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The life of a plastic butter tub in riverine environments

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ABSTRACT

Plastic pollution in the world’s ocean is one of the major environmental challenges that affects the society today, due to their persistence at sea, adverse consequences to marine life and being potentially harmful to human health. Rivers are now widely recognized as being the major input source of land-based plastic waste into the seas. Despite their key role in plastic transportation, riverine plastic pollution research is still in its infancy and plastic sources, hot-spots and degradation processes in riverine systems are to date poorly understood. In this contribution, we introduce a novel concept of following the aging of polypropylene based post-consumer goods placed in known trapping and mobility zones of macroplastics on a fluvial point bar, which was determined through repeated field surveys of macroplastic densities on this bar. As a proof-of-concept, we followed the degradation of 5 identical plastic butter tubs in 5 different locations on a riverbank and significant differences in the aging of the tubs were observed. The degree of aging of the tubs can to some extent be correlated to their proximity to the main river channel, exposure to natural conditions, such as solar radiation, and its storage time on land.

Keywords: polymers, Allier river, storage, riparian vegetation, degradation

46 **1. Introduction**

47 Global models of river plastic emissions based on mismanaged plastic waste predict that
48 between 0.4-2.75 million metric tons (MT) of plastic enter the world's ocean from rivers
49 annually (Schmidt et al., 2018; Lebreton et al., 2017). On the other hand, Mai *et al.* (2020)
50 recently developed a model based on human development index which estimates a global
51 plastic outflow from rivers in the range of 57,000-265,000 MT year⁻¹. Despite these
52 discrepancies in riverine plastic outputs, it is widely agreed that rivers are the most dominant
53 source of plastic input into the sea (van Emmerik and Schwarz, 2020). Contradictorily, field-
54 data based models estimate that approximately a total of 250,000 MT plastic debris currently
55 afloats at sea, which only accounts for a fraction of what is predicted to have accumulated in
56 the sea over the years since the start of plastic production in the 1950s (Lebreton et al., 2019).
57 This mass-imbalance between plastic litter supplied to and observed in the ocean suggests a
58 missing “sink” (van Sebille et al., 2012; ter Halle et al., 2016). While crude estimates of
59 riverine plastic pollution have been attempted, a more detailed understanding of the sources,
60 accumulations, fluxes and fate is now required urgently in order to address one of the most
61 pressing question in ocean plastic pollution research; *where is the missing plastic?* (Blettler et
62 al., 2018; van Emmerik and Schwarz, 2020; van Emmerik et al., 2019)

63 Rivers are often regarded as channels that transport materials to the ocean; a perspective
64 that overlooks their retentive nature. To date, most research on riverine plastic pollution have
65 focused on floating plastic and microplastic debris in the river channel (Lebreton et al., 2017;
66 van Emmerik and Schwarz, 2020; van Emmerik et al., 2019; Dris et al., 2015). However
67 recent studies suggest that natural characteristics of river catchments such as hydrological
68 processes, channel morphology, and riparian vegetation control the storage, input and
69 transport of plastic debris in fluvial systems (Dris et al., 2015; Liro et al., 2020; Hurley et al.,
70 2020). For example, studies on the Seine river in France showed that the time which riverine

71 plastic spend stranded on land next to the river largely exceeds the time the plastic spent in the
72 river (Tramoy et al., 2020a; Tramoy et al., 2020b). Nevertheless, with only a handful of
73 studies examining the trapping potential of riverine systems, there is limited knowledge
74 regarding riverine plastic sources, storage, dynamics, associated risks and potential solutions
75 for reducing plastic input into the ocean (van Emmerik and Schwarz, 2020; Hurley et al.,
76 2020; Tramoy et al., 2020a; Tramoy et al., 2020b; Dris et al., 2020). The storage duration of
77 plastic debris in fluvial environments must be emphasized, especially in relation to the
78 trapping function of riparian vegetation (Ivar do Sul et al., 2014) and spatial variations in the
79 vegetation roughness (based on the vegetation age, density and spatial structure) must be
80 considered.

81 Although field surveys contribute to our understanding of riverine plastic pathways, they
82 provide ‘snap-shots’ of the macroplastics’ journey in the environment at the time of sampling.
83 Once introduced into riverine systems, plastics will be exposed to natural conditions such as
84 moisture, heat, solar radiation and microbial actions, causing the plastic to ‘age’ and degrade
85 into smaller pieces (eventually into microplastics) as well as cleaved into small molecules
86 (Chamas et al., 2020). Stranded plastic debris is subjected to degradation, which include
87 mechanical, thermal, hydrolytic, photo- and biodegradation (Harvey, 2005). In particular,
88 photoaging of a polymeric material is an oxidative process and leads to structural changes of
89 the polymer backbone, such as oxidations leading to the formation of carbonyl functional
90 groups, chain scission and cross-linking (Grossette et al., 2002). These transformations at the
91 molecular level affect the overall mechanical properties of the plastic and favor leaching of
92 degradation products, embrittlement and fragmentation, leading to the generation of micro-
93 and nano-plastics (Commereuc et al., 2013; Commereuc et al., 2010). The extent of aging of
94 riverine plastics in important environmental sinks could determine its degradative state and

95 shape as it will be released back into the river stream to eventually complete its journey to the
96 ocean.

97 Understanding the aging of riverine plastic debris is fundamental for the assessment of
98 plastic transportation in riverine systems, the related risks they pose on the environment, the
99 development of effective clean-up and mitigation actions (Liro et al., 2020). Here we develop
100 a proof-of-concept, which demonstrates that the aging of plastic debris on a fluvial point bar
101 varies when placed in various trapping zones along a lateral gradient of hydraulic connectivity
102 and vegetation roughness. We follow the aging of polypropylene based post-consumer goods,
103 more specifically- plastic butter tubs, with respect to their location and storage time on Mariol
104 point bar next to the Allier river for up to 4.5 years. The focus of this study lies in monitoring
105 the long-term degradation rate and mechanism of identical post-consumer macroplastics in
106 different trapping zones, by periodically taking a number of sub-samples of the same
107 macroplastics as they are aged for analysis. These post-consumer wastes were chosen since it
108 is known that the oxidative mechanism of polypropylene leads mainly to chain scission
109 arising from tertiary primary hydroperoxide decomposition and consequently forming
110 carbonyl groups (Bateman, 1954; Bolland and Gee, 1946). The aging of polypropylene based
111 material can therefore be followed relatively straightforwardly through changes in physical
112 (e.g. viscoelastic properties) and chemical properties (e.g. the rise of carbonyl degradation
113 products). We envision that this novel concept of monitoring the degradation pathway of
114 macroplastics in various known trapping zones in the environment can be employed to a
115 variety of plastic debris, using relatively simple methods demonstrated herein, in order to
116 develop more statistical analyses and models of plastic degradation pathways in important
117 environmental sinks.

118 **2. Materials and method**

119 *2.1. Materials*

120 Polypropylene butter tubs (Saint Hubert brand), see figure S1 in the Supplementary
121 Information, SI, were used as representative post-consumer plastic materials that can be found
122 in the environment. The laboratory analyses were performed on different pieces that were
123 sub-sampled of the plastic butter tubs, which allowed to follow the degradation of the same
124 tub. The sub-sampling and analysis of the tubs were taken of the same side of the tubs to
125 ensure that pieces had similar thickness. It is also worth noting that the study was based on
126 identical post-consumer goods, which limited the number of plastic butter tubs used for this
127 study.

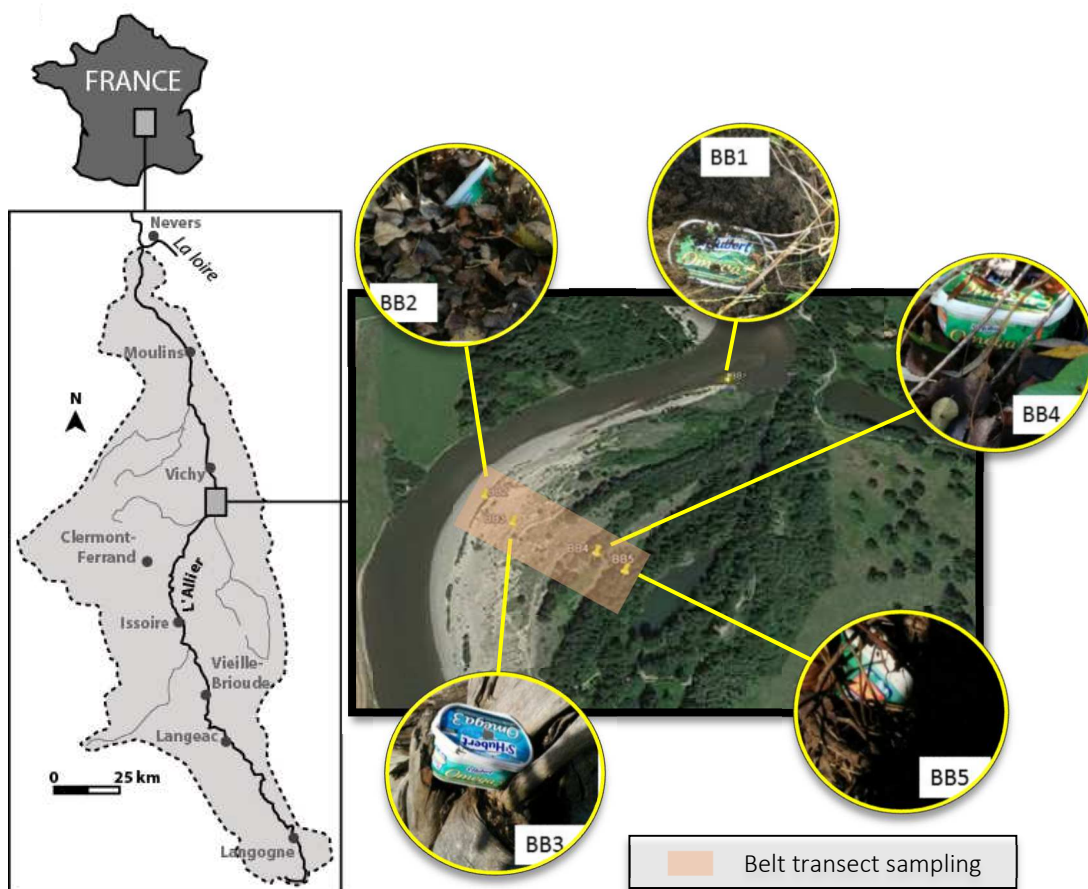
128 2.2. *Surveying the spatial density and mobility of plastic waste on alluvial bars*

