the ecosystem is
904 thus not influenced by mask ageing.



905

906 **Figure 7.** Survival and gut content analysis of *G. roeselii* fed on 4 conditioned resource type: leaf litter
 907 (alder), unaged mask (pristine), 1 day (1d) and 3 days (3d) aged mask. **(A)** Kaplan-Meier curves for the
 908 time-to-death of organisms fed on the 4 resources type. **(B)** Gut filling and relative proportion of the 4
 909 items found in the gut of gammarids fed on the 4 resources type. Lowercase letters a, ab and b in
 910 histograms indicate significant differences ($p < 0.05$). **(C)** Example of the items observed in gammarids
 911 gut content by optical microscopy. The displayed items correspond to those found at least once in the
 912 analysed guts of the gammarids sacrificed at the end of the experiment. Diatoms and CPOM were not
 913 found. Size of observed fibres are in agreement with those constituting the 3-layers masks.

914

915 4. Conclusions.

916 Results reported in this work evidence that face masks should be viewed as peculiar plastic waste
 917 as they consist of fibres whose surface area well exceeds that of solid plastic objects of equivalent
 918 mass. We show that mask photodegradation in its early stage is associated with generation of micron-
 919 and nanometre-sized fragments. Surprisingly, the loss of mechanical properties leading to such
 920 fragments does not correlate with changes of most of the bulk material properties monitored over
 921 time by e.g. X-ray diffraction and infrared spectroscopy. The main changes recorded after UV-exposure
 922 involve the production of new chemical groups (carbonyl functions) symptomatic of oxidation process.

923 For the mask intermediate layer, these newly formed chemical functions are detectable after just a
924 few days of UV-exposure. For all three layers, their quantity is significant at 28 days, as evidenced by
925 the variation in the carbonyl index. Analysis of the colloidal features of released fragments reveals that
926 dispersion of these fragments in 1-250 mM salinity solution is possible even at moderate UV dose (3
927 days exposure), meaning that mask debris have gained significant polarity. Remarkably, the
928 dependence of electrophoretic mobility of mask debris on salinity features a similar 'banana' shape,
929 regardless of the crystalline form of the polymer and the advancement of the degradation reaction.
930 SEM observations and chemical analysis further reveal the presence of additives in released fibres,
931 especially TiO₂ nanoparticles located both at the surface and in the bulk of the fibres. Fragmentation
932 that follows degradation increases the exposure of these polluting additives towards aquatic biota, a
933 feature that adds to the well-reported issue of fibres ingestion and intestinal damage in living aquatic
934 organisms. This finding is supported by our observation of a change in the distribution of fluorescent
935 entities upon degradation, from homogeneous to heterogeneous in the form of localized blisters at
936 the fibre surface. Reactivity of pristine and photodegraded masks towards aquatic biota is further
937 addressed in terms of organism diversity/abundance in mask-supported biofilms grown in the Moselle
938 River, and survival of gammarids species fed with these biofilms. Overall, mask ageing primarily
939 reduces the abundance of algae (mainly diatoms) and poorly affects both bacteria abundance and
940 microbial community structure. In addition, the mortality of gammarids is found to increase when
941 feeding on biofilms grown on aged masks, mainly because of a deficiency in food resource quality.

942 Beyond the results briefly summarized above, originality of this work lies in its recourse to a suite
943 of techniques for probing fragments properties versus UV radiation exposure conditions, from the
944 molecular, to colloidal and bulk macroscopic scale. Extensions of this work include additional
945 qualitative and/or quantitative analyses to correlate changes of the different mask properties at short
946 time (i.e. within a few days UV-exposure conditions) with corresponding variations in their colonization
947 by organisms and ecotoxicity effects. Options include the recourse to fluorescence imaging with
948 dedicated molecular probes so as to evaluate hydrophobicity of masks. Establishing firmly specific and
949 mechanistic connections between masks composition/property and effects on biota would further
950 require working with reference samples with simpler chemical composition, like polypropylene
951 particles differing in terms of e.g. organic compounds and inorganic elements.

952 It is expected that the underlying methodology can be applied to other (potentially) hazardous
953 materials, i.e. all objects made of polypropylene fabrics and found outdoors like big bags employed in
954 the construction sector for waste collection or in the agrifood industry to transport grains, or mulching
955 clothes used in gardens to prevent weed growth.

956

957 **CRedit authorship contribution statement**

958 **I.B.:** Conceptualization, Methodology, Validation, Investigation, Writing – original draft, review &
959 editing, Visualization, Supervision, Project administration, Funding acquisition. **R.G.:** Investigation,
960 Supervision. **L.G., A.B., A.R., M.B., D.B., C.B., C.C., P.M., M.Z., F.J., B.G., P.B., C.N.:** Investigation. **M.D.,**
961 **V.F.:** Investigation, Validation, Writing – original draft, Supervision. **C.P.:** Conceptualization,
962 Investigation, Validation, Writing – original draft, Supervision, Funding acquisition. **J.F.L.D.:**
963 Conceptualization, Methodology, Validation, Investigation, Writing – original draft, review & editing,
964 Supervision.

965

966 **Declaration of Competing Interest**

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

969

970 **Data Availability**

971 Data are available upon requests.

972

973

974 **Acknowledgement**

975 This work was financially supported by the Observatoire Terre et Environnement de Lorraine (OTELo)
976 from Nancy, France (Interdisciplinary Project BAlesMASques). This work was performed with
977 ressources from the Pôle de Compétences en Physico-Chimie de l'Environnement, Pôle de
978 Compétences en Chimie Analytique Environnementale, and Pôle de Compétences en Biologie
979 Environnementale, ANATELo, LIEC laboratory, UMR 7360 CNRS – Université de Lorraine. The LERMAB
980 laboratory (EA 4370-Université de Lorraine) is thanked for providing the accelerated ageing chamber.
981 The scanning electron micrographs were acquired on a microscope of the SCMEM-GEORESSOURCES
982 (UMR 7360 CNRS-Université de Lorraine) with assistance of Andreï Lecomte. Christophe Cloquet from
983 the SARM (CRPG, CNRS-Université de Lorraine) is thanked for his contribution to elemental chemical
984 analysis. WAXS experiments were performed on a diffractometer from the Centre de Compétences X-
985 Gamma (IJL, UMR 7198 CNRS-Université de Lorraine). Maria Cellamare (Phyto-Quality, Paris-France) is
986 thanked for the taxonomic identification of algae in biofilms. Yves Waldvogel (Université de Lorraine,
987 CNRS, LIEC, Nancy-France) is thanked for his contribution to electrokinetic and granulometry
988 experiments.

989

990 **Appendix A-N. Supporting Information**

991 Supplementary data associated with this article can be found in the online version.

992

993 **References**

- 994 Alimi, O.S., Claveau-Mallet, D., Lapointe, M., Biu, T., Liu, L., Hernandez, L.M., Bayen, S., Tufenkji, N.,
995 2023. Effects of weathering on the properties and fate of secondary microplastics from a
996 polystyrene single-use cup. *J. Hazard. Mater.* 459, 131855.
- 997 Al-Malaika, S., Axtell, F., Rothon, R., Gilbert, M., 2017. Chapter 7 - Additives for Plastics. In: Gilbert, M.
998 (Ed.), *Brydson's Plastics Materials (Eighth Edition)*. Butterworth-Heinemann, pp. 127–168.
- 999 Almond, J., Sugumaar, P., Wenzel, M.N., Hill, G., Wallis, C., 2020. Determination of the carbonyl index
1000 of polyethylene and polypropylene using specified area under band methodology with ATR-
1001 FTIR spectroscopy. *E-Polym.* 20, 369–381.
- 1002 Ammendolia, J., Saturno, J., Brooks, A.L., Jacobs, S., Jambeck, J.R., 2021. An emerging source of plastic
1003 pollution: Environmental presence of plastic personal protective equipment (PPE) debris
1004 related to COVID-19 in a metropolitan city. *Environ. Pollut.* 269, 116160.
- 1005 Andrady, A.L., 2017. The plastic in microplastics: A review. *Mar. Pollut. Bull.* 119, 12–22.
- 1006 Androsch, R., Di Lorenzo, M.L., Schick, C., Wunderlich, B., 2010. Mesophases in polyethylene,
1007 polypropylene, and poly(1-butene). *Polymer* 51, 4639–4662.
- 1008 Aragaw, T.A., 2020. Surgical face masks as a potential source for microplastic pollution in the COVID-
1009 19 scenario. *Mar. Pollut. Bull.* 159, 111517.
- 1010 Aranberri-Askargorta, I., Lampke, T., Bismarck, A., 2003. Wetting behavior of flax fibers as
1011 reinforcement for polypropylene. *J. Colloid Interface Sci.* 263, 580–589.
- 1012 Aslanzadeh, S., Haghghat Kish, M., 2010. Photo-oxidation of polypropylene fibers exposed to short
1013 wavelength UV radiations. *Fibers Polym.* 11, 710–718.
- 1014 Au, S.Y., Bruce, T.F., Bridges, W.C., Klaine, S.J., 2015. Responses of *Hyalella azteca* to acute and chronic
1015 microplastic exposures: Effects of Microplastic Exposure on *Hyalella azteca*. *Environ. Toxicol.*
1016 *Chem.* 34, 2564–2572.

- 1017 Benítez, A., Sánchez, J.J., Arnal, M.L., Müller, A.J., Rodríguez, O., Morales, G., 2013. Abiotic degradation
1018 of LDPE and LLDPE formulated with a pro-oxidant additive. *Polym. Degrad. Stab.* 98, 490–501.
- 1019 Benson, N.U., Basse, D.E., Palanisami, T., 2021. COVID pollution: impact of COVID-19 pandemic on
1020 global plastic waste footprint. *Heliyon* 7, e06343.
- 1021 Blais, P., Carlsson, D.J., Wiles, D.M., 1972. Surface changes during polypropylene photo-oxidation: A
1022 study by infrared spectroscopy and electron microscopy. *J. Polym. Sci. [A1]* 10, 1077–1092.
- 1023 Blarer, P., Burkhardt-Holm, P., 2016. Microplastics affect assimilation efficiency in the freshwater
1024 amphipod *Gammarus fossarum*. *Environ. Sci. Pollut. Res.* 23, 23522–23532.
- 1025 Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem.*
1026 *Soc.* 60, 309–319.
- 1027 Celina, M., George, G.A., Billingham, N.C., 1993. Physical spreading of oxidation in solid polypropylene
1028 as studied by chemiluminescence. *Polym. Degrad. Stab.* 42, 335–344.
- 1029 Chae, Y., Kim, D., Kim, S.W., An, Y.-J., 2018. Trophic transfer and individual impact of nano-sized
1030 polystyrene in a four-species freshwater food chain. *Sci. Rep.* 8, 284.
- 1031 Chow, K.Y., Grant, D.J.W., 1988. Surface analysis of griseofulvin powders by krypton adsorption:
1032 Evaluation of specific surface area, BET constant C and polanyi adsorption potential. *Powder*
1033 *Technol.* 56, 209–223.
- 1034 Chowdhury, H., Chowdhury, T., Sait, S.M., 2021. Estimating marine plastic pollution from COVID-19
1035 face masks in coastal regions. *Mar. Pollut. Bull.* 168, 112419.
- 1036 Cooksey, K.E., Wigglesworth-Cooksey, B., 1995. Adhesion of bacteria and diatoms to surfaces in the
1037 sea: a review. *Aquat. Microb. Ecol.*
- 1038 Crenier, C., Arce-Funck, J., Bec, A., Billoir, E., Perrière, F., Leflaive, J., Guérol, F., Felten, V., Danger, M.,
1039 2017. Minor food sources can play a major role in secondary production in detritus-based
1040 ecosystems. *Freshw. Biol.* 62, 1155–1167.
- 1041 de Sá, L.C., Oliveira, M., Ribeiro, F., Rocha, T.L., Futter, M.N., 2018. Studies of the effects of
1042 microplastics on aquatic organisms: What do we know and where should we focus our efforts
1043 in the future? *Sci. Total Environ.* 645, 1029–1039.
- 1044 Duval, J.F.L., Farinha, J.P.S., Pinheiro, J.P., 2013. Impact of Electrostatics on the Chemodynamics of
1045 Highly Charged Metal–Polymer Nanoparticle Complexes. *Langmuir* 29, 13821–13835.
- 1046 Duval, J.F.L., Leermakers, F.A.M., van Leeuwen, H.P., 2004. Electrostatic Interactions between Double
1047 Layers: Influence of Surface Roughness, Regulation, and Chemical Heterogeneities. *Langmuir*
1048 20, 5052–5065.
- 1049 Duval, J.F.L., Ohshima, H., 2006. Electrophoresis of Diffuse Soft Particles. *Langmuir* 22, 3533–3546.
- 1050 Felske, A., Akkermans, A.D.L., De Vos, W.M., 1998. Quantification of 16S rRNAs in Complex Bacterial
1051 Communities by Multiple Competitive Reverse Transcription-PCR in Temperature Gradient Gel
1052 Electrophoresis Fingerprints. *Appl. Environ. Microbiol.* 64, 4581–4587.
- 1053 Felten, V., Tixier, G., Guérol, F., De Crespín De Billy, V., Dangles, O., 2008. Quantification of diet
1054 variability in a stream amphipod: implications for ecosystem functioning. *Fundam. Appl.*
1055 *Limnol.* 170, 303–313.
- 1056 Felten, V., Toumi, H., Masfarau, J.-F., Billoir, E., Camara, B.I., Féral, J.-F., 2020. Microplastics enhance
1057 *Daphnia magna* sensitivity to the pyrethroid insecticide deltamethrin: Effects on life history
1058 traits. *Sci. Total Environ.* 714, 136567.
- 1059 Ferreira, I., Venâncio, C., Lopes, I., Oliveira, M., 2019. Nanoplastics and marine organisms: What has
1060 been studied? *Environ. Toxicol. Pharmacol.* 67, 1–7.
- 1061 Fries, E., Dekiff, J.H., Willmeyer, J., Nuelle, M.-T., Ebert, M., Remy, D., 2013. Identification of polymer
1062 types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning
1063 electron microscopy. *Environ. Sci. Process. Impacts* 15, 1949.
- 1064 Gigault, J., Halle, A. ter, Baudrimont, M., Pascal, P.-Y., Gauffre, F., Phi, T.-L., El Hadri, H., Grassl, B.,
1065 Reynaud, S., 2018. Current opinion: What is a nanoplastic? *Environ. Pollut.* 235, 1030–1034.
- 1066 Goikhman, A.S., Kirichenko, V.I., Budnitskii, G.A., 1984. X-Ray diffraction measurements of the
1067 crystallinity of polypropylene fibres. *Polym. Sci. USSR* 26, 974–981.

