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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<sup>-1</sup>. 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.

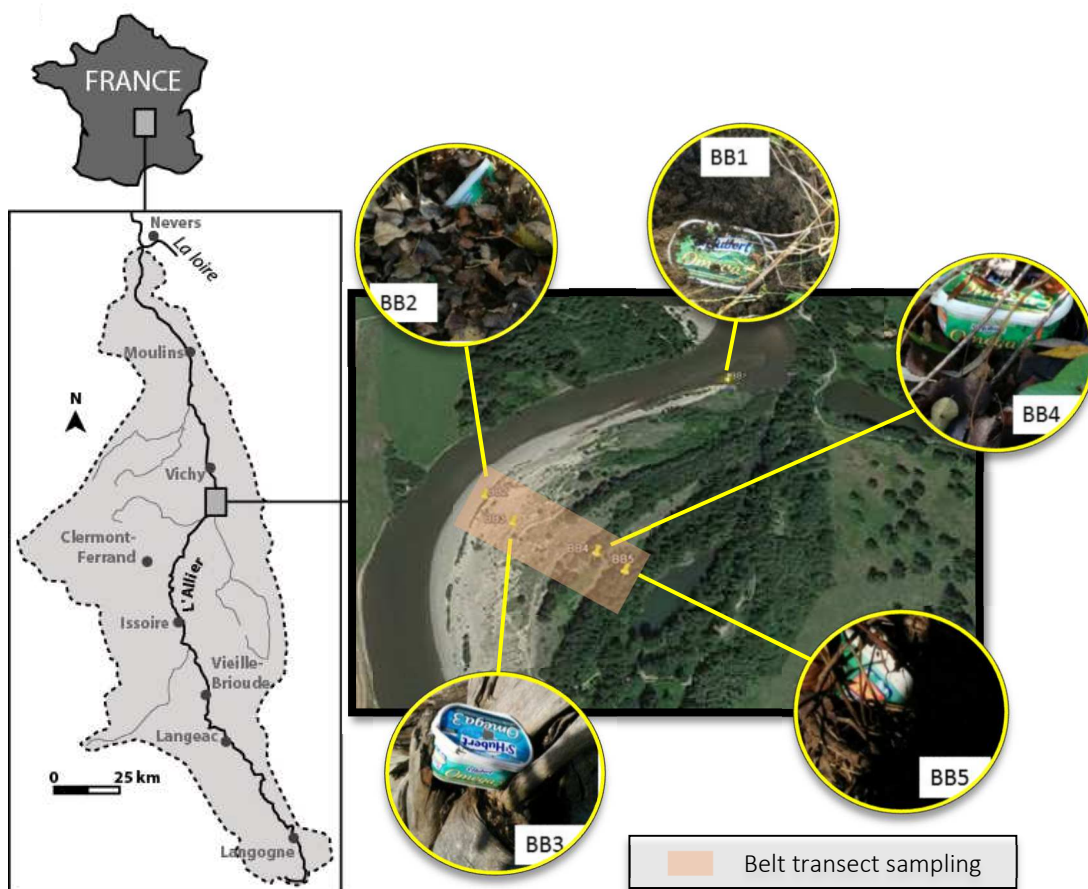
## 128 2.2. *Surveying the spatial density and mobility of plastic waste on alluvial bars*

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 23<sup>rd</sup> of May 2016, 17<sup>th</sup> of November 2016, 10<sup>th</sup> of March 2017 and 29<sup>th</sup> 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  $\pm 20$  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 23<sup>rd</sup> 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 (17<sup>th</sup> of November 2016), 371 (10<sup>th</sup> of March 2017), 506 (11<sup>th</sup> of October  
184 2017) and 1600 (9<sup>th</sup> 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*