129 The Allier river is a natural, unregulated river and its downstream section is
130 considered as one of the last highly mobile rivers in Europe (Garófano Gómez et al., 2017).
131 Since the mid-1990s, the Mariol point bar has grown via lateral accretion and has been
132 increasingly covered by riparian tree species, which trap sediment and macroplastic waste. In
133 order to determine whether the spatial density and mobility of plastic waste on the Mariol
134 point bar show a spatial pattern related to the riparian vegetation structure and the proximity
135 to the main channel, a repeated survey of plastic waste was developed. Using a belt transect
136 sampling approach, perpendicular to the main Allier river flow (figure 1), plastic debris were
137 counted on the 23rd of May 2016, 17th of November 2016, 10th of March 2017 and 29th of May
138 2017. For each sampling date, a group of 6 aligned people (spacing of 10 m) surveyed the belt
139 transect (50 m width and 200 m long) from the right bank of the Allier river to the abandoned
140 channel. The locations of surveyed plastic waste were recorded using two Trimble GEO7X
141 differential GPS. GNSS signals were post-treated in order to compute precise locations (under
142 ± 20 cm). Within a GIS software, the belt transect was divided into 20 bands of 10 m width in
143 order to compute the plastic waste density (number of macroplastic per surface unit) of each
144 band for each date (see figure 2 for the belt transect division). Based on these 4 surveys, the

145 sum and relative standard deviation (RSD) of plastic waste density were computed for each
146 band in order to highlight hot spots of trapping capacity and plastic waste mobility,
147 respectively. Based on field prospections and the 2016 aerial photographs mission provided
148 by the IGN (Institut National de l'Information Géographique et Forestière), the percentages
149 of vegetation cover for each band were calculated in order to investigate a possible correlation
150 between vegetation cover and the density and mobility of macroplastic waste (see table S1 in
151 the SI for percentage vegetation coverage in the belt transect used in the field-surveys).

152 2.3. *Plastic butter tubs positioning*

153 Based on the results from the belt transect-survey, plastic butter tubs were placed in
154 zones where a high density of plastic debris was observed. Five butter tubs (BB1, BB2, BB3,
155 BB4 and BB5) were placed in 5 different locations as shown in figure 1 along the Allier river
156 on the 23rd of May 2016, their GPS positions were noted.



157

158 **Fig. 1. Mariol meander and its associated point bar.** The belt transect sampling along the
159 Mariol point bar for density and mobility survey of plastic debris is highlighted in the orange
160 rectangle. Five identical plastic butter tubs, nominated BB1, BB2, BB3, BB4 and BB5, were
161 placed in 5 different zones along the Mariol point bar. BB1 was buried in the sediment by the
162 riverbank, BB2 was placed in the vegetation in the young riparian trees, BB3 was positioned
163 on a fallen tree trunk on the bare point bar, BB4 was placed by the foot of an old riparian tree
164 and BB5 was placed in a bush in the old riparian tree zone. The GPS locations of each tub
165 were noted and the tubs were sampled periodically.

166 One of the tubs, BB1, was buried in the sediment near the river channel after being
167 artificially pre-weathered in laboratory conditions (24 hours in an accelerated photoaging
168 chamber based on a SEPAP 12-24 device, the function of this device is described below), this
169 was done in order to replicate the solar radiation that the plastic butter tub is likely to have
170 been exposed to prior to being buried in the sediment. Although the butter tub is buried and
171 therefore exposed to no solar radiation, it has previously been shown that plastic materials
172 continue to degrade even in the absence of UV radiation after initial exposure to UV radiation
173 (Vogt and Kleppe, 2009). Another two tubs, BB2 and BB3 were placed on the riverbank, BB2
174 in the young riparian vegetation (<7yrs) with low exposure to solar radiation and BB3 on a
175 tree trunk with high exposure to solar radiation on the bare point bar. It should be noted that
176 BB3 was artificially attached onto the tree trunk in order to prolong its exposure as much as
177 possible. The remaining two tubs, BB4 and BB5, were placed further away from the river
178 channel, among the old riparian trees (>17 years), where BB4 was placed next to a tree with
179 intermediate exposure to solar radiation and BB5 was placed in a bush by the foot of a tree
180 with low exposure to solar radiation. Each of the locations of the tubs are shown in figure 1.
181 At each position, the temperature and humidity were recorded hourly using iButtons®.
182 Samples of a few cubic centimeters were cut off of the tubs and subjected to laboratory

183 analysis after 167 (17th of November 2016), 371 (10th of March 2017), 506 (11th of October
184 2017) and 1600 (9th of October 2020) days.

185 2.4. *Accelerated photoaging*

186 BB1 was exposed to UV radiation at 60 °C in dry air in an accelerated photoaging
187 device (based on SEPAP 14-24 device), aging of polymers in this device is described by
188 Lemaire and Lacoste (Lemaire and Lacoste, 1988). The device is equipped with a “medium
189 pressure” mercury source filtered by a borosilicate envelope (Mazda type MA 400) emitting
190 polychromic radiation of wavelengths longer than 300 nm. The inside of the chamber is made
191 of highly reflecting aluminum. The mercury source is located along the focal axis of a
192 cylinder with an elliptical base and BB1 was fixed on aluminum holders, turned around the
193 other focal axis. The temperature of the butter tub was controlled by a thermocouple
194 connected with a temperature regulator device which controls a fan.

195 2.5. *Rheology*

196 Changes in the molecular structure of the plastic tubs after being exposed to natural
197 conditions were monitored over time by melt viscoelasticity experiments in oscillatory shear
198 mode using a rotational controlled strain rheometer (ARES/Rheometric Scientific) equipped
199 with parallel plates geometry. The diameter of the plates was 8 mm and the gap between the
200 plates was approximately 1 mm. A strain amplitude of 10% was applied and in all
201 measurements, the values of the strain amplitude were checked to ensure that all
202 measurements were conducted within the linear viscoelastic region. A frequency sweep
203 extending from 0.1 to 100 rad/s was performed. All experiments were carried out under dry
204 airflow and at a fixed temperature of 180 °C.

205 2.6. *Scanning Electron Microscopy*

206 Samples of outer and inner faces of the 5 plastic butter tubs were metallized with gold
207 for surface morphology analysis with a scanning electron microscopy, SEM, (Hirox SH-
208 4000M using acceleration of 15 kV) that was equipped with a scattering electron detector.