1068 Gooch, J.W., 2002. Analysis and Deformulation of Polymeric Materials, Topics in Applied Chemistry.
1069 Kluwer Academic Publishers, Boston.

1070 Gopmandal, P.P., Duval, J.F.L., 2022. Electrostatics and electrophoresis of engineered nanoparticles
1071 and particulate environmental contaminants: Beyond zeta potential-based formulation. *Curr.*
1072 *Opin. Colloid Interface Sci.* 60, 101605.

1073 Guo, Y., Liu, Y., Xiang, T., Li, J., Lv, M., Yan, Y., Zhao, J., Sun, J., Yang, X., Liao, C., Fu, J., Shi, J., Qu, G.,
1074 Jiang, G., 2023. Disposable Polypropylene Face Masks: A Potential Source of
1075 Micro/Nanoparticles and Organic Contaminates in Humans. *Environ. Sci. Technol.* 57, 5739–
1076 5750.

1077 Hu, T., Shen, M., Tang, W., 2022. Wet wipes and disposable surgical masks are becoming new sources
1078 of fiber microplastic pollution during global COVID-19. *Environ. Sci. Pollut. Res.* 29, 284–292.

1079 Hughes, R.H., 1969. The determination of the isotacticity of polypropylene in the 90–100% range by
1080 infrared spectroscopy. *J. Appl. Polym. Sci.* 13, 417–425.

1081 Isasi, J.R., Mandelkern, L., Galante, M.J., Alamo, R.G., 1999. The degree of crystallinity of monoclinic
1082 isotactic poly(propylene). *J. Polym. Sci. Part B Polym. Phys.* 37, 323–334.

1083 Ismail, M.F., Islam, M.A., Khorshidi, B., Sadrzadeh, M., 2021. Prediction of surface charge properties on
1084 the basis of contact angle titration models. *Mater. Chem. Phys.* 258, 123933.

1085 Jacobasch, H.-J., 1984. Characterization of the adhesion properties of polymers by electrokinetic
1086 measurements. *Angew. Makromol. Chem.* 128, 47–69.

1087 Klindworth, A., Pruesse, E., Schweer, T., Peplies, J., Quast, C., Horn, M., Glöckner, F.O., 2013. Evaluation
1088 of general 16S ribosomal RNA gene PCR primers for classical and next-generation sequencing-
1089 based diversity studies. *Nucleic Acids Res.* 41, e1.

1090 Košíková, B., Revajová, A., Demianová, V., 1995. The effect of adding lignin on modification of surface
1091 properties of polypropylene. *Eur. Polym. J.* 31, 953–956.

1092 Kotek, J., Kelnar, I., Baldrian, J., Raab, M., 2004. Structural transformations of isotactic polypropylene
1093 induced by heating and UV light. *Eur. Polym. J.* 40, 2731–2738.

1094 Labeled-Veydert, T., Danger, M., Felten, V., Bec, A., Laviale, M., Cellamare, M., Desvillettes, C., 2022.
1095 Microalgal food sources greatly improve macroinvertebrate growth in detritus-based
1096 headwater streams: Evidence from an instream experiment. *Freshw. Biol.* 67, 1380–1394.

1097 Lacoste, J., Vaillant, D., Carlsson, D.J., 1993. Gamma-, photo-, and thermally-initiated oxidation of
1098 isotactic polypropylene. *J. Polym. Sci. Part Polym. Chem.* 31, 715–722.

1099 Lambert, S., Scherer, C., Wagner, M., 2017. Ecotoxicity testing of microplastics: Considering the
1100 heterogeneity of physicochemical properties: Ecotoxicity Testing of Microplastics. *Integr.*
1101 *Environ. Assess. Manag.* 13, 470–475.

1102 Lambert, S., Wagner, M., 2016. Formation of microscopic particles during the degradation of different
1103 polymers. *Chemosphere* 161, 510–517.

1104 Lee, Q.-Y., Li, H., 2021. Photocatalytic Degradation of Plastic Waste: A Mini Review. *Micromachines* 12,
1105 907.

1106 Lima, M.F.S., Vasconcellos, M.A.Z., Samios, D., 2002. Crystallinity changes in plastically deformed
1107 isotactic polypropylene evaluated by x-ray diffraction and differential scanning calorimetry
1108 methods. *J. Polym. Sci. Part B Polym. Phys.* 40, 896–903.

1109 Liu, X., Cao, W., Xie, L., Sun, C., Jiang, F., 2022. Photoaging Characteristics of Disposable Masks under
1110 UV Irradiation. *J. Mar. Sci. Eng.* 10, 170.

1111 Lund, J.W.G., Kipling, C., Le Cren, E.D., 1958. The inverted microscope method of estimating algal
1112 numbers and the statistical basis of estimations by counting. *Hydrobiologia* 11, 143–170.

1113 Luongo, J.P., 1960. Infrared study of polypropylene. *J. Appl. Polym. Sci.* 3, 302–309.

1114 Ma, J., Chen, F., Xu, H., Jiang, H., Liu, J., Li, P., Chen, C.C., Pan, K., 2021. Face masks as a source of
1115 nanoplastics and microplastics in the environment: Quantification, characterization, and
1116 potential for bioaccumulation. *Environ. Pollut.* 288, 117748.

1117 Ma, J., Chen, F., Xu, H., Liu, J., Chen, C.C., Zhang, Z., Jiang, H., Li, Y., Pan, K., 2022. Fate of face masks
1118 after being discarded into seawater: Aging and microbial colonization. *J. Hazard. Mater.* 436,
1119 129084.

1120 Machado, G., Denardin, E.L.G., Kinast, E.J., Gonçalves, M.C., de Luca, M.A., Teixeira, S.R., Samios, D.,
1121 2005. Crystalline properties and morphological changes in plastically deformed isotactic
1122 polypropylene evaluated by X-ray diffraction and transmission electron microscopy. *Eur.*
1123 *Polym. J.* 41, 129–138.

1124 Mateos-Cárdenas, A., O'Halloran, J., van Pelt, F.N.A.M., Jansen, M.A.K., 2020. Rapid fragmentation of
1125 microplastics by the freshwater amphipod *Gammarus duebeni* (Lillj.). *Sci. Rep.* 10, 12799.

1126 Men, C., Liu, R., Xu, F., Wang, Q., Guo, L., Shen, Z., 2018. Pollution characteristics, risk assessment, and
1127 source apportionment of heavy metals in road dust in Beijing, China. *Sci. Total Environ.* 612,
1128 138–147.

1129 Morgana, S., Casentini, B., Amalfitano, S., 2021. Uncovering the release of micro/nanoplastics from
1130 disposable face masks at times of COVID-19. *J. Hazard. Mater.* 419, 126507.

1131 Muller, E.I., Souza, J.P., Muller, C.C., Muller, A.L.H., Mello, P.A., Bizzi, C.A., 2016. Microwave-assisted
1132 wet digestion with H₂O₂ at high temperature and pressure using single reaction chamber for
1133 elemental determination in milk powder by ICP-OES and ICP-MS. *Talanta* 156–157, 232–238.

1134 Natta, G., Corradini, P., 1960. Structure and Properties of Isotactic Polypropylene. *Nuovo Cimento Suppl*
1135 40–51.

1136 Nishida, K., Okada, K., Asakawa, H., Matsuba, G., Ito, K., Kanaya, T., Kaji, K., 2012. In situ observations
1137 of the mesophase formation of isotactic polypropylene—A fast time-resolved X-ray diffraction
1138 study. *Polym. J.* 44, 95–101.

1139 Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L.,
1140 Santos, E.M., Paull, G.C., Van Look, K.J.W., Tyler, C.R., 2009. A critical analysis of the biological
1141 impacts of plasticizers on wildlife. *Philos. Trans. R. Soc. B Biol. Sci.* 364, 2047–2062.

1142 Ogonowski, M., Schür, C., Jarsén, Å., Gorokhova, E., 2016. The Effects of Natural and Anthropogenic
1143 Microparticles on Individual Fitness in *Daphnia magna*. *PLOS ONE* 11, e0155063.

1144 Ohtani, B., Adzuma, S., Miyadzu, H., Nishimoto, S., Kagiya, T., 1989. Photocatalytic degradation of
1145 polypropylene film by dispersed titanium dioxide particles. *Polym. Degrad. Stab.* 23, 271–278.

1146 Parashar, N., Hait, S., 2021. Plastics in the time of COVID-19 pandemic: Protector or polluter? *Sci. Total*
1147 *Environ.* 759, 144274.

1148 Patrício Silva, A.L., Prata, J.C., Walker, T.R., Campos, D., Duarte, A.C., Soares, A.M.V.M., Barcelò, D.,
1149 Rocha-Santos, T., 2020. Rethinking and optimising plastic waste management under COVID-19
1150 pandemic: Policy solutions based on redesign and reduction of single-use plastics and personal
1151 protective equipment. *Sci. Total Environ.* 742, 140565.

1152 Pereira, L.S.F., Pedrotti, M.F., Miceli, T.M., Pereira, J.S.F., Flores, E.M.M., 2016. Determination of
1153 elemental impurities in poly(vinyl chloride) by inductively coupled plasma optical emission
1154 spectrometry. *Talanta* 152, 371–377.

1155 Philippart, J.-L., Sinturel, C., Arnaud, R., Gardette, J.-L., 1999. Influence of the exposure parameters on
1156 the mechanism of photooxidation of polypropylene. *Polym. Degrad. Stab.* 13.

1157 Philippart, J.-L., Sinturel, C., Gardette, J.-L., 1997. Influence of light intensity on the photooxidation of
1158 polypropylene. *Polym. Degrad. Stab.* 58, 261–268.

1159 Prata, J.C., Silva, A.L.P., Walker, T.R., Duarte, A.C., Rocha-Santos, T., 2020. COVID-19 Pandemic
1160 Repercussions on the Use and Management of Plastics. *Environ. Sci. Technol.* 54, 7760–7765.

1161 Qiao, R., Deng, Y., Zhang, S., Wolosker, M.B., Zhu, Q., Ren, H., Zhang, Y., 2019. Accumulation of
1162 different shapes of microplastics initiates intestinal injury and gut microbiota dysbiosis in the
1163 gut of zebrafish. *Chemosphere* 236, 124334.