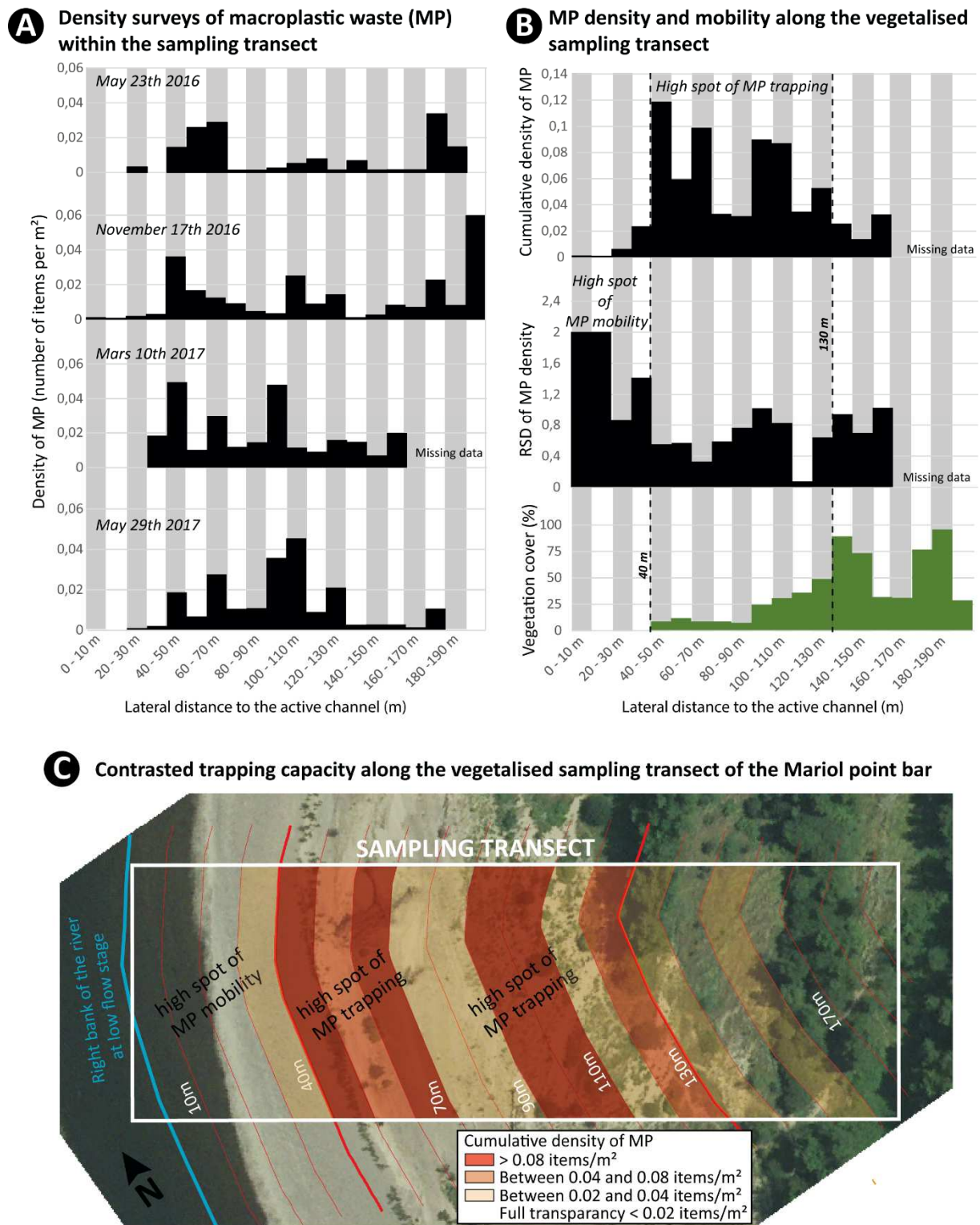
210 The mechanism by which oxidation of PP occurs is fairly well-understood and is  
211 assumed to follow free radical chain mechanisms as the ones formulated by Bolland (Bolland  
212 and Gee, 1946) and Bateman (Bateman, 1954). The main degradation products from  
213 photooxidation of polypropylene 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  $4000 \text{ cm}^{-1}$  and  $643 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  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 23<sup>rd</sup> of May 2016, 17<sup>th</sup> of November 2016, 10<sup>th</sup> of March 2017 and 29<sup>th</sup> 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/km<sup>2</sup> (May  
248 2016), 10300 items/km<sup>2</sup> (November 2016), and finally, 15500 items/km<sup>2</sup> (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.**

<b>Butter