209 2.7. *Infrared spectroscopy*

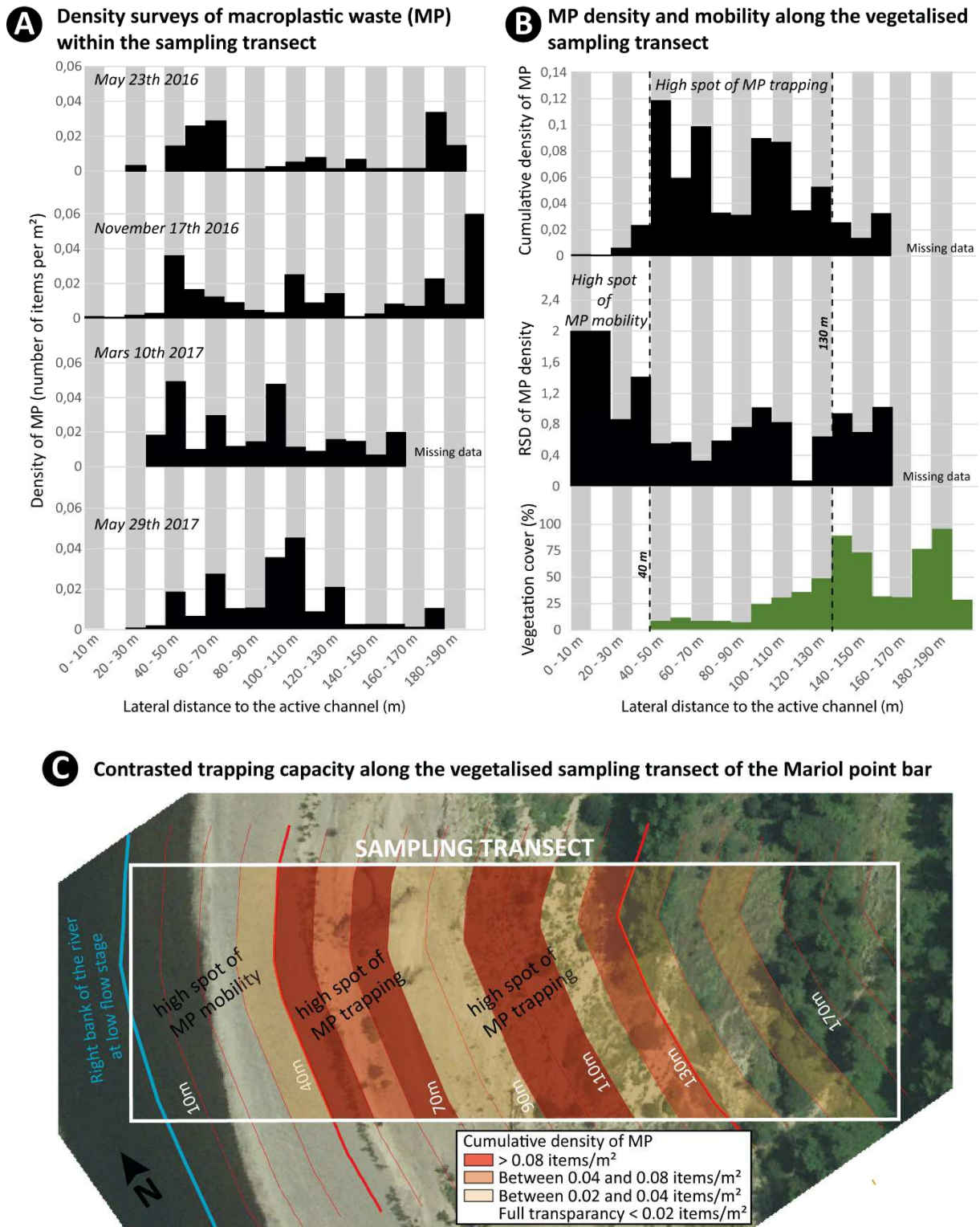
210 The mechanism by which oxidation of PP occurs is fairly well-understood and is
211 assumed to follow free radical chain mechanisms as the ones formulated by Bolland (Bolland
212 and Gee, 1946) and Bateman (Bateman, 1954). The main degradation products from
213 photooxidation of polypropylene are carbonyl containing products such as esters, ketones and
214 carboxylic acids and hydroxyl products such as hydroperoxide, alcohols and carboxylic acid
215 (Gallo et al., 2006). Infrared (IR) spectroscopy is particularly sensitive for detecting polar
216 functional groups such as carbonyl and hydroxyl groups which appear as intense peaks in the
217 range of $1700 - 1800 \text{ cm}^{-1}$, and $3600 - 3200 \text{ cm}^{-1}$, respectively (Chamas et al. 2020;
218 Rajakumar et al., 2009). IR spectra of polymeric materials can thus readily detect the
219 appearance and disappearance of certain functional groups in polymers as a result of their
220 degradation processes or release of additives (Chamas et al. 2020).

221 Attenuated total reflectance infrared spectroscopy, ATR-IR, was used to investigate the
222 appearances and disappearances of functional groups over time within the polymeric material.
223 The spectra were recorded between 4000 cm^{-1} and 643 cm^{-1} with a resolution of 4 cm^{-1} and 32
224 scans, on a Nicolet 380 IR Thermo Electron Corporation with a Golden Gate™ Single Reflection
225 Diamond ATR SPECAC. The reported spectra are of the outer face of the plastic butter tubs, if
226 not otherwise stated. Baseline correction was performed on all of the IR spectra with the OMNIC
227 software.

228 **3. Results**

229 3.1. *Spatial patterns and mobility of plastic debris at Mariol point bar*

230 Based on the 4 field-surveys along the belt transect, the sum and standard deviation of
231 plastic waste density were calculated for each band in order to highlight hot spots of trapping
232 and mobility zones of macroplastics. The spatial patterns of collected plastic debris for the
233 field-surveys are shown in figure 2A (raw data of the quantity of macrodebris collected per
234 band are in table S2 in the SI).



235

236 **Fig. 2. Trapping and mobility zones of plastic debris at Mariol point.** A. Density of
 237 macroplastic (MP) based on sampling of MP during four field surveys at Mariol point bar on
 238 the 23rd of May 2016, 17th of November 2016, 10th of March 2017 and 29th of May 2017. B.
 239 Cumulative MP data and the mobility of MP in the belt transect was calculated from the sum

240 of the density and the standard deviation based on the four field-surveys of MP, respectively.
241 This revealed hotspots of MP accumulation and mobility. The percentage coverage of
242 vegetation in the belt transect is also highlighted. C. The belt transect used for the repeated
243 field-surveys was perpendicular to the main Allier river flow and divided in 20 bands of 10 m
244 width, from the right bank of the Allier river to the abandoned channel. The sampling was
245 carried out by a group of 6 aligned persons (spacing of 10 m) prospected the belt transect (50
246 m width and 200 m long). The identified macroplastic hotspots are highlighted.

247 The values of the overall densities of macroplastic collected were 7350 items/km² (May
248 2016), 10300 items/km² (November 2016), and finally, 15500 items/km² (March 2017)
249 revealing significant accumulation of macroplastic during this one year period. The daily
250 mean discharge of the river (represented in figure S2 in the SI) reveals three events of high
251 flows, which could explain the supply of accumulated riverine litter to the riverbank. The sum
252 of the collected macroplastic for each band during the 4 field surveys are represented in the
253 top graph in figure 2B, where hotspots of macroplastic trapping are highlighted. Furthermore,
254 high mobility zones of macroplastics were identified by plotting the relative standard
255 deviation of the macroplastics sampled across the 4 field survey as a function of distance from
256 the river channel, see the second top graph in figure 2B.

257 Large variations in density and mobility of macroplastics were observed along a lateral
258 distance from the river channel. The mobility and cumulative density of surveyed
259 macroplastics were compared with the percentage of vegetation coverage on the mariol point
260 bar. Mariol point bar is bordered by sand, riparian grass and young (<7 years) riparian trees
261 while further in towards land a dense forest of old (>17 years) riparian trees encloses an
262 abandoned channel. The rate of vegetation in the belt transect for the field sampling is shown
263 in the bottom graph in figure 2B. Comparing the percentage of vegetation cover with the
264 mobility and cumulative density of macroplastic in the mariol point bar it becomes clear that

265 the mobility of the plastic waste is to some extent correlated to the vegetal density and
266 proximity to the river channel, see figure 2B and 2C. Two distinct trapping zones of
267 macroplastics were identified and correspond to the young riparian trees, which had higher
268 plastic debris density but lower residence time than the old riparian trees which were at a
269 greater distance from the river channel and allowed longer storage time of macroplastics. We
270 interpret this phenomenon as follows: the renewal of the trapped plastic in the vegetal area is
271 high in close proximity to the river, resulting in relatively high density and high mobility of
272 macroplastic, whereas the renewal is low in the more dense vegetated areas further away from
273 the river and consequently leading to relatively high macroplastic density but low mobility of
274 macroplastic. Our main conclusions of the field-study of the mobility and density of
275 macroplastic at the mariol point bar are illustrated in figure 2C.

276 3.2. *Plastic butter tub sampling and their surrounding environments*

277 The plastic butter tubs were deliberately placed along the belt transect in which the
278 field survey took place and one was buried at the tip of the point bar, to represent
279 macroplastic trapped in the sediment of riverbanks. At each position the temperatures were
280 recorded hourly using iButtons®. Unfortunately, the iButtons® placed by BB3 and BB5 were
281 lost and the temperature fluctuations overtime could not be retrieved. However, considering
282 their close positions in the alluvial environment, we can assume that the BB3 experienced
283 similar temperatures as BB2, and that BB5 was exposed to temperatures much like the ones
284 that BB4 was exposed to. The measured hourly temperatures are shown in figures S3 in the SI
285 and the average, maximum and minimum of the daily average temperatures are summarized
286 in table 1 together with their position in the alluvial environment. The average measured UV
287 radiation measured at the Puy-Dôme region for the time of sampling is shown in figure S4 in
288 the SI.

289

Table 1. Average daily temperature ranges, standard deviations, maximum and minimum temperatures measured at the locations where the plastic butter tubs were placed.