1164 R Core Team, 2019. A Language and Environment for Statistical Computing. R Foundation for Statistical
1165 Computing, <https://www.R-project.org/>.

1166 Rao, T.S., Rani, P.G., Venugopalan, V.P., Nair, K.V.K., 1997. Biofilm formation in a freshwater
1167 environment under photic and aphotic conditions. *Biofouling* 11, 265.

1168 Rathinamoorthy, R., Balasaraswathi, S.R., 2022. Disposable tri-layer masks and microfiber pollution –
1169 An experimental analysis on dry and wet state emission. *Sci. Total Environ.* 816, 151562.

1170 Ren, Z., Shanks, R.A., Rook, T.J., 2002. Processing and Properties of Polypropylene Composites with
1171 High Filler Content. *Polym. Compos.* 10, 10.

1172 Rochman, C.M., Hoh, E., Hentschel, B.T., Kaye, S., 2013. Long-Term Field Measurement of Sorption of
1173 Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic Marine Debris.
1174 *Environ. Sci. Technol.* 47, 1646–1654.

1175 Rollin, M., Coulaud, R., Danger, M., Sohm, B., Flayac, J., Bec, A., Chaumot, A., Geffard, O., Felten, V.,
1176 2018. Additive effect of calcium depletion and low resource quality on *Gammarus fossarum*
1177 (Crustacea, Amphipoda) life history traits. *Environ. Sci. Pollut. Res. Int.* 25, 11264–11280.

1178 Rouillon, C., Bussiere, P.-O., Desnoux, E., Collin, S., Vial, C., Therias, S., Gardette, J.-L., 2016. Is carbonyl
1179 index a quantitative probe to monitor polypropylene photodegradation? *Polym. Degrad. Stab.*
1180 128, 200–208.

1181 Saliu, F., Veronelli, M., Raguso, C., Barana, D., Galli, P., Lasagni, M., 2021. The release process of
1182 microfibers: from surgical face masks into the marine environment. *Environ. Adv.* 4, 100042.

1183 Severini, F., Gallo, R., Ipsale, S., 1988. Environmental degradation of polypropylene. *Polym. Degrad.*
1184 *Stab.* 22, 185–194.

1185 Shrivastava, A., 2018. 4 - Additives for Plastics. In: Shrivastava, A. (Ed.), *Introduction to Plastics*
1186 *Engineering, Plastics Design Library*. William Andrew Publishing, pp. 111–141.

1187 Škvarla, J., 2007. Hard versus Soft Particle Electrokinetics of Silica Colloids. *Langmuir* 23, 5305–5314.

1188 Slepíčka, P., Vasina, A., Kolská, Z., Luxbacher, T., Malinský, P., Macková, A., Švorčík, V., 2010. Argon
1189 plasma irradiation of polypropylene. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact.*
1190 *Mater. At.*, 19th International Conference on Ion Beam Analysis 268, 2111–2114.

1191 Song, J., Duval, J.F.L., Cohen Stuart, M.A., Hillborg, H., Gunst, U., Arlinghaus, H.F., Vancso, G.J., 2007.
1192 Surface Ionization State and Nanoscale Chemical Composition of UV-Irradiated
1193 Poly(dimethylsiloxane) Probed by Chemical Force Microscopy, Force Titration, and
1194 Electrokinetic Measurements. *Langmuir* 23, 5430–5438.

1195 STATISTA, 2022. Face Masks - Worldwide | Statista Market Forecast [WWW Document]. URL
1196 <https://www.statista.com/outlook/cmo/tissue-hygiene-paper/face-masks/worldwide>
1197 (accessed 12.13.22).

1198 Wang, Z., An, C., Chen, X., Lee, K., Zhang, B., Feng, Q., 2021. Disposable masks release microplastics to
1199 the aqueous environment with exacerbation by natural weathering. *J. Hazard. Mater.* 417,
1200 126036.

1201 WHO, 2021. When and how to use masks [WWW Document]. URL
1202 [https://www.who.int/emergencies/diseases/novel-coronavirus-2019/advice-for-](https://www.who.int/emergencies/diseases/novel-coronavirus-2019/advice-for-public/when-and-how-to-use-masks)
1203 [public/when-and-how-to-use-masks](https://www.who.int/emergencies/diseases/novel-coronavirus-2019/advice-for-public/when-and-how-to-use-masks) (accessed 1.6.23).

1204 Wright, R.J., Erni-Cassola, G., Zadjelovic, V., Latva, M., Christie-Oleza, J.A., 2020. Marine Plastic Debris:
1205 A New Surface for Microbial Colonization. *Environ. Sci. Technol.* 54, 11657–11672.

1206 Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine
1207 organisms: A review. *Environ. Pollut.* 178, 483–492.

1208 Wu, P., Li, J., Lu, X., Tang, Y., Cai, Z., 2022. Release of tens of thousands of microfibers from discarded
1209 face masks under simulated environmental conditions. *Sci. Total Environ.* 806, 150458.

1210 Zimmermann, R., Dukhin, S., Werner, C., 2001. Electrokinetic Measurements Reveal Interfacial Charge
1211 at Polymer Films Caused by Simple Electrolyte Ions. *J. Phys. Chem. B* 105, 8544–8549.

1212

APPENDIX - Supporting Information

Photodegradation of disposable polypropylene face masks: physicochemical properties of debris and implications for the toxicity of mask-carried river biofilms.

Isabelle Bihannic,^{a,*} Renaud Gley,^a Lucas Gallo,^a Apolline Badura,^a Angelina Razafitianamaharavo,^a Maximilien Beuret,^b David Billet,^a Clément Bojic,^b Céline Caillet,^a Philippine Morlot,^b Marie Zaffino,^b Fatina Jouni,^b Béatrice George,^c Pascal Boulet,^d Camille Noûs,^e Michael Danger,^b Vincent Felten,^b Christophe Pagnout,^b Jérôme F.L. Duval^{a,*}

a. Université de Lorraine, CNRS, LIEC, F-54000 Nancy, France.

b. Université de Lorraine, CNRS, LIEC, F-57000 Metz, France.

c. Université de Lorraine, INRAE, LERMAB, F-54000 Nancy, France.

d. Université de Lorraine, CNRS, IJL, F-54000 Nancy, France.

e. Cogitamus Laboratory, Paris, France.

* Corresponding authors. Email: isabelle.bihannic@univ-lorraine.fr, jerome.duval@univ-lorraine.fr

This document contains 23 pages and 17 supplementary figures and 1 supplementary table.

OUTLINE.

A. Materials and Methods.

B. Experimental set up for mask exposure in the Moselle river.

C. Aspect of masks after photodegradation.

D. Complementary Wide-Angle X-ray Scattering (WAXS) results.

E. Complementary Scanning Electron Microscopy (SEM) results.

F. Complementary Atomic Force Microscopy (AFM) results.

G. Complementary gas adsorption results.

H. Complementary electrophoretic mobility results.

I. Characterization of nanoparticles released from polypropylene granulates.

J. Determination of the amount of released carboxylic acids by ion chromatography.

K. Analysis of bacterial community composition in freshwater biofilms grown on masks.

L. Analysis of phytoplankton community composition in freshwater biofilms grown on masks.

M. Additional illustrative confocal microscopy images of freshwater biofilms grown on masks.

N. Observation of mineral deposits in the freshwater biofilm grown on masks.

O. References.

A. Materials and Methods

Preamble. The question of the very significance of reporting standard deviations for the different indexes (Cl_x , HC_{IR} and Cal_{IR}) provided in **Table 1** (in main text) for the bulk properties of polypropylene masks is debatable, as judged by previous studies/comments published in journals focusing on polymer chemistry and degradation. In particular, concerning carbonyl index, Celina et al. (2021) extensively details the "significant error margins in carbonyl quantification, with exact carbonyl species and extinction coefficients already being major contributors on their own". The authors further argue that "experimental variances depend on the combination of uncertainty in exact carbonyl species, extinction coefficient, contributions from neighboring convoluting peaks, matrix interaction phenomena and instrumental variations in primary IR spectral acquisition (refractive index and penetration depth for ATR measurements)". Given the inherent heterogeneity of composition of pristine masks from one sample to another, and the obvious heterogeneity of masks composition/structure brought by photodegradation process from molecular to macroscopic scale (cf. e.g. **Figures 2**, and **Figures C.1(b)** and **E.3** in this **Supporting Information**), a question to be asked is how many mask samples must be tested to provide statistically meaningful standard deviation information. That question has no obvious answer. Probably the amount of required pristine masks (subsequently subjected to UV treatment) to be tested should be sufficiently large so as to cover the entire spectrum of heterogeneities of their physicochemical and elemental composition properties, i.e. surely more than $N=3$ or 4 , and most probably a few hundreds or more, that is the amount typically considered to check reproducibility of large-scale mask production. Accordingly, and given the costs of the multi-technique measurements we provide, it is not practically feasible and scientifically meaningful to provide statistically relevant standard deviations for the indexes pertaining to bulk mask properties (Cl_x , HC_{IR} and Cal_{IR}).

Wide Angle X-ray scattering (WAXS).

Wide angle X-ray scattering pattern were recorded with a 2D BRUKER APEX II detector. Obtained images of dimension 512×512 pixels (pixel size of $75 \times 75 \mu\text{m}^2$, binning of 8) were collected with a 60 s acquisition time. Samples were positioned at the centre of the goniometer with help of a goniometer head. The mechanical strength of most of the photodegraded materials made it possible to stack 4 layers at the centre of the sample-holder. For the most degraded samples (i.e. after 28 days of UV treatment), two Kapton windows were required to close the sample holder. Scattering from the background (air and/or Kapton windows) was recorded and removed after transmission correction. One-dimensional diffraction curves were calculated from the two-dimensional WAXS patterns according to an angular averaging procedure.

Data processing consisted in decomposing the whole WAXS diagram on the angular domain covering the 11 to $24-2\theta$ degrees range. The experimental curves were decomposed into the sum of peaks associated with crystallized phases, plus an additional contribution corresponding to the amorphous halo. Each peak marking the presence of a crystallized phase was fitted to a pseudo-Voigt function, and the amorphous halo was adjusted to a split Gaussian component. Data were analysed using the open-source fitting software Fityk (Wojdyr, 2010).

Fourier Transform Infrared spectroscopy (FTIR).

For pristine mask specimens (unexposed to UV) and short time UV-treated specimens (1, 2 or 3 days), fibers were pulled out from layers with tweezers. Approximately 1 mg of the fibre samples was sandwiched homogeneously between two layers of ground KBr powder of 100 mg each (Reference

221864-25G FT-IR, grade \geq 99% trace metals basis, SIGMA-MERCK) and compressed to form 13 mm diameter pellets. For mask layers highly degraded by UV exposition (e.g. after 28 days in the QUV tester), around 1 mg of powdery samples was mixed with KBr powder and ground in an agate mortar before compression in 13 mm pellets.

Gas adsorption.

Gas adsorption experiments were conducted using krypton. The choice of this gas probe as adsorbate is motivated by the expected small SSA of the materials of interest in this work. Prior to adsorption measurement, about 250 mg of samples was outgassed overnight at 60°C under turbo pump vacuum, until a vacuum of 10^{-5} Pa was achieved. High Purity Krypton (Kr N48, purity $>$ 99.995%) used for the experiments was provided by Alphagaz (France). Specific surface areas were estimated on the basis of the Brunauer-Emmet-Teller (BET) equation (Brunauer et al., 1938) adopting 21 \AA^2 for the effective cross-sectional area occupied by an adsorbed krypton atom (Sing, 1985). The relative pressure window used for the calculation ranges from 0.05 to 0.3. Regular analyses performed on a certified reference material (SiO_2 BAM-PM-101 purchased from the Federal Institute for Materials Research and Testing, Germany) with a SSA of $0.177 \pm 0.004 \text{ m}^2\text{g}^{-1}$ led to a $0.02 \text{ m}^2\text{g}^{-1}$ precision on that sample.

Atomic Force Microscopy (AFM).

A few drops of ethanol suspension containing mask fragments were deposited onto a cleaned borosilicate glass slide and immediately dried at ambient temperature. AFM probes used for measurements were NPG Silicon Nitride tips (30 nm apex curvature radius) with nominal spring constant value $0.32 \pm 0.2 \text{ N/m}$.

Electrokinetics.

Suspensions were prepared for electrokinetic measurements by collecting 18 mg of photodegraded mask debris and dispersing them into 80 mL of a so-called 'very soft' water. The very soft water was prepared by adding 24 mg of NaHCO_3 , 15 mg of CaSO_4 and MgSO_4 , and 1 mg of KCl to 2 L of ultra-pure water. Prior to electrophoretic mobility measurements, the debris suspension (pH 7.35) was agitated for 1 hour on a rocking table. The first point of the mobility versus $[\text{KNO}_3]$ curve was recorded on this suspension. Then, KNO_3 salt concentration in the debris suspension was varied upon proper addition of 2 M KNO_3 aliquots so as to reach a solution ionic strength we varied in the range 0.57 mM (ionic strength of very soft water) to 250 mM. In a last series of experiments, we measured the dependence of the electrophoretic mobility of plastic debris on solution pH (3 to 10) adjusted with proper addition of 1 M HNO_3 solution (one batch, pH 7 to 3) or 1 M NaOH solution (second batch, pH 7 to 10) in 12 mM KNO_3 solution.

16S rRNA gene quantification.

The qPCR reactions were performed in 20 μL with 400 nM reverse and forward primers, 0.6 $\mu\text{g}/\mu\text{L}$ BSA, 1% dimethylsulfoxide, 10 μL Fast SYBR Green master mix (Invitrogen) and 2 μL of extracted DNA at 2.5 $\text{ng}/\mu\text{L}$, or 1 μL of linear plasmid used as standard or milliQ water for negative control. Amplification conditions were 30 s at 95°C and 40 cycles of 95°C for 30 s, 30 s at 60°C, and 72°C for 30 s, followed by a final extension of 7 min at 72°C. Melting curves were generated from 52°C to 95°C with an increase of 0.5°C every 5 s. For each sample, melting curves were manually checked to verify amplification specificity. A standard curve was constructed from a 10-fold serial dilution (10^9 to 10^1 gene copies per μL) of PstI linearized pJET1.2 plasmids containing the 16S rRNA gene of *E. coli* JM109.

Toxicity assay.

All food resource discs were freeze-dried and weighed to the nearest 0.01 mg (with a Perkin Elmer AD6 Autobalance) before and after being offered to gammarids. A set of 72 juvenile *G. roeseli* was sorted according to their body length and was photographed under a stereomicroscope ($\times 6$ to $\times 40$ magnification) in their curved state. Length was recorded from the base of the first antenna to the base of the telson (carried by the third uromere) by following the upper part of the pereiomere using SigmaScan Image Analysis Version 5.000 (SPSS Inc, Chicago, IL, USA; linear state = $0.88 \times$ curved state [mm]; $R^2 = 0.98$). Initial total body length of gammarids did not differ between the 4 tested conditions (mean size \pm SD: 5.07 ± 0.66 mm; $F_{3,68} = 0.45$; $p > 0.05$; one-way ANOVA). Juvenile gammarids were randomly transferred in replicates to initiate the experiment.

B. Experimental set-up for mask exposure in the Moselle River.



Figure B.1. Masks were sandwiched between two transparent polymethyl methacrylate sheets. The upper sheet was openwork to allow mask colonization by microorganisms during exposure in the river. This experimental device was weighted and horizontally immersed in the Moselle River for 4 weeks.

C. Aspect of masks after photodegradation.

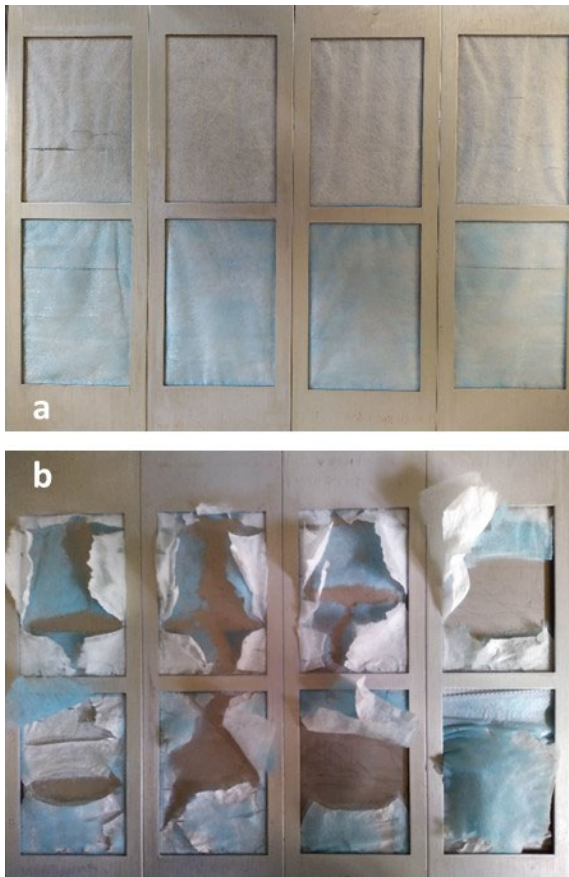


Figure C.1 Aspects of masks on sample holders immediately after their removal from the UV-ageing chamber. The size of the opening in the sample holder is 6 cm×9 cm. **(a)**: masks after 3 days UV-exposure. **(b)**: masks after 28 days UV-exposure.

D. Complementary Wide Angle X-ray Scattering (WAXS) results.

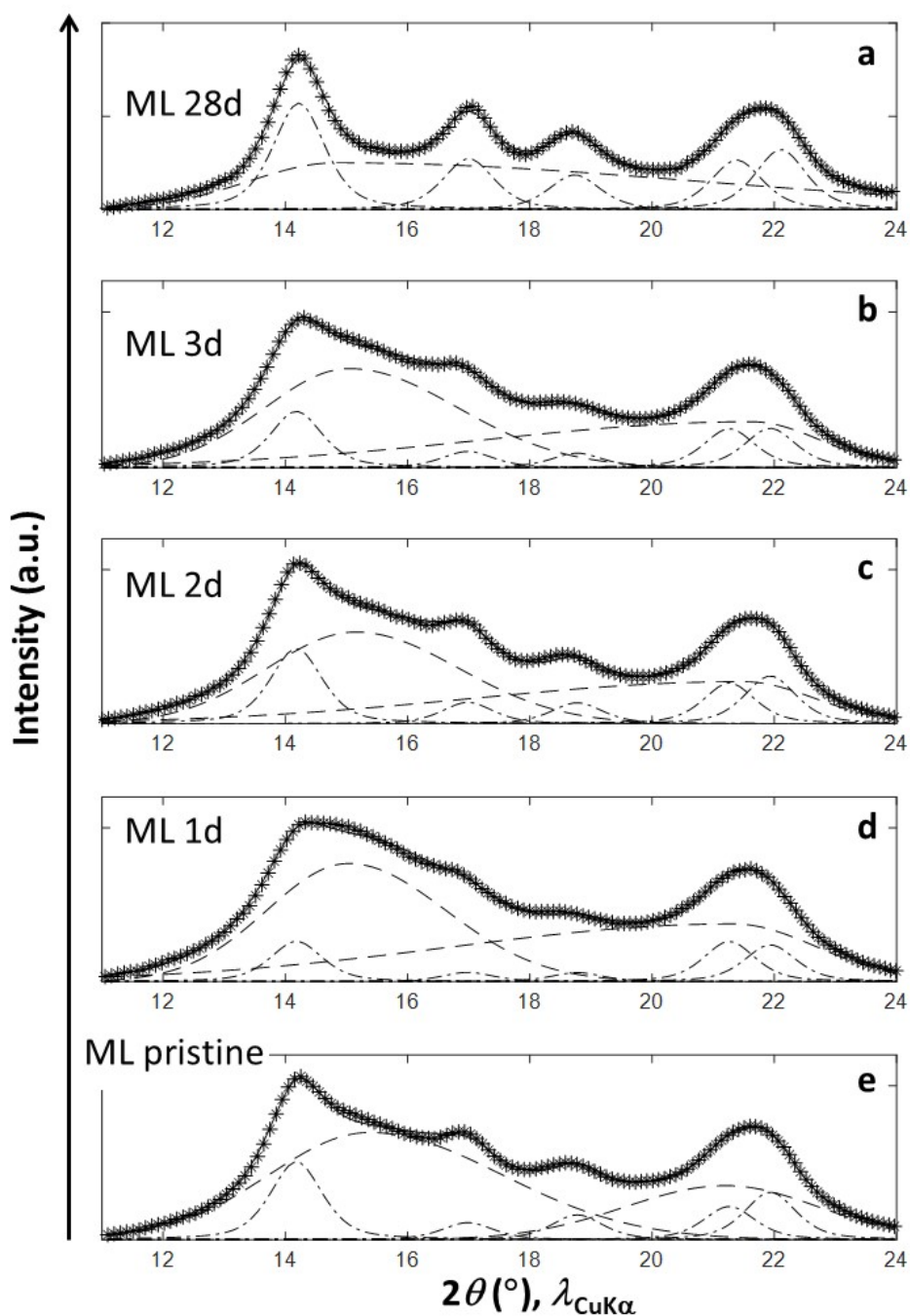


Figure D.1. Decomposition of the Wide-Angle X-rays Scattering (WAXS) curves recorded for the middle layer (ML) in pristine state or after ageing (indicated). For UV exposure duration shorter or equal to 3 days ((b) to (e)), each experimental curve (-*) is decomposed using 5 contributing peaks at fixed angular positions (indicated) corresponding to the α -monoclinic phase, plus two additional broad contributions (indicated) corresponding to the amorphous phase.

E. Complementary Scanning Electron Microscopy (SEM) results.

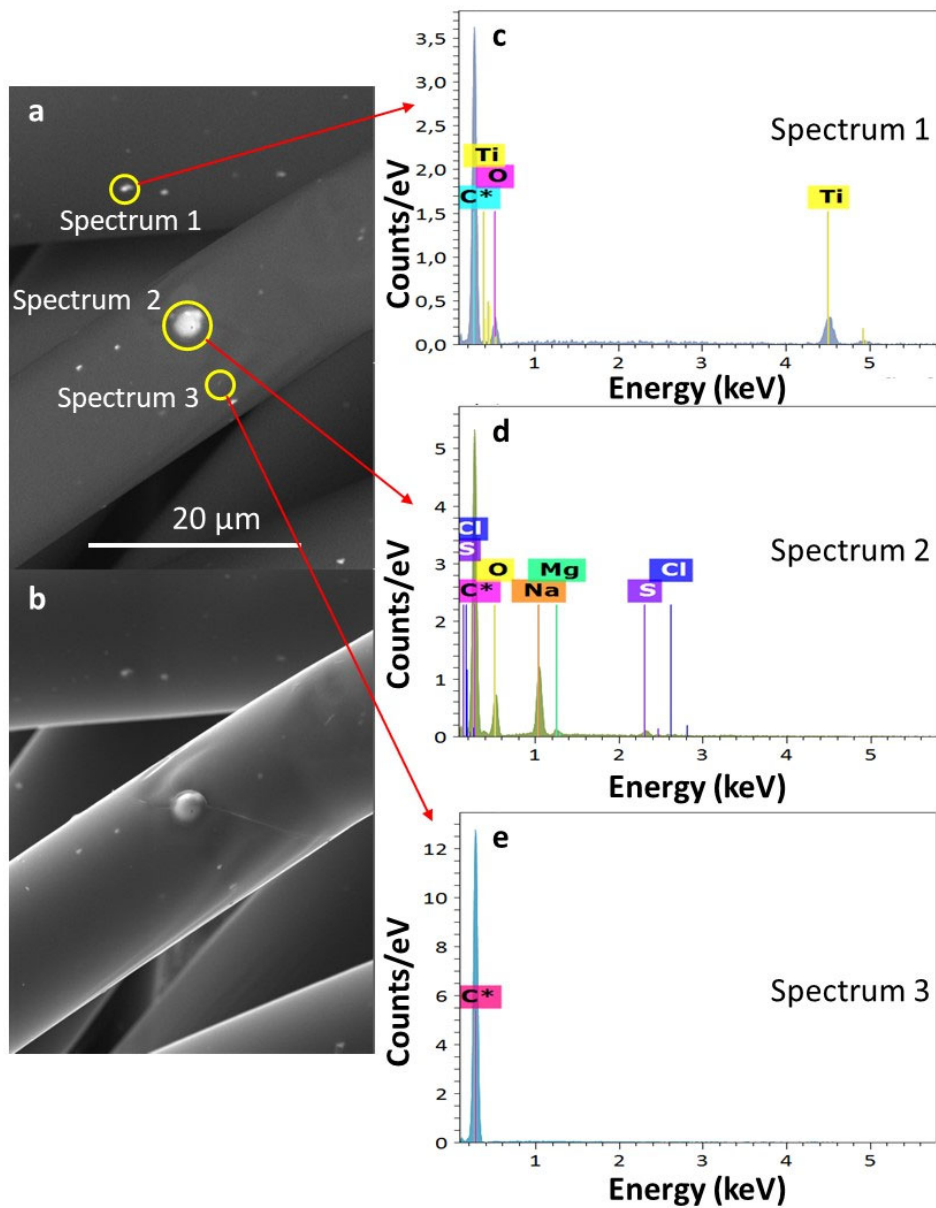


Figure E.1. (a) Illustrative Scanning electron micrographs (SEM) of pristine inner layer (IL). (b) Detection of backscattered electrons (BSE) corresponding to (a). (c)-(e) Detection of secondary electrons (SE) (corresponding analysed areas are identified in (a)) and elemental analysis by energy dispersive X-ray spectroscopy (EDS). Ca element was also detected in some of the spectra corresponding to the condition in panel (d).