Butter tub	Alluvial environment	Average daily temperature	Daily temperature standard deviation	Maximum temperature	Minimum temperature
BB1	Highly connected to the active channel buried by sediment	1.3 °C	1.4 °C	15.1 °C	1.0 °C
BB2 + BB3	Highly connected to the active channel and below the younger (<7yrs) riparian forest (BB2) or over the bare fluvial deposit (BB3)	12.3 °C	5.9 °C	37.1 °C	-12.5 °C
BB4 + BB5	Poorly connected to the channel and below the older (>17 years) riparian forest	6.8 °C	3.6 °C	27.6°C	-6.5 °C

290

291 The plastic butter tubs experienced vastly different fluctuations of temperature. BB2
292 and BB3 were exposed to higher temperature fluctuations and a wider temperature range.
293 BB4 and BB5 experienced a near half temperature range experienced by BB2 and BB3, and
294 thus less extreme temperatures. On the other hand, BB1 which was buried in the sediment did
295 not experience much fluctuation in temperature and experienced the lowest average
296 temperature. In contrast to BB2 and BB3, BB4 and BB5 were placed in a zone with high
297 vegetation density, which could provide a buffering effect to temperature fluctuations.
298 Although the solar radiation was not measured directly at each location, the differences in

299 solar radiation experienced by the plastic butter tubs could to some extent be indirectly
300 observed in the differences in temperature at each location due to heat build-up as a result of
301 solar radiation (Andrady et al., 1998).

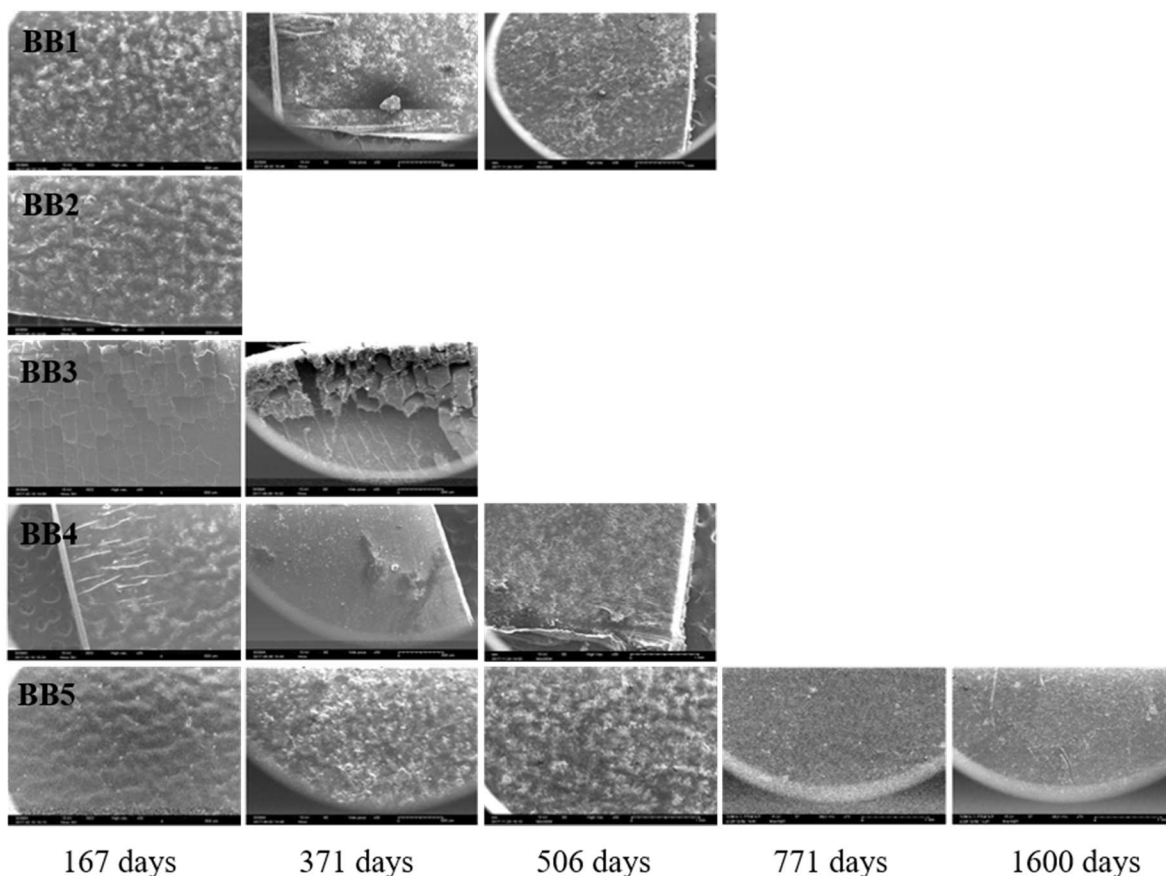
302 Samples of the tubs were taken for laboratory analysis after 167 days (17th of
303 November 2016), 371 days (10th of March 2017), 506 days (11th of October 2017) and 1600
304 days (9th of October 2020) of being placed on the Mariol point bar. After 371 days only four
305 out of the five tubs were recovered, BB2 was lost and is likely to have been washed away by
306 the river after a flooding that occurred sometime between 167-371 days after being placed in
307 the environment. BB4 and BB1 were lost between 506 and 771 days, and only BB3 and BB5
308 were recovered after 771 days. After 1600 days only BB5 was recovered and BB3 was lost
309 between 771-1600 days of being placed in the environment.

310 3.3. *Surface morphology*

311 Surface modification of polymers during degradation can be detected with Scanning
312 Electron Microscopy, SEM, and directly shows topographical changes at the polymer surface,
313 such as the formation of holes and cracks, greater roughness, or even attachment of microbes
314 to the surface as a result of degradative processes. The changes in surface morphology of the
315 plastic butter tubs over time is shown in the SEM images in figure 3. The images show the
316 most representative changes observed on the outer faces of the pieces sub-sampled
317 periodically. The most significant differences were observed between plastic butter tubs that were
318 openly exposed to sunlight, e.g. BB3, and did not have, for example, vegetation protecting it from
319 the sunlight compared to the plastic butter tubs that were protected by leaves, trees and sediment
320 such as BB5. This is exemplified in the SEM images of BB3 which showed degradation indicators
321 such as fractures and cracks after 167 days of exposure in the environment, see figure 3. It should
322 be noted that the 506- and 771 day samples of BB3 showed a very advanced state of degradation,
323 which rendered the samples too unstable under electronic bombardment during SEM

324 measurements and it was therefore not possible to get SEM images of these samples. This is
325 consistent with previous reports which also observed cracks and cavity formations for
326 polypropylene based polymers aged in landfills and naturally weathered PP (Longo et al., 2011;
327 Romano et al., 2018; Gallo et al., 2006).

328 The loss of mechanical properties as a consequence of the degradative processes could
329 explain the defects such as cracks and fractioning of the plastic material. It has previously been
330 observed that UV-radiation accelerates the formation of fractioning at the surfaces of polymeric
331 materials, which is in line with our observation (Gallo et al., 2006). BB3 was exposed to high
332 solar radiation and BB4 was exposed to medium solar radiation as it was covered by riparian
333 vegetation in the old forest (see figure 3 for SEM images of BB4). On the other hand, for BB5,
334 which was located by the foot of a tree by the old riparian trees, showed no significant changes on
335 its surface topology even after being exposed to the environment for 1600 days, only dust and
336 impurities on the surface were observed. In contrast to BB3, BB5 was exposed to low solar
337 radiation which could explain the difference in the evolution of changes in their surface
338 morphologies. BB2 was exposed to low solar radiation as it was placed in the young riparian
339 vegetation, and no significant surface modifications were observed up to 167 days of exposure.
340 Significant surface modifications were also found on BB1, characterized as dents and scratches,
341 which seem to be caused by mechanical abrasion by the sand sediment in which it was buried.