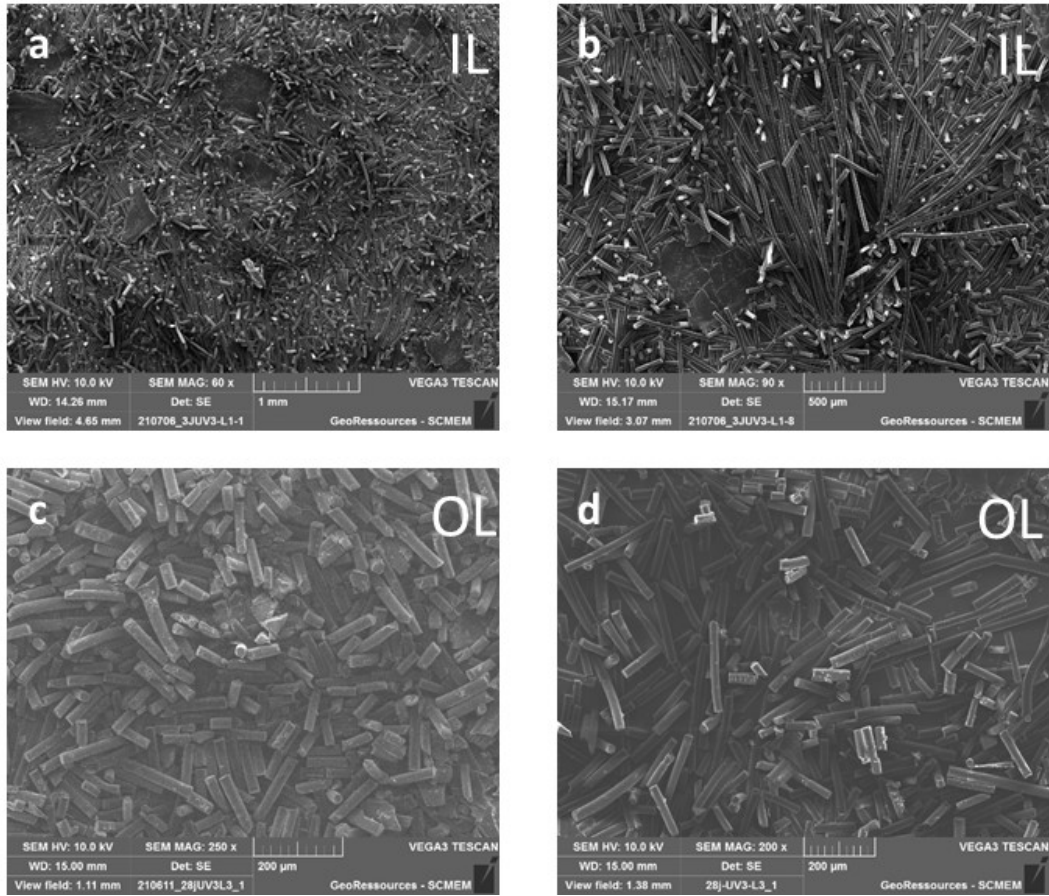


Figure E.2. Scanning electron micrographs of 3 days UV-exposed inner layer ((a)-(b)) and outer layer ((c)-(d)). Micrographs correspond to secondary electrons (SE) detection mode.

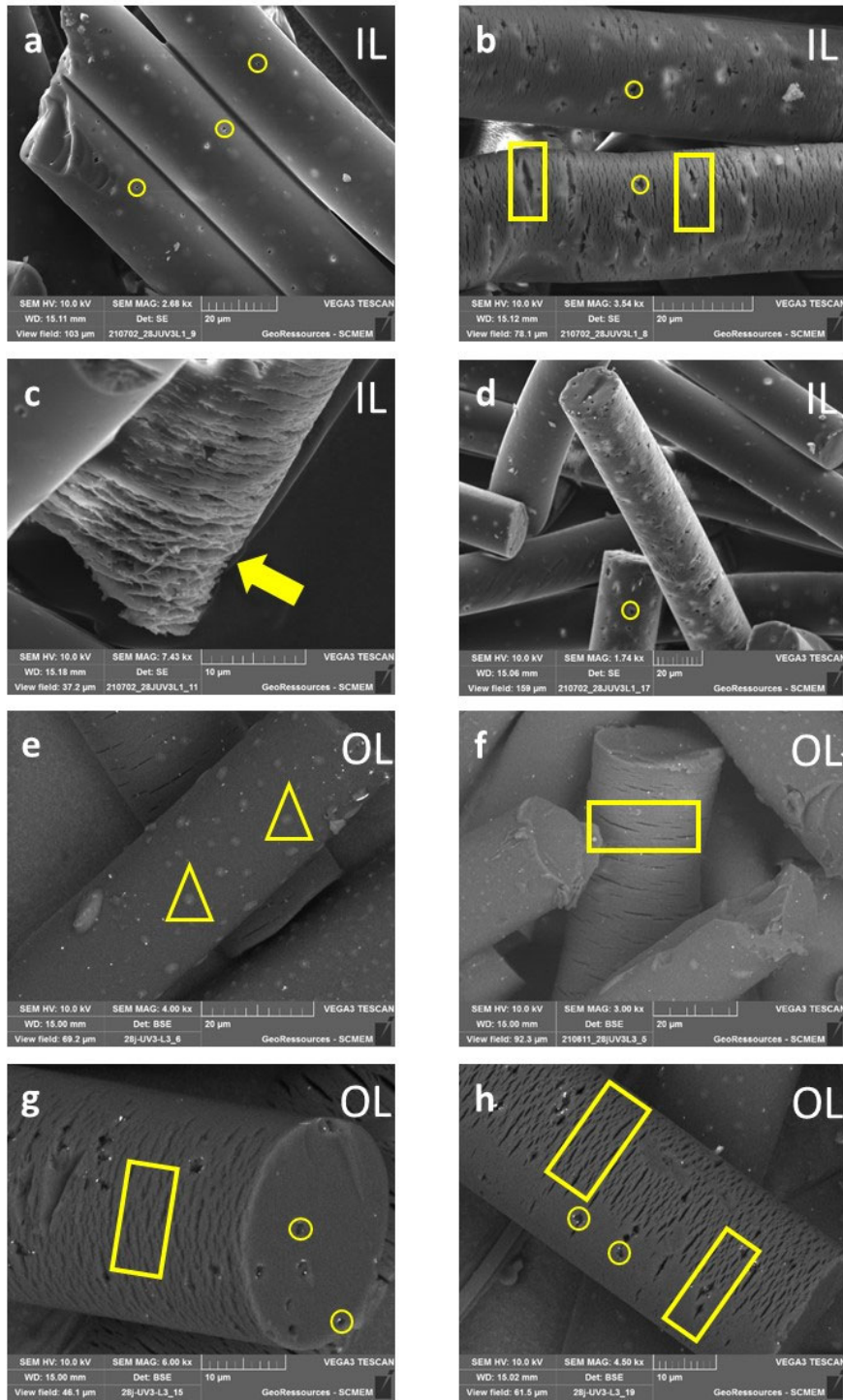


Figure E.3. Scanning electron micrographs of 28 days UV-exposed inner and outer layers (IL and OL, indicated). Illustration for the presence of cavities (circles), cracks (rectangles), blisters (diamonds) and laminated texture (arrows). For the sake of clarity, only some of the most characteristic defaults are highlighted here. BSE: backscattered electrons – SE: secondary electrons. See main text for details.

F. Complementary Atomic Force Microscopy (AFM) results.

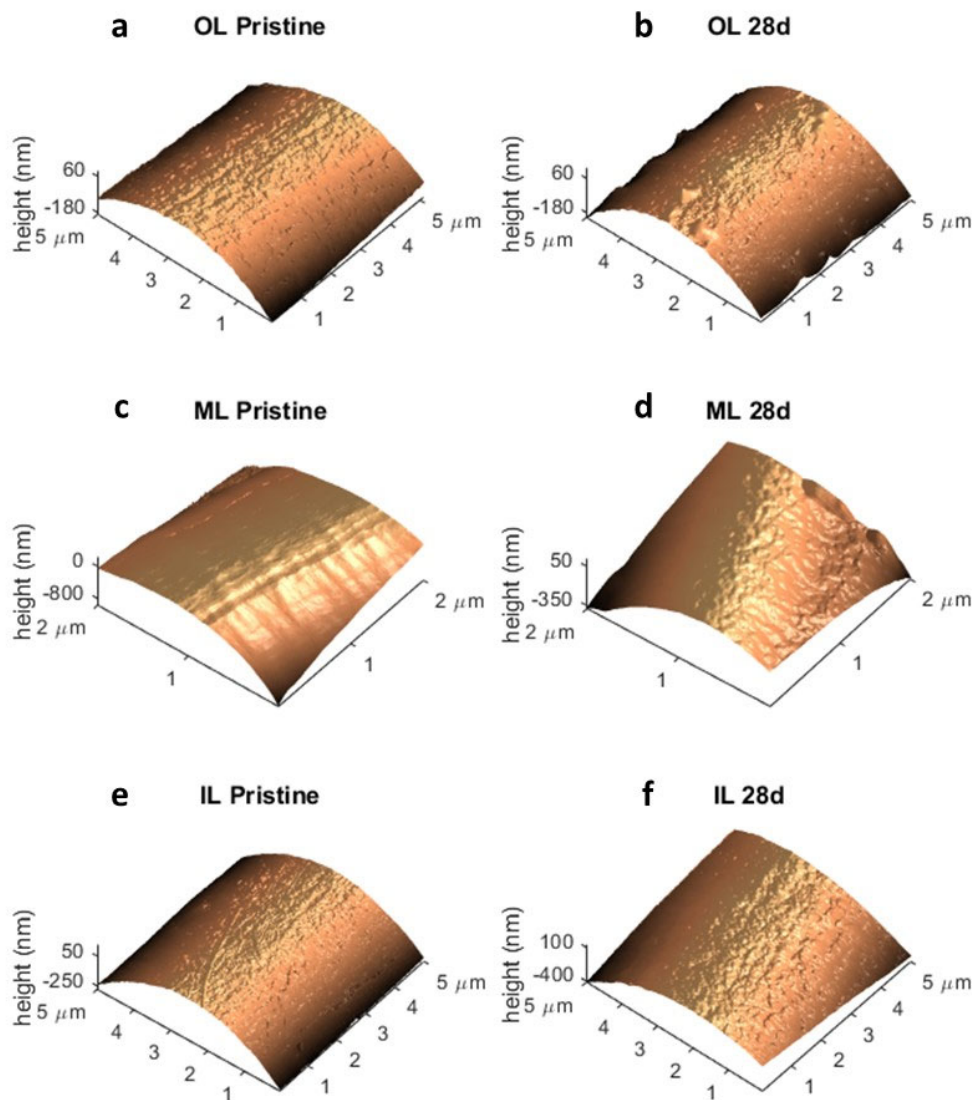


Figure F.1. Representative AFM height sensor images for the outer layer (OL, **(a)-(b)**), middle layer (ML, **(c)-(d)**) and inner layer (IL, **(e)-(f)**), in pristine state (no UV exposure) or after 28 days UV exposure (28d) (indicated). The size of the images is scaled according to the fibre diameters, i.e. images of $5 \times 5 \mu\text{m}$ for the inner and outer layers, and $2 \times 2 \mu\text{m}$ for the middle layer. AFM images shown here are those where roughness evaluation was performed (cf. Table 1 in the main text).

G. Complementary gas adsorption results.

In order to address the possible impact of generated cracks on BET results, we computed theoretical SSA for materials consisting of an ensemble of cylinders defined by different lengths and diameters (**Figure G.1**). Considering a density (d) of 0.9 g cm^{-3} , the obtained specific surface area of $50 \text{ }\mu\text{m}$ -long cylinder was ca. 0.6 , 0.32 and $0.27 \text{ m}^2 \text{ g}^{-1}$ for a radius of 4 , 8 and $10 \text{ }\mu\text{m}$, respectively, in agreement with results derived from BET measurements. For a cylinder length above a threshold value of a few hundreds of microns, the calculated SSA reached asymptotically a plateau whose value corresponded to the contribution of the lateral surface to the whole SSA (situation of an infinite cylinder). Indeed, for cylinders of radius R and length L , SSA has 2 components, one associated with the 2 basal surfaces and the other with the cylinder lateral surface. These components contribute to the total SSA according to $2/(dL)$ and $2/(dR)$, respectively. This demonstrates that for debris with sufficiently large aspect ratio, the contribution of lateral surfaces in the overall SSA overwhelms that from basal surfaces. In turn, cracks do not contribute much to the overall SSA.

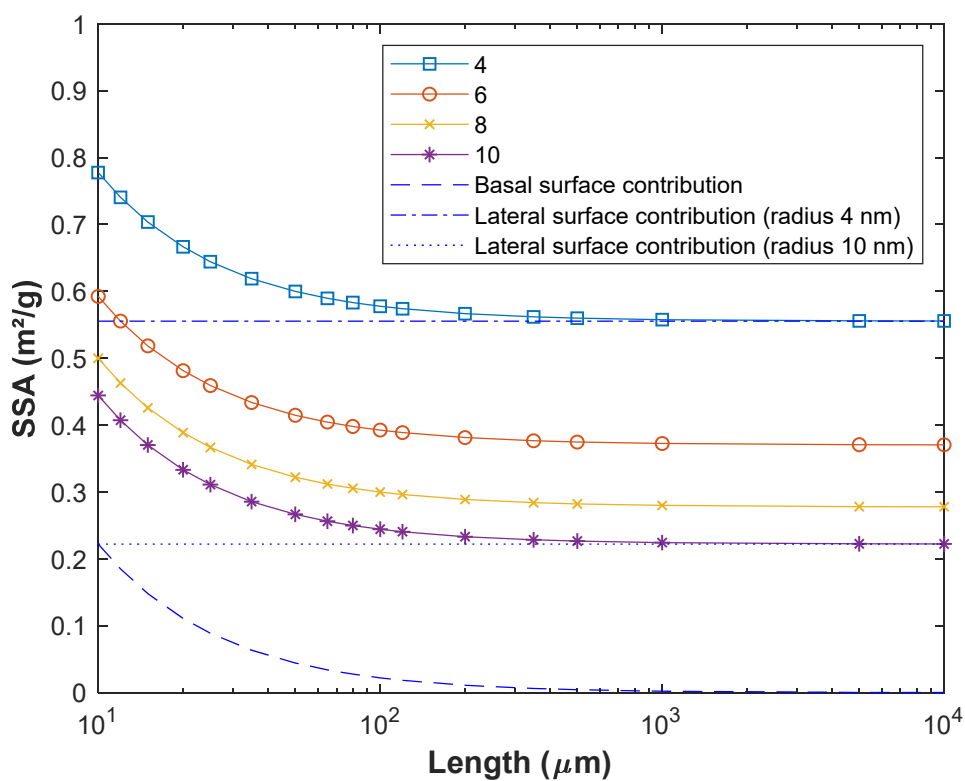


Figure G.1. Theoretical specific surface areas (SSA) calculated for cylinders with different radii (R) in the range 4 to $10 \text{ }\mu\text{m}$ (indicated). SSA is reported as a function of the cylinder length (L). The total SSA of a cylinder is the sum of two components. The first contribution corresponds to the 2 basal surfaces and is proportional to $2/L$, and the second one corresponding to the lateral surface is proportional to $2/R$.

H. Complementary electrophoretic mobility results.

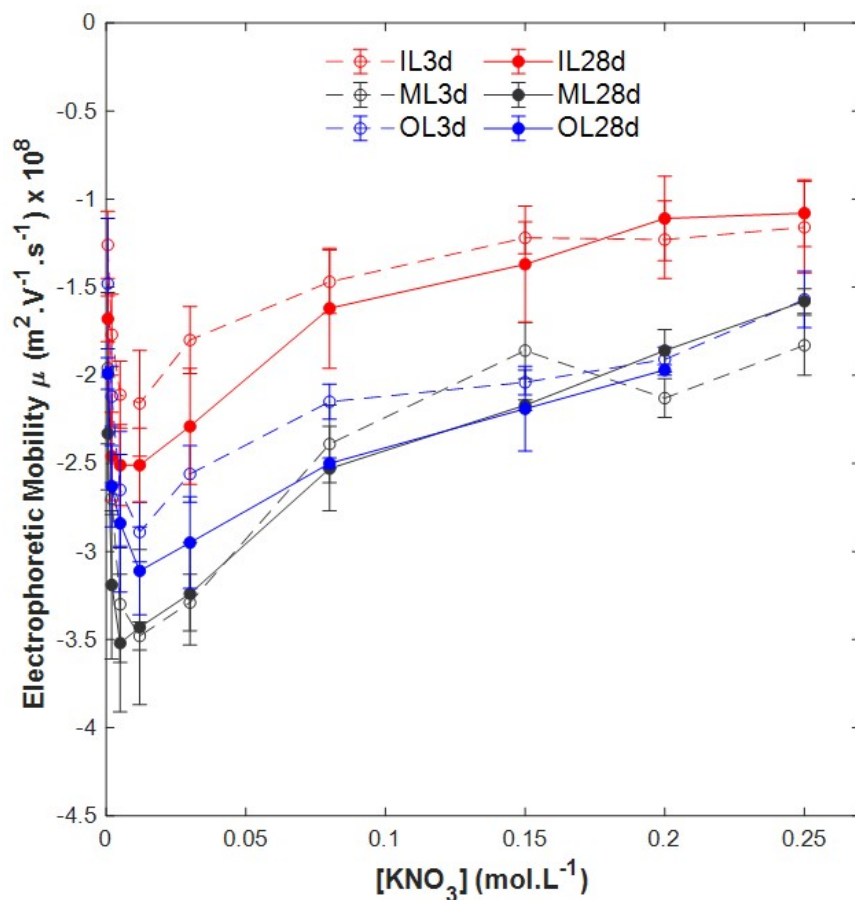


Figure H.1. Electrophoretic mobility measured on masks debris (specified) as a function of KNO_3 concentration at pH 7.35. IL: inner layer, ML: middle layer, OL: outer layer. 3d, 28d: after 3 days and 28 days UV-exposure, respectively. Data correspond to those reported in Figure 3A and are plotted here according to linear scale in KNO_3 concentration.

I. Characterization of nanoparticles released from polypropylene granulates.

Additional photodegradation experiments were carried on polypropylene (PP) beads purchased from GOOVEAN FIBERS Ltd (<https://gooveanfibres.com/>). The received granulates of 90 μm size were poured in a crystallizer so as to cover its surface and then placed under a UV lamp (Benda, at 366 nm, 6 W). The exposure protocol consisted in 7 cycles of 24 hours with alternating 16 hours UV radiation followed by 8 hours in dark. After exposure, 56 mg of granulates were dispersed in 350 mL of very soft water prepared by adding 24 mg of NaHCO_3 , 15 mg of CaSO_4 and MgSO_4 , 1 mg of KCl to 2 L of ultra-pure water with a conductivity of $0.055 \mu\text{S}\cdot\text{cm}^{-1}$. After one hour agitation, the smallest colloidal fraction was collected by filtering the suspension with glass fibre filters of $0.7 \mu\text{m}$. The size of the nanoparticles and their electrophoretic mobility were measured by Dynamic Light Scattering and Phase Analysis Light Scattering techniques, respectively, both run with a Nano-ZS Malvern Instrument. Measurements were done with increasing KNO_3 concentration along the lines detailed in Materials and Methods section relative to the electrokinetic characterization of masks debris by electrophoresis. Electrophoresis and size results are provided below in **Figures I.1** and **I.2**, respectively.

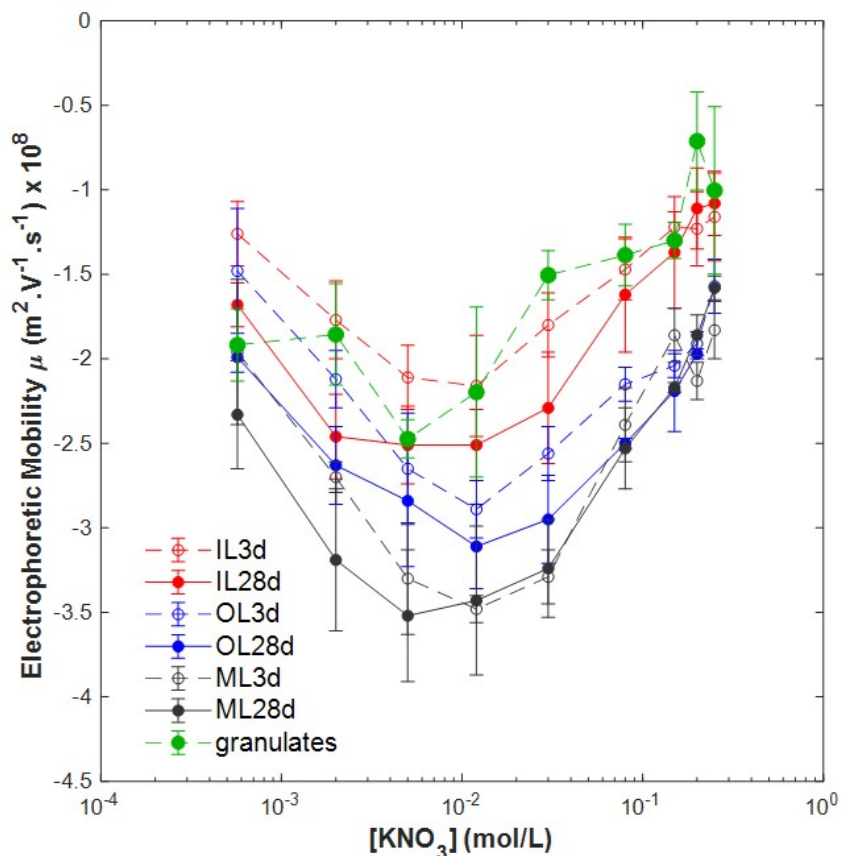


Figure I.1. Electrophoretic mobility measured on masks fragments as a function of KNO_3 concentration at pH 7.35. IL: inner layer, ML: middle layer, OL: outer layer. 3d, 28d: after 3 days or 28 days UV-exposure, respectively. The green curve corresponds to measurements performed on the filtered ($<0.7 \mu\text{m}$) fraction of a suspension of PP granulates recovered after dispersion in water of 90 μm beads exposed to UV for 7 days. Error bars correspond to triplicate measurements.