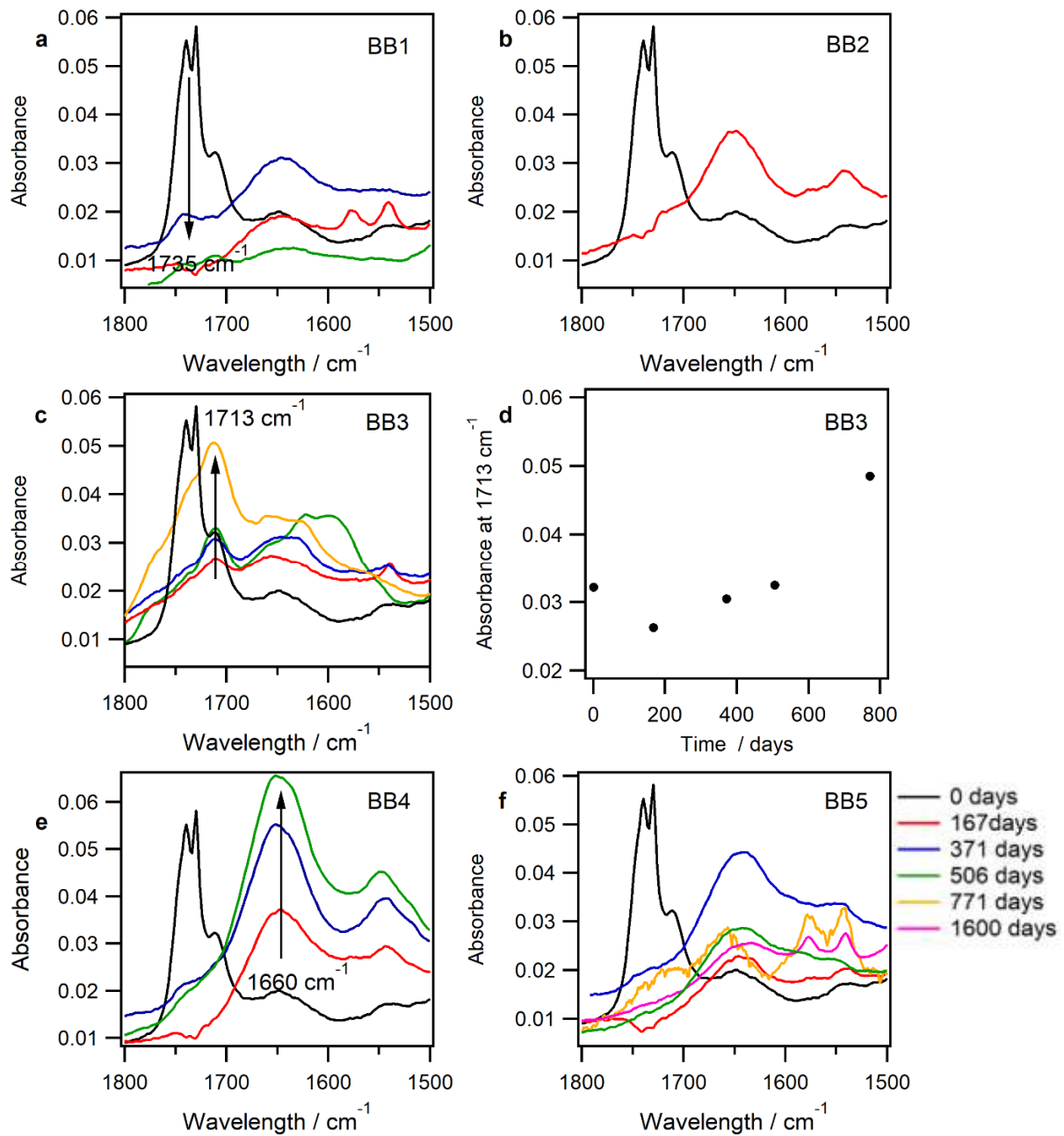
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343 **Fig. 3. SEM images of aged plastic butter tub samples.** Images taken from the outer faces
 344 of BB1, BB2, BB3, BB4 and BB5 after exposure to natural weathering for 167, 371, 506, 771
 345 and 1600 days by the Allier river. The SEM images are taken with a magnification of x50.
 346 Images of the inner and outer faces of the BB1, BB2, BB3, BB4 and BB5 are shown in
 347 figures S5-S9 in the SI.

348 *3.4. Infrared Spectroscopy*

349 The evolution of carbonyl groups is shown in the IR spectra of the samples of plastic
 350 butter tubs over time in figure 4. The full infrared spectra of the plastic butter tubs are shown
 351 in figure S10 in the SI and it should be noted that all of the IR spectra have been baseline
 352 corrected. For all the plastic butter tubs a sharp decrease in a peak at 1735 cm^{-1} was observed
 353 after only 167 days of exposure in the environment, which is believed to be the loss of an
 354 additive (likely to be in the ink, as this peak is not observed in the spectra on the inside

355 surface of the plastic butter tubs, see SI figure S11). For most of the plastic butter tubs, the
356 loss of the peak at 1735 cm^{-1} showed the most significant change in their spectra, however for
357 BB3 a broad peak at 1713 cm^{-1} in the carbonyl region (1700 cm^{-1} and 1800 cm^{-1}) appeared
358 after 371 days, see figure 4c. The increase in the peak at 1713 cm^{-1} as a function of time in the
359 environment is shown in figure 4d. A similar trend was observed in the study of naturally
360 weathered PP at Messina (Italy) by Gallo *et al.*, 2006. The rather broad peak appearing in the
361 carbonyl region during the degradation of PP is likely to be due to the result of different
362 products of degradation such as lactone, esters, ketones and carboxylic acids (Romano *et al.*,
363 2018). Furthermore, Rajakumar *et al.*, 2009, observed, through SEM imaging, surface cracks
364 of weathered PP appeared when the concentration of carbonyl products sharply increased.
365 This is consistent with our results, in that cracks appeared in the surface of the polymer and a
366 peak appearing in the carbonyl region were observed for BB3 after some time in the
367 environment. No peak appeared between 1700 cm^{-1} and 1800 cm^{-1} for BB1, BB2, BB4 and
368 BB5, see figure 4a, 4b, 4e and 4f, respectively, which again is likely to be a result of these
369 tubs being more protected from sunlight by vegetation and could therefore have a slower
370 degradation rate than that of BB3. The peak at 1660 cm^{-1} in the spectra of BB1, BB2, BB4
371 and BB5 is characteristic of O-H-O scissor bending of water, which is likely to be due to
372 water contamination of the sample (Zhuang *et al.*, 2020). In addition, the characteristic broad
373 peak of O-H stretching of water at around 3400 cm^{-1} was also observed in these spectra,
374 which can be seen in the full spectra in figure S10 in the SI. The formation of hydroxyl
375 products, such as hydroperoxide, alcohols and carboxylic acid, has previously been observed
376 in IR analyses of naturally weathered PP in the $3600\text{--}3200\text{ cm}^{-1}$ region (Rajakumar *et al.*,
377 2009). However, as a result of water being present in the plastic butter tub samples, it is likely
378 that the peaks appearing as a result of the formation of hydroxyl degradation products are
379 swamped by the peaks resulting from the H-O stretching peak of the water contamination.



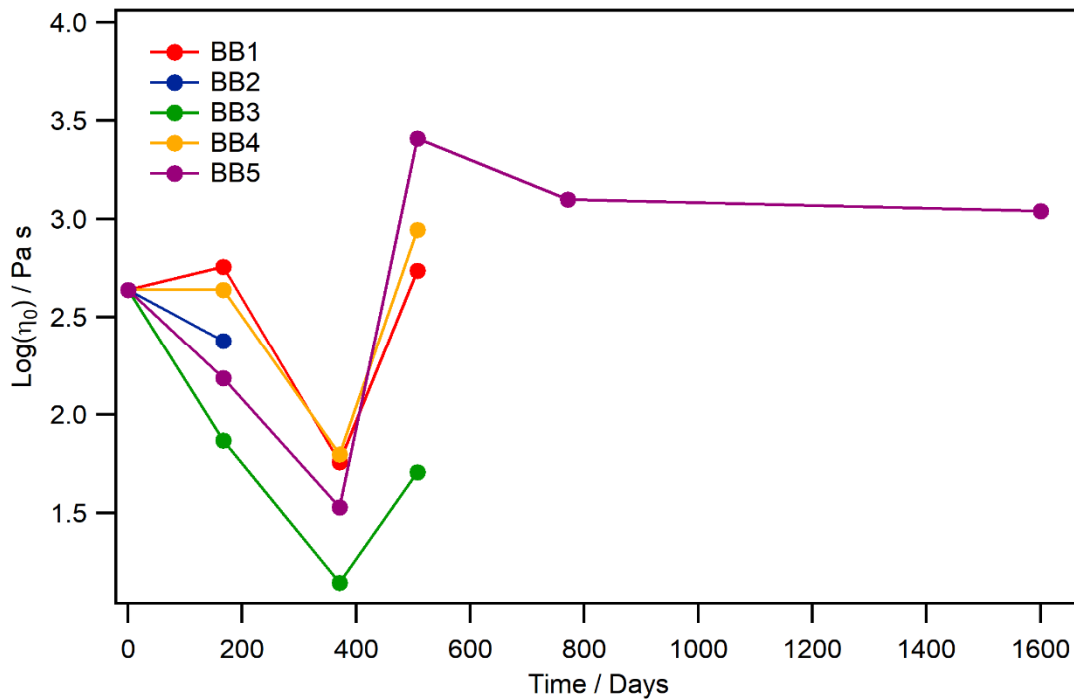
380

381 **Fig. 4. Infrared spectra of the plastic butter tubs after various exposure time in the**
 382 **environment.** The infrared spectra shows the formation of oxidation products in the 1700-
 383 1800 cm⁻¹ region after being exposed to the environment for 167, 371, 506, 771 and 1600
 384 days of **a. BB1, b. BB2, c. BB3 e. BB4 and f. BB5.** The increase of the peak at 1713 cm⁻¹ in
 385 the carbonyl region of BB3 is demonstrated in **d.** The peaks at 1660 cm⁻¹ are due the presence
 386 of water (Zhuang et al., 2020). The loss of additive can be observed from the disappearance of
 387 the peak at around 1735 cm⁻¹ for all the plastic butter tubs.