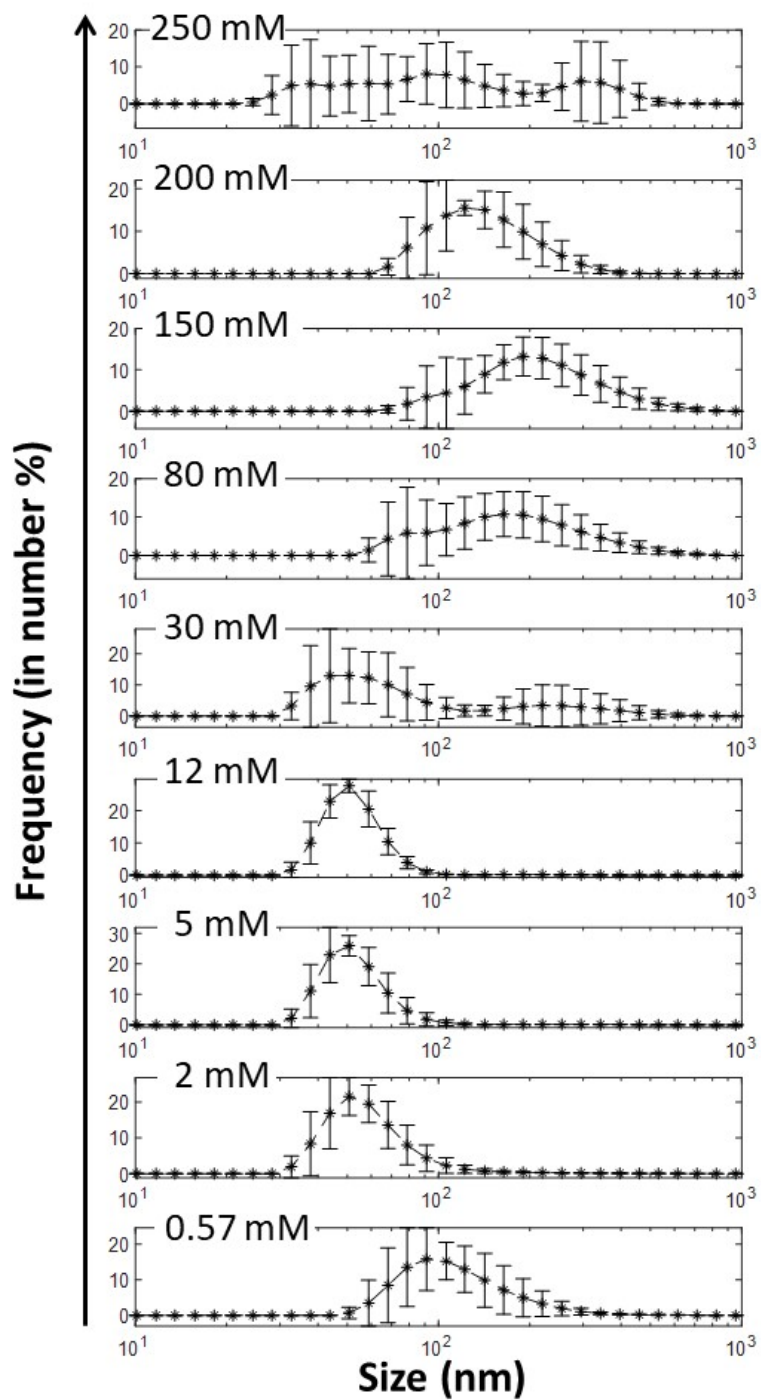


Figure I.2. Particle size distributions (expressed in number %) obtained by Dynamic Light Scattering (DLS) on the filtered ($<0.7 \mu\text{m}$) fraction of a PP granulates suspension after dispersion in water of $90 \mu\text{m}$ beads exposed to UV for 7 days. Each distribution corresponds to a green point in Figure I.1., i.e. a different concentration of KNO_3 (indicated). Error bars correspond to triplicate measurements.

J. Determination of the amount of released carboxylic acids by ion chromatography.

To determine the amount of carboxylic acid release in water by UV exposed mask layers, 18 mg of each layer UV-aged for 3 days and 28 days were dispersed in a bottle filled with 80 mL of very soft water. Bottles were left on a shaking table under natural light condition at room temperature for 3 months. Regularly, a volume of 2 mL was collected (i.e. after 1 h, 5 h, and 1, 2, 4, 7, 46, 58 and 91 days). The sampled solutions were then analysed using a compact high-pressure ion chromatography system (ICS-5000+ - Thermo), coupled with an ISQ EM single quadrupole mass spectrometer. Results are provided below in **Figure J.1**.

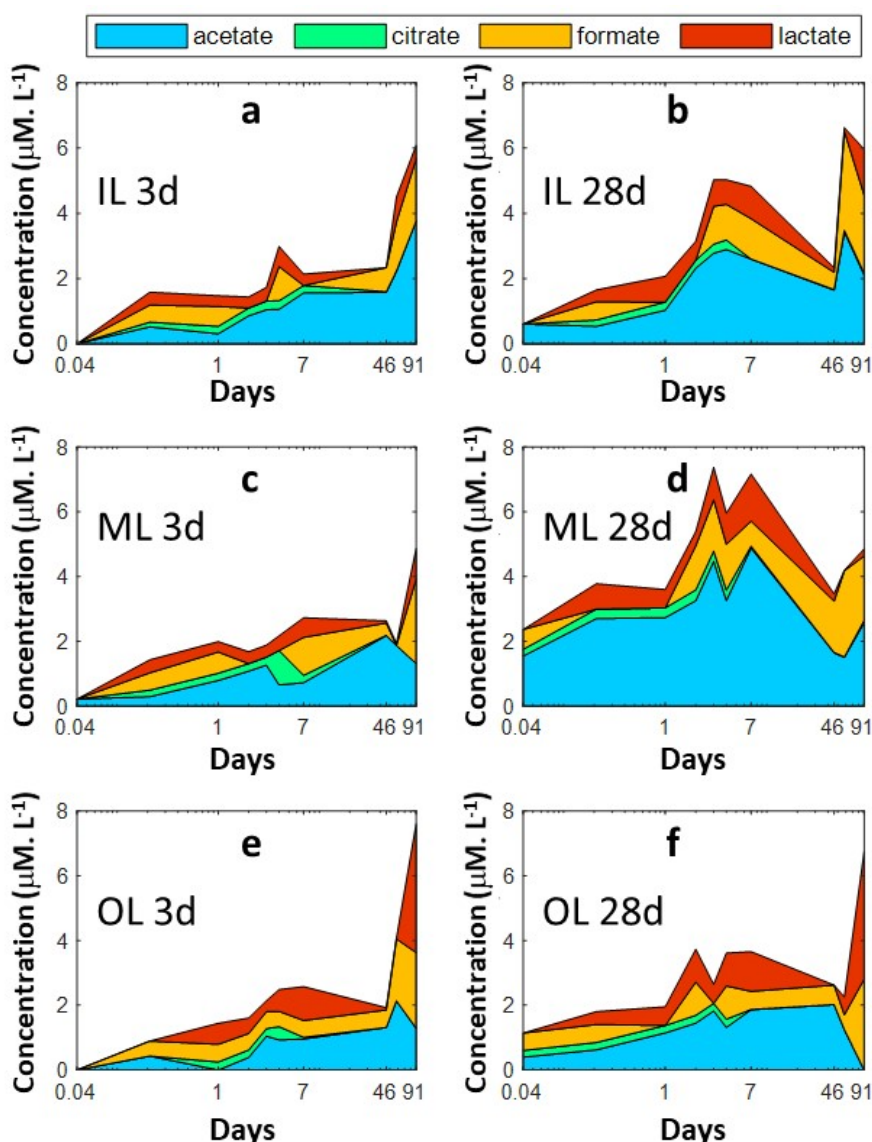


Figure J.1. Determination of the amount of carboxylic acids (from acetate, citrate, formate and lactate, as specified) released in solution by UV-aged masks debris under agitation condition (maximum duration of agitation: 91 days). IL: inner layer, ML: middle layer, OL: outer layer. 3d, 28d: layers after 3 days or 28 days UV-exposure, respectively.

K. Analysis of bacterial community composition in freshwater biofilms grown on masks.

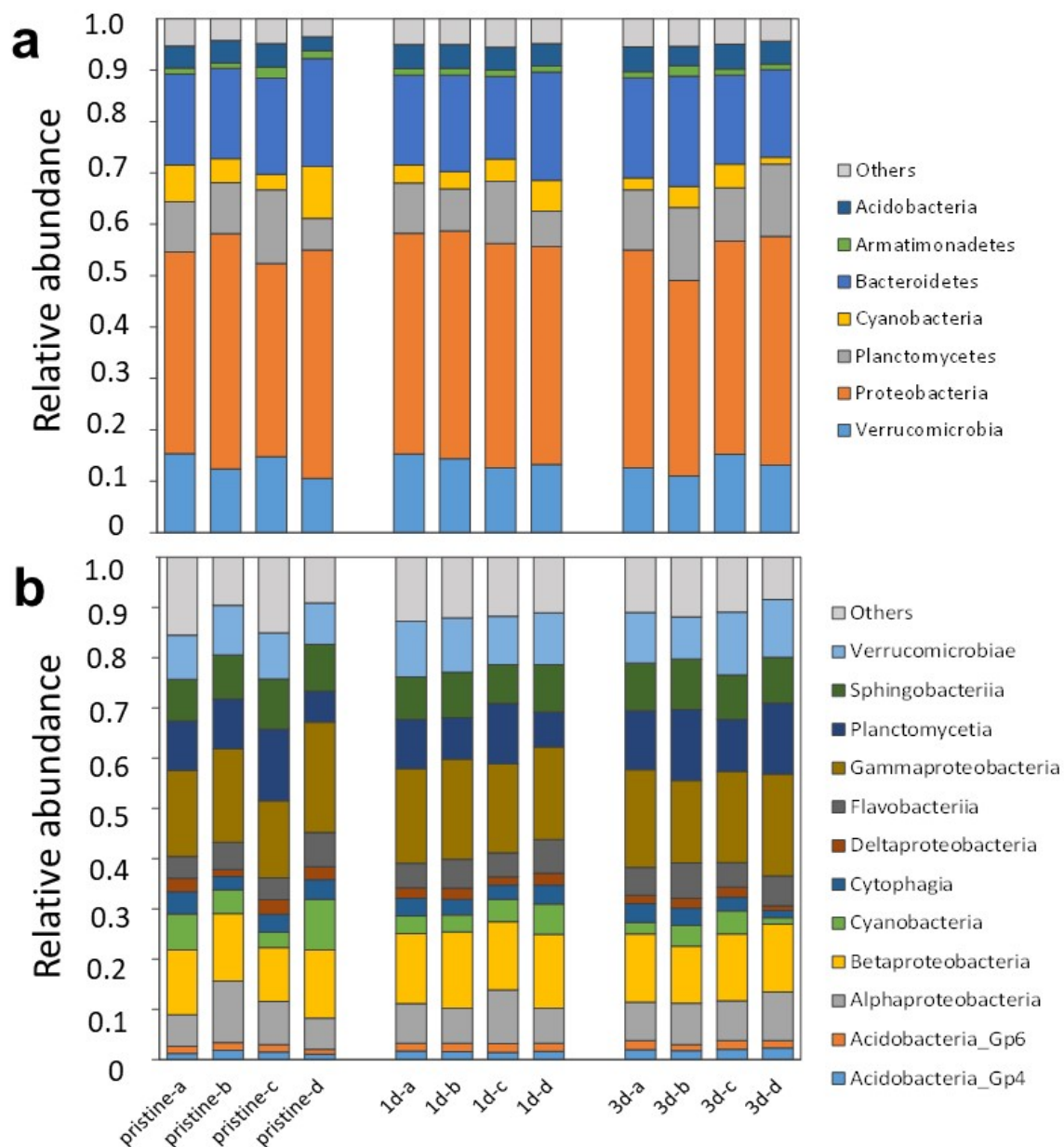


Figure K.1. Bacterial taxonomic distribution at the phylum (**a**) and class (**b**) levels. Pristine: no exposure; 1d, 3d: masks after 1 day and 3 days UV-exposure, respectively. For each condition tested, 4 independent replicates are analysed and reported here (designed by the letters a, b, c, d).

L. Analysis of phytoplankton community composition in freshwater biofilms grown on masks.

Table L.1. Relative abundance of Bacillariophytes (diatoms), Chlorophytes and Cyanophytes in biofilms.

	Pristine-a	Pristine-b	Pristine-c	1d-a	1d-b	1d-c	3d-a	3d-b	3d-c
Bacillariophytes									
Small pennate diatoms (<i>Achnanthydium</i> and others) - 10-11 μ	43	85	9	50	34	16	45	37	32
<i>Gr. Achnanthydium</i>	1	8	4	4	3	4	7	3	2
<i>Gr. Encyonema / Amphora</i>	3			16	10	1	18	7	13
<i>Gomphonema</i> spp.	5			5	7	2	7		
<i>Humidophila</i>					7				
<i>Fragilaria</i>	2								
<i>Navicula</i>		8				1			
<i>Nitzschia</i>	1					4			
<i>Odontidium mesodon</i>					7				
<i>Planorhynchium</i>				3	17	1			3
Pennate diatoms (connective vision)	1				7		2		7
<i>Rhoicosphenia</i>						3			
Chlorophytes									
<i>Characium</i>			24			4			
<i>Chaetophorales (Stigeoclonium and others)</i>	2		2			23			
<i>Chlamydomonadales</i>	19		10			22	3	3	
<i>Ulotrichales (Tetraciella)</i>			34			6			
Cyanophytes									
<i>Chamaesiphon</i>	0.5			1.2				15.5	1
<i>Synechococcales (Leptolyngbya, Heteroleibleinia)</i>	18.4		10	13.4		13.8	10.2	27.5	31.2
<i>Pseudanabaena catenata</i>	0.7				3.4	2.5			0.2
Others	2		7	6	6		8	6	9

M. Additional illustrative confocal microscopy images of freshwater biofilms grown on masks.

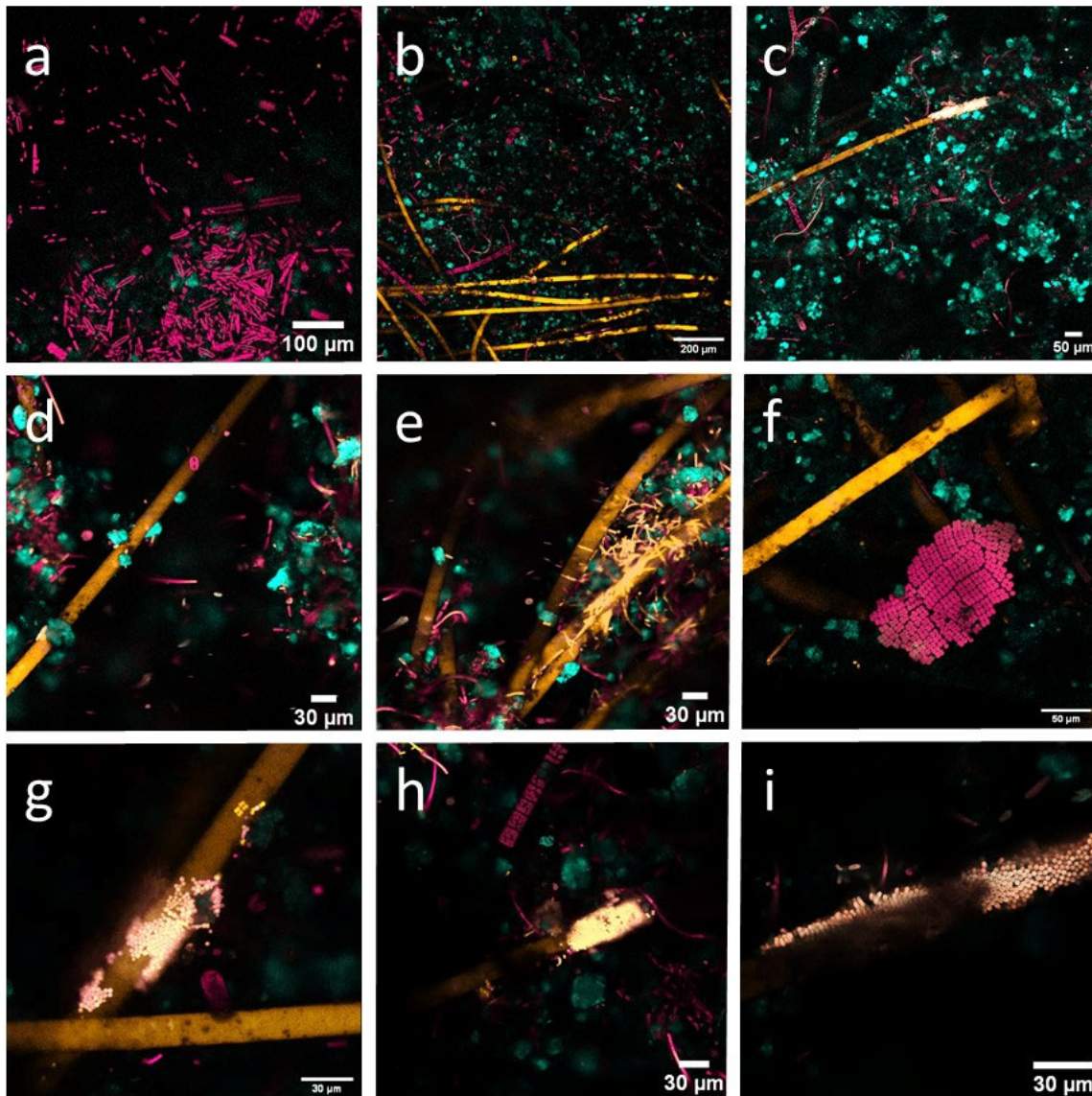


Figure M.1. Confocal laser scanning microscopy of freshwater biofilms developed on mask after a stay of 4 weeks in the Moselle River. Pictures are merged from the three channels used to collect autofluorescence (C1 – Exc 488 nm/Em: 499-561 nm, C2 – Exc 561 nm/Em: 570-632 nm, C3 – Exc 633 nm/Em: 641-694 nm). **(a)** Pristine mask, picture recorded on the coverslip focal plane. **(b)** 1d-mask. **(c)** 3d-mask. **(d),(e)** Pristine mask. **(f),(g)** 1d-mask. **(h),(i)** 3d-mask. Pristine: no exposure; 1d, 3d: samples after 1 day and 3 days UV-exposure, respectively. The colour adopted for each channel corresponds to the median detection wavelength in that channel.

N. Observation of mineral deposits in the freshwater biofilm grown on masks.

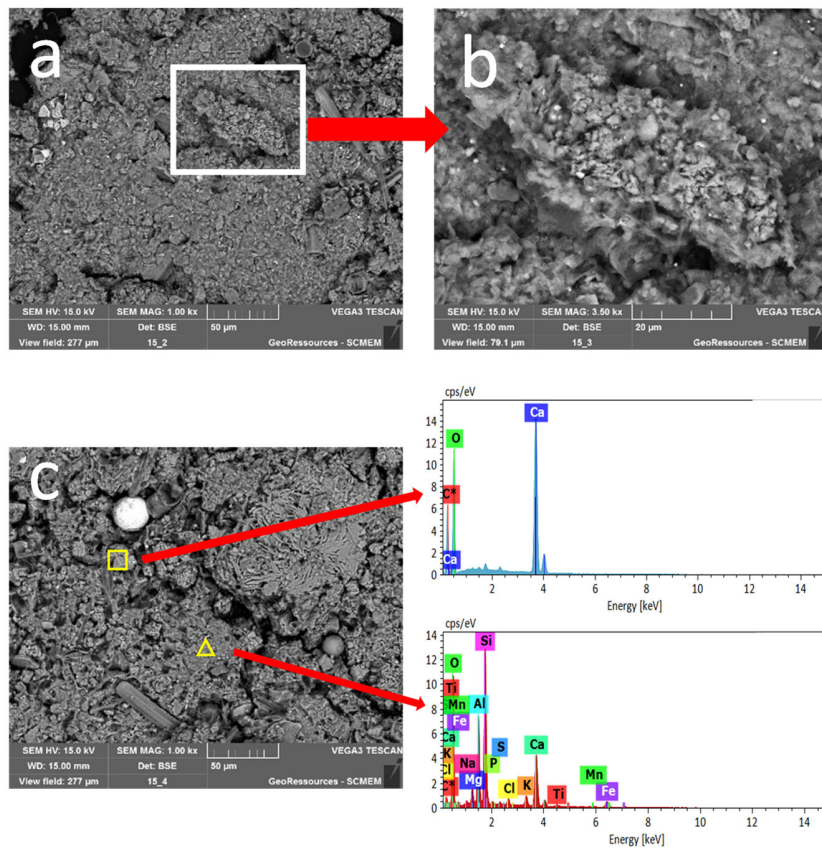


Figure N.1. Illustrative Scanning electron micrographs (SEM) of particles on a pristine mask after 4 weeks in the Moselle River. **(a)** Assembly of aggregates sampled on a pristine mask, **(b)** enlarged view of an aggregate, **(c)** elemental analysis by energy dispersive X-ray spectroscopy (EDS).

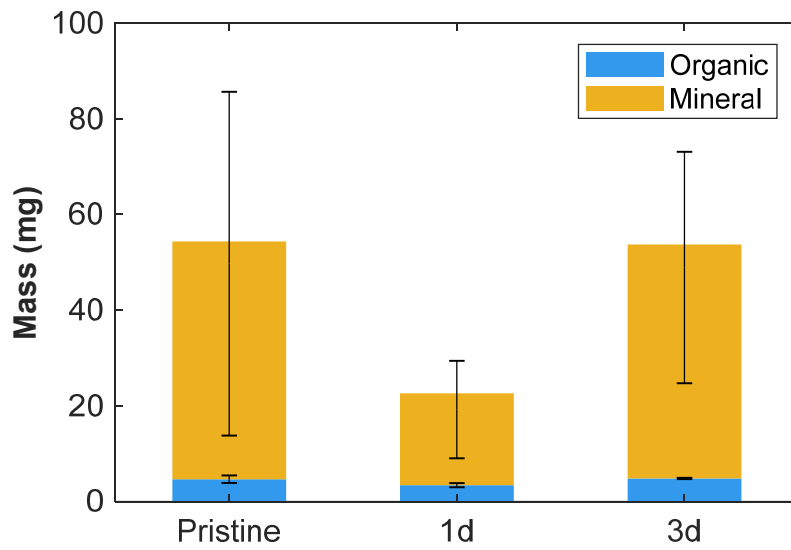


Figure N.2. Evaluation of organic and mineral mass after loss on ignition of masks incubated 4 weeks in the Moselle River. Experiments were performed to reveal the possible presence of mineral phases in the biofilms. The experimental procedure we followed was adapted from the protocol by Mathieu and Pieltain (2003). Briefly, 2 cm diameter disks cut from pristine, 1 day or 3 days-aged masks immersed for 4 weeks in Moselle River were first dehydrated for 16 hours at 220°C and then calcined for 4 hours at 450°C. Two replicates were averaged per condition.

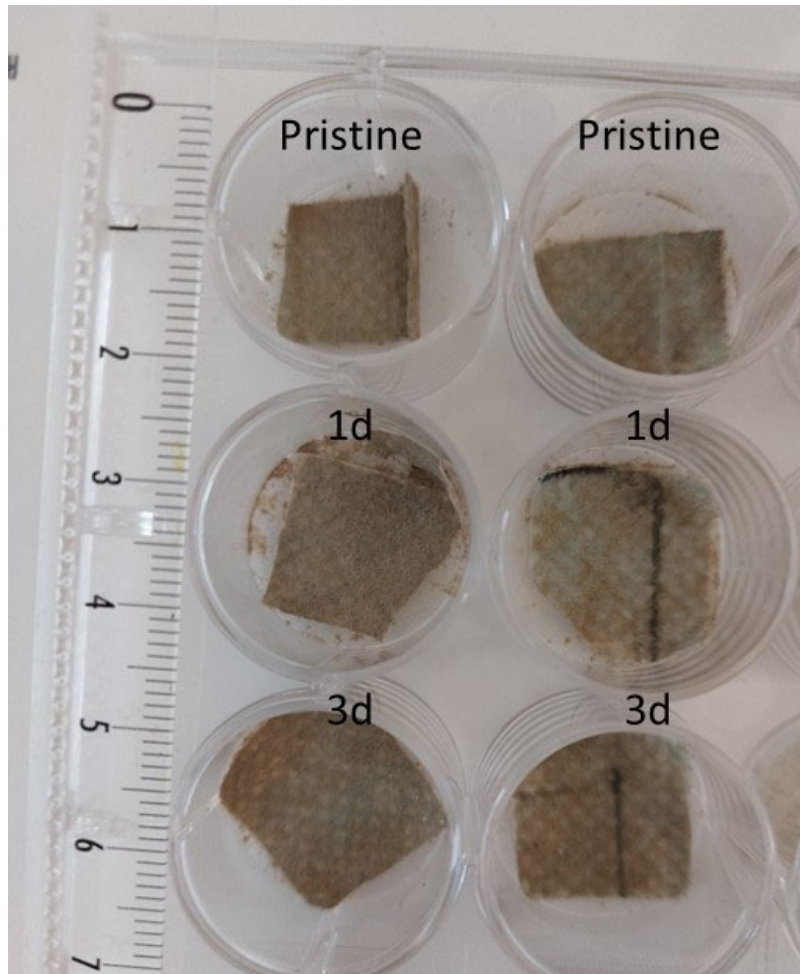


Figure N.3. Macroscopic view of masks incubated 4 weeks in the Moselle River. Mask pieces were placed in a multi-well plate for CLSM measurements.

O. References.

- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* 60, 309–319.
- Celina, M.C., Linde, E., Martinez, E., 2021. Carbonyl Identification and Quantification Uncertainties for Oxidative Polymer Degradation. *Polym. Degrad. Stab.* 188, 109550.
- Mathieu, C., Pieltain, F., 2003. Analyse chimique des sols. Méthodes choisies. Tec & doc; Lavoisier, France.
- Sing, K.S.W., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl. Chem.* 57, 603–619.
- Wojdyr, M., 2010. Fityk: a general-purpose peak fitting program. *J. Appl. Crystallogr.* 43, 1126–1128.