388 The infrared spectra reveal both similarities and differences between the butter tubs
389 aged in different locations. The sub-sampling of the plastic butter tubs for IR analyses were
390 taken on different pieces and despite being on different areas of the plastic butter tub, a trend
391 could be observed in for example BB3, where the carbonyl peaks increased over time and it
392 did not for the other plastic butter tubs. The main focus of this study is to develop a proof-of-
393 concept to see if the degradation of the same plastic material varies as a function of its storage
394 location and time on land, it was therefore a strategic choice to follow the degradation of the
395 same butter tubs. However, it is clear that the inclusion of replicates is needed to truly
396 corroborate the variability of aging of riverine plastics with their storage location and time.
397 Despite the low replication in this study, we hope that this study has evoked interest and
398 envision that this concept can be applied in future studies employing more replicates and
399 consequently providing statistical data of the degradation pathway of plastic waste in the
400 environment.

401 3.5. Rheology

402 Melt rheology was used to calculate the zero shear viscosity, η_0 , of the butter tub samples.
403 The η_0 depends on the molecular weight (M_w) of a polymer, (Commereuc *et al.*, 2013;
404 Commereuc *et al.*, 2010), the relationship is described in the SI, and can be used to determine
405 whether a polymer degrades *via* chain scission or chain recombination mechanisms. Figure 5
406 shows the variation of η_0 of all the plastic butter tubs as a function of the time exposed to the
407 environment.



408

409 **Fig. 5. Changes of η_0 of plastic butter tubs.** η_0 of aged plastic butter tubs obtained through
 410 extrapolation of cole-cole plots.

411 Any alteration in η_0 of a polymeric material from its initial η_0 suggests that the polymer
 412 has been subjected to a change at the molecular level and can be considered as degraded.
 413 Interestingly, all the samples follow roughly the same degradation mechanism with
 414 differences in the intensity of the variations. For all plastic butter tubs, there is an initial drop
 415 in η_0 until 371 days (and until 167 days for BB2) of exposure in the environment, this is then
 416 followed by an increase in η_0 . The initial drop in η_0 suggests that there is a chain scission
 417 mechanism occurring within the polymer in the first year in the environment. The drop in η_0 is
 418 the most pronounced in BB3. The increase in η_0 indicates a chain recombination process
 419 (Commereuc et al., 2013; Commereuc et al., 2010), and the increase in η_0 is the most
 420 pronounced for BB5 after 506 days of exposure. After 771 days of being placed in the
 421 environment, only BB3 and BB5 were recovered. The 771 day samples of BB3 and BB5 were
 422 both subjected to mechanical analyses, however the viscosity of BB3 had dropped
 423 significantly, that even its mechanical properties could not be measured at the same

424 conditions it was measured in the prior rheological analyses. The loss of mechanical
425 properties was also observed visually, as BB3 would crumble with very light applied force.
426 This sharp drop in η_0 suggests that there is, again, a chain scission mechanism occurring
427 (Commereuc et al., 2013; Commereuc et al., 2010). The mechanical properties of BB5,
428 however, could be measured and showed a slight decrease in viscosity after 1600 days of
429 being placed in the environment.

430 The strongest ambiguity comes from the increase in viscosity observed during the
431 sampling period of the tubs after 506 days in the environment. The increase in viscosity is an
432 unusual behavior for polypropylene degradation, since polypropylene is usually reported to
433 degrade by chain scission due to the presence of hydrogen linked to a tertiary carbon in the
434 backbone chain (Longo et al., 2011; Canevarolo, 2000). It is possible that the initial stage for
435 degradation is photooxidative causing chain scission, and thereafter processes such as
436 microbial actions or the presence of impurities could initiate other degradation processes
437 causing chain recombination processes. This unusual behavior of polypropylene demonstrates
438 the complexity of natural conditions that plastic debris are exposed to, which are difficult to
439 replicate in laboratory settings.

440 The results of each plastic butter tub are summarized in table 2.

Table 2. Summary of plastic butter tubs placed on the Mariol point bar with its observed changes in surface morphology, infrared spectroscopy, rheological properties and mobility.

Butter tub	Position	Solar radiation	Temperature	Mobility	SEM	IR	Rheology
BB1	Buried in sediment, high mobility zone	Pre-irradiated, then no exposure	Avg. 1.3 °C Max. 15.1 °C Min. 1.0 °C	Lost after 506 days	Some cavities and modifications to the surface from mechanical abrasions	Departure of the ink additive at 1735 cm ⁻¹ . A small peak appeared in carbonyl region between 0-371 days, then a drop again at 506 days.	Initial decrease in Newtonian viscosity, then followed by an increase in viscosity
BB2	By riverbank in young (<7 yrs) vegetation, high mobility zone	Low exposure	Avg. 12.3 °C Max. 37.1 °C Min. -12.5 °C	Lost after 167 days	Little modification to the surface morphology	Departure of the ink additive at 1735 cm ⁻¹ .	Decrease in Newtonian viscosity.
BB3	By riverbank, on bare alluvial deposit, medium mobility zone	High exposure	Avg. 12.3 °C Max. 37.1 °C Min. -12.5 °C	Lost after 771 days	Cracking and fractioning at surface after 167 days.	Departure of the ink additive at 1735 cm ⁻¹ . A small peak appeared in carbonyl region at 1660 cm ⁻¹ and increased from 371 days to 771 days	Initial decrease in Newtonian viscosity, then followed by an increase in viscosity, and then a drastic decrease in viscosity after 771 days.
BB4	Further away from river, in older (<17 years) vegetation, medium to low mobility zone	Low to medium exposure	Avg. 6.8 °C Max. 27.6 °C Min. -6.5 °C	Lost after 506 days	Cracks and fractioning appears after 506 days	Departure of the ink additive at 1735 cm ⁻¹ . Very little changes in the carbonyl and hydroxyl region.	Initial decrease in Newtonian viscosity, then followed by an increase in viscosity
BB5	Further away from river, in older (>17 years) vegetation, low mobility zone	Low exposure	Avg. 6.8 °C Max. 27.6 °C Min. -6.5 °C	Still in initial location	Relatively intact, only dust/impurities were detected	Departure of the ink additive at 1735 cm ⁻¹ . No changes in the carbonyl and hydroxyl region.	Initial decrease in Newtonian viscosity, then followed by an increase in viscosity and then a slight decrease in viscosity.

441 **4. Discussion**

442 With the outset of developing a proof-of-concept study, we deliberately placed 5 identical
443 plastic butter tubs in 5 different mobility and trapping zones (determined from the repeated
444 belt-transect surveys). The storage time of these 5 plastic butter tubs when trapped in the
445 identified mobility and storage zones were therefore expected to vary sufficiently to allow us
446 to assess the aging of the same plastic butter tubs in these storage locations. To the best of our
447 knowledge, no study has followed the degradation of riverine plastic debris as a function of
448 their storage time on land. Our initial study reveals variability in the aging of plastic debris
449 stored in different trapping zones, however, future studies including replicates are necessary
450 to better corroborate this conclusion.

451 From the repeated belt-transect surveys we could see that the retention time of plastic
452 debris in the fluvial system varies as a function of proximity to the river channel and the
453 density of riparian vegetation. Logically, the retention time for plastic near the active channel
454 is expected to be shorter than the retention time for plastic trapped in the distal parts of the
455 river floodplains. Thus, BB2's close proximity to the channel increases the likelihood of
456 mobility and explains its relatively early departure from the riverbank. Although BB1 was
457 also placed in close proximity to the river channel, it was not as mobile as BB2 and could be
458 retrieved even after 506 days being in the environment before it was mobilized, possibly
459 through riverbank erosion. Burying BB1 under the sediment protects it from certain natural
460 mobilization actions such as winds or low magnitude floods. Furthermore, already we can see
461 that if a plastic material is trapped further in towards land and in areas of densely packed
462 vegetation, such as BB4 and BB5, it could be trapped there for years and maybe even
463 permanently. For example, BB5 has now been in the same location for almost 5 years.
464 Needless to say, the use of more replicates per location could improve the certitude of the
465 mobility and storage time of macroplastics in these zones.

466 As previously mentioned, the focus of this study is on following the aging of
467 macroplastics as a function of their storage time in different locations along a river channel.
468 The 5 butter tubs, were placed in locations in which the storage time could be sufficiently
469 different and therefore allowing us to follow the degradation of the identical butter tubs for
470 varying storage time. The mobility and storage time of macroplastics will determine the
471 amount of time the plastic will be exposed to natural degradative conditions on land, which
472 will in turn determine the extent of aging of the plastic when stored in this sink. Additionally,
473 the intensity of natural conditions to which the plastic is exposed to will determine the rate of
474 degradation, as exemplified by the differences in degradation states of the 771 day samples of
475 BB3 and BB5. BB3 was in a more advanced state of degradation after 771 days in the
476 environment than BB5, which was clearly observed in the differences in their SEM images,
477 infrared spectroscopies and rheological properties, as well as visually. The different degrees
478 of degradation can be explained by their different protection of natural conditions, for
479 example BB3, was openly exposed to natural conditions such as solar radiation and
480 temperature fluctuations, as seen in the daily average temperature ranges and standard
481 deviations in table 1, whereas the dense forest in which BB5 was located provided protection
482 from natural conditions, such as sunlight, and consequently buffered the aging of BB5.

483 Notably, the sharp decrease in the carbonyl peak observed in the infrared spectroscopy of
484 all plastic butter tubs, which is believed to be the ink additive (see figure S11), suggests that
485 the additive has leached out into their surrounding environments after only 167 days of being
486 in the environment. For BB3, we could also see the generation of carbonyl groups, suggesting
487 that degradation products have formed, which could also lead to chemical leachates.
488 Monitoring the appearance and disappearance of peaks in IR spectra could provide vital
489 information when studying the ecotoxicity of plastics in the environment, since the presence

490 of plastic leachates can raise threats to the quality of the water in rivers, land users next to
491 rivers and the well-being of wildlife which aggregate in riparian areas.

492 In this study, we demonstrated that relatively simple analytical techniques such as IR,
493 SEM imaging and rheology are sensitive tools in terms of detecting degradation of plastics.
494 Even early sampling of the tubs (after 167 days of being in the environment) revealed
495 differences in the degree of degradation of the plastic, these initial degradation evolutions
496 were particularly clear in their rheological properties. Investigations on degradation pathways
497 and the extent of degradation of plastic waste in relation to their positioning and exposure to
498 natural conditions can provide important information on its future transformations in a
499 specific environment. As a result of placing the butter tubs in different trapping zones along
500 the Allier river, the plastic materials or pieces of the plastic will have entered the river stream
501 in diverse shapes and degrees of degradation. The advancement of the aging of plastic debris
502 is clearly important to consider as these will determine how they will be re-trapped by riverine
503 vegetation further along the river stream, transported in the river, and its future degradation
504 pathways which will ultimately determine the state and how much of the riverine plastic
505 actually enters the ocean.

506 Considering that riverine plastic debris spends a weighty proportion of its lifetime
507 stranded (Tramoy et al., 2020a; Tramoy et al., 2020b), the degradation it undergoes whilst
508 stranded is likely to play a significant role in its overall lifetime. As observed in this study,
509 after 2 years in the environment BB3 had become extremely brittle and we can assume that it
510 was “lost” as microplastic, as a result of mechanical forces acting on it (e.g. wind or rainfall).
511 Understanding how much and where macroplastic is “lost” as microplastic during its journey
512 from land to ocean *via* rivers, would not only improve the certitude of global estimates of
513 riverine outputs of macro- and microplastic, but also guide mitigation actions to prioritise
514 areas for macroplastic cleanup. As highlighted in numerous reviews and studies, plastic

515 material in the environment exhibit a wide variety of degradation pathways and rates as a
516 result of the vast plastic materials existing today, the various natural conditions the material is
517 exposed to and its path in the environment (Pinheiro *et al.*, 2021, Zhang *et al.*, 2021, Chamas
518 *et al.*, 2020). Thus, local observational studies of monitoring plastic degradation during their
519 storage time in known environmental sinks such as the one described herein and Ter Halle *et*
520 *al.* (2017) which studied the degradation of polyethylene based ocean microplastic, as well as
521 including more polymer shapes and types are needed to better understand the range of
522 transformations and transformation rates that plastic waste can undertake in important
523 environmental sinks.

524 **5. Conclusion**

525 Through our proof-of-concept study of following the aging of identical plastic butter tubs
526 at different locations along a riverine system, we have demonstrated that the amount of time
527 that plastic debris is stored and aged by natural conditions prior to re-mobilization seems to
528 depend on its position with respect to the river channel as well as the riparian vegetation age,
529 roughness and structure. Plastic waste can be retained on riverbanks for years, accumulate,
530 degrade and fragment, which could drastically lower the global estimates of plastic emissions
531 from rivers into the ocean. Understanding how riverine plastic debris are aged and
532 transformed in these temporary sinks, as well as the time-scale of storage, can help in gaining
533 more knowledge of marine plastic pollution sources and pathways, and possibly in part
534 answering the question *where is the missing plastic?* Furthermore, long-term marine debris
535 monitoring using relatively simple methods could provide crucial information for developing
536 effective mitigation and clean-up activities, which could reduce both riverine plastic and
537 ultimately marine plastic.

538

539

540

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545

546 **References**

547 Andrady, A. L., Hamid, S. H., Hu, X., Torikai, A., 1998. Effects of increased solar ultraviolet
548 radiation on materials, *J. Photochem. Photobiol. B.* 46, (1-3): 96-103.
549 [https://doi.org/10.1016/S1011-1344\(98\)00188-2](https://doi.org/10.1016/S1011-1344(98)00188-2).

550

551 Bateman, L., 1954. Olefin oxidation. *Q. Rev. Chem. Soc.* 8:147–167.
552 <https://doi.org/10.1039/QR9540800147>.

553

554 Blettler, M. C. M., Abrial, E., Khan, F. R., Sivri, N., Espinola, L. A., 2018. Freshwater plastic
555 pollution: recognizing research Biases and identifying knowledge gaps. *Water Res.* 143:416-
556 424. <https://doi.org/10.1016/j.watres.2018.06.015>.

557

558 Bolland, J. L.,Gee, G., 1946. Kinetic studies in the chemistry of rubber and related materials.
559 II. The kinetics of oxidation of unconjugated olefins. *Trans. Faraday Soc.* 42:236–243.
560 <https://doi.org/10.1039/TF9464200236>.

561

562 Canevarolo, S. V., 2000. Chain scission distribution function for polypropylene degradation
563 during multiple extrusions. *Polym. Degrad. Stabil.* 70 (1): 71–76.
564 [https://doi.org/10.1016/S0141-3910\(00\)00090-2](https://doi.org/10.1016/S0141-3910(00)00090-2).

565
566 Chamas, A. Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J. H., Abu-Omar, M., Scott, S.
567 L., and Suh S., 2020. Degradation rates of plastics in the environment. *ACS Sustain. Chem.*
568 *Eng.* 8 (9): 3494–3511. <https://doi.org/10.1021/acssuschemeng.9b06635>.

569
570 Commereuc, S., Askanian, H., Verney, V., Celli, A., Marchese, P., 2010. About durability of
571 biodegradable polymers: structure/degradability relationships. *Macromol. Symp.* 296 (1):378–
572 387. <https://doi.org/10.1002/masy.201051052>.

573
574 Commereuc, S. Askanian, H., Verney, V., Celli, A., Marchese, P., Berti, C., 2013. About the
575 end life of novel aliphatic and aliphatic-aromatic (co)polyesters after UV-weathering:
576 structure/degradability relationships. *Polym. Degrad. Stabil.* 98 (7):1321–1328.
577 <https://doi.org/10.1016/j.polymdegradstab.2013.03.030>.

578
579 Dris, R., Imhof, H., Sanchez, W., Gasperi, J., Galgani, F., Tassin, B., Laforsch, C., 2015.
580 Beyond the ocean: contamination of freshwater ecosystems with (micro-)plastic
581 particles. *Environ. Chem.* 12 (5):539-550. <https://doi.org/10.1071/EN14172>.

582
583 Dris, R., Tramoy, R., Alligant, S., Gasperi, J., Tassin, B., 2020. Plastic Debris Flowing from
584 Rivers to Oceans: The Role of the Estuaries as a Complex and Poorly Understood Key
585 Interface, in: Rocha-Santos, T., Costa, M., Mouneyrac, C. (Eds.), *Handbook of Microplastics*

586 in the Environment. Springer, Cham, pp. 1–28. [https://doi.org/10.1007/978-3-030-10618-8_3-](https://doi.org/10.1007/978-3-030-10618-8_3-1)
587 1.

588

589 Gallo, R., Brambilla, L., Castiglioni, C., Severini, F., 2006. Characterization of naturally
590 weathered polypropylene plates. *J Macromol Sci Pure Appl Chem. A.* 43 (3):535–554.
591 <https://doi.org/10.1080/10601320600575280>.

592

593 Garófano Gómez, V., Metz, M., Egger, G., Díaz-Redondo, M., Hortobágyi, B., Geerling, G.,
594 Corenblit, D., Steiger, J., 2017. Vegetation succession processes and fluvial dynamics of a
595 mobile temperate riparian ecosystem: the lower Allier river (France). *Geomorphol. Relief,*
596 *Process. Environ.* 23 (3):187–202. <https://doi.org/10.4000/geomorphologie.11805>.

597

598 Geyer, R., Jambeck, J. R., Law, K. L., 2017. Production, use, and fate of all plastics ever
599 made. *Sci. Adv.* 3 (7):1700782. <https://doi.org/10.1126/sciadv.1700782>.

600

601 Grossetete, T., Gonon, L., Verney, V., 2002. Submicrometric characterization of the
602 heterogeneous photooxidation of polypropylene by microthermal analysis. *Polym. Degrad.*
603 *Stabil.* 78 (2):203–210. [https://doi.org/10.1016/S0141-3910\(02\)00134-9](https://doi.org/10.1016/S0141-3910(02)00134-9).

604

605 Harvey, J. A., 2005. Chemical and Physical Aging of Plastics, in: Kutz, M. (ed.), *Handbook*
606 *of Environmental Degradation of Materials.* William Andrew Publishing, Norwich, pp. 153-
607 163. <https://doi.org/10.1016/B978-081551500-5.50009-4>.

608

609 Hurley, R., Horton, A., Lusher, A., Nizzetto, L., 2020. Plastic Waste in the Terrestrial
610 Environment, in: Letcher, T. M. (ed.), *Plastic Waste and Recycling*. Academic Press, Stratton
611 on the Fosse, pp. 163–193. <https://doi.org/10.1016/B978-0-12-817880-5.00007-4>.

612 Lebreton, L., Egger, M., Slat, B., 2019. A global mass budget for positively buoyant
613 macroplastic debris in the ocean. *Sci. Rep.* 9:15611. [https://doi.org/10.1038/s41598-019-](https://doi.org/10.1038/s41598-019-49413-5)
614 49413-5.

615

616 Lebreton, L. C. M., van der Zwet, J., Damsteg, J. –W., Slat, B., Andrady, A., Reisser, J.,
617 2017. River plastic emissions to the world's oceans. *Nat. Commun.* 8:15611.
618 <https://doi.org/10.1038/ncomms15611>.

619

620 Lemaire, J., Arnaud, R., Lacoste, J., 1988. The Prediction of the Long-Term Photoageing of
621 Solid Polymers. *Acta Polym.* 39 (2): 27–32. <https://doi.org/10.1002/actp.1988.010390106>.

622

623 Liro, M., Emmerik, T. van, Wyżga, B., Liro, J., Mikuś, P., 2020. Macroplastic storage and
624 remobilization in rivers. *Water.* 12 (7): 2055. <https://doi.org/10.3390/w12072055>.

625

626 Longo, C., Savaris, M., Zeni, M., Brandalise, R., Grisa, A., 2011. Degradation study of
627 polypropylene (PP) and bioriented polypropylene (BOPP) in the environment. *Mater. Res.* 14
628 (4):442–448. <https://doi.org/10.1590/S1516-14392011005000080>.

629

630 Mai, L., Sun, X. -F., Xia, L. -L., Bao, L. -J., Liu, L. -Y., Zeng, E. Y., 2020. Global Riverine
631 Plastic Outflows. *Environ. Sci. Technol.* 54 (16): 10049-10056.
632 <https://doi.org/10.1021/acs.est.0c02273>.

633

634 Pinheiro, L., M., Agostini, V. O., Lima, A., R., A., Ward, R., D., Pinho, G., L., L., 2021. The
635 fate of plastic litter within estuarine compartments: An overview of current knowledge for the
636 transboundary issue to guide future assessments. *Environ. Pollut.*, 279: 1169085.
637 <https://doi.org/10.1016/j.envpol.2021.116908>.

638

639 Rajakumar, K., Sarasvathy, V., Thamarai Chelvan, A., Chitra, R., Vijayakumar, C. T., 2009.
640 Natural Weathering Studies of Polypropylene. *J. Polym. Environ.* 17 :191.
641 <https://doi.org/10.1007/s10924-009-0138-7>.

642

643 Romano, R. S. G., Oliani, W. L., Parra, D. F., Lugao, A. B., 2018. Accelerated environmental
644 degradation of gamma irradiated polypropylene and thermal analysis. *J. Therm. Anal.*
645 *Calorim.* 131:823–828. <https://doi.org/10.1007/s10973-017-6653-1>.

646

647 Schmidt, C., Krauth, T., Wagner, S., 2018. Export of Plastic Debris by Rivers into the Sea.
648 *Environ. Sci. Technol.* 51 (21):12246–12253. <https://doi.org/10.1021/acs.est.7b02368>.

649

650 ter Halle, A., Ladirat, L., Gendre, X., Goudouneche, D., Pusineri, C., Routaboul, C.,
651 Tenailleau, C., Duployer, B., Perez, E., 2016. Understanding the fragmentation pattern of

652 marine plastic debris. *Environ. Sci. Technol.* 50 (11):5668–5675.
653 <https://doi.org/10.1021/acs.est.6b00594>.
654
655 ter Halle, A., Ladirat, L., Martignac, M., Mingotaud, A. F., Boyron, O., Perez, E., 2017. To
656 what extent are microplastics from the open ocean weathered?. *Environ. Pollut.* 227: 167-174.
657 <https://doi.org/10.1016/j.envpol.2017.04.051>.
658
659 Tramoy, R., Gasperi, J., Colasse, L., Tassin, B., 2020. Transfer dynamic of macroplastics in
660 estuaries - new insights from the Seine estuary: Part 1. Long term dynamic based on date-
661 prints on stranded debris. *Mar. Pollut. Bull.* 152:110894.
662 <https://doi.org/10.1016/j.marpolbul.2020.110894>.
663
664 Tramoy, R., Gasperi, J., Colasse, L., Silvestre, M., Dubois, P., Noûs, C., Tassin, B., 2020.
665 Transfer dynamics of macroplastics in estuaries – new insights from the Seine estuary: Part 2.
666 Short-term dynamics based on GPS-trackers. *Mar. Pollut. Bull.* 160:111566.
667 <https://doi.org/10.1016/j.marpolbul.2020.111566>.
668
669 van Sebille, E., England, M. H., Froyland, G., 2012. Origin, dynamics and evolution of ocean
670 garbage patches from observed surface drifters. *Environ. Res. Lett.* 7:044040.
671 <https://doi.org/10.1088/1748-9326/7/4/044040>.
672
673 van Emmerik, T., Schwarz, A., 2020. Plastic debris in rivers. *WIREs Water.* 7(1):1398.
674 <https://doi.org/10.1002/wat2.1398>.
675

676 van Emmerik, T., Strady, E., Kieu-Le, T.-C., Nguyen, L., Gratiot, N., 2019. Seasonality of
677 riverine macroplastic transport. *Sci. Rep.* 9:13549. [https://doi.org/10.1038/s41598-019-50096-](https://doi.org/10.1038/s41598-019-50096-1)
678 1.

679

680 Vogt, N. B., Kleppe, E. A., 2009. Oxo-biodegradable polyolefins show continued and
681 increased thermal oxidative degradation after exposure to light. *Polym. Degrad. Stabil.*
682 94(1):659–663. <https://doi.org/10.1016/j.polymdegradstab.2009.01.002>.

683

684 Zhang, K., Hamidian, A. H., Tubić, A., Zhang, Y., Fang, J., K., H., Wu, C., Lam, P., K., S.,
685 2021. Understanding plastic degradation and microplastic formation in the environment: A
686 review. *Environ. Pollut.*, 274:116554. <https://doi.org/10.1016/j.envpol.2021.116554>.

687

688 Zhuang, J., Li, M., Pu, Y., Ragauskas, A. J., Yoo, C. G., 2020. Observation of potential
689 contaminants in processed biomass using Fourier transform infrared spectroscopy. *Appl. Sci.*
690 10(12):4345. <https://doi.org/10.3390/app10124345>.

691

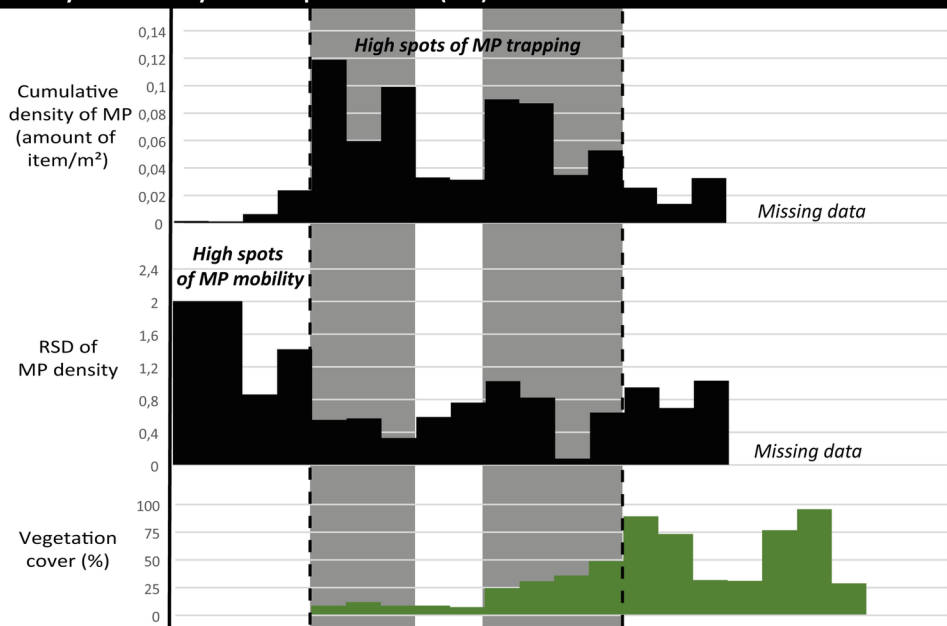
692 **Author contributions.**

693 A. E. D. conceptualization, data curation, formal analysis, investigation, methodology,
694 writing- original draft, review & editing. G. B. K. conceptualization, data curation, formal
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696 Supervision, conceptualization, methodology, writing- editing & reviewing.

697 **Competing interests.**

698 The authors declare that they have no known competing financial interests or personal
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Density and mobility of macroplastic waste (MP) in the riverine environment



Aging of plastic butter tubs along the riverine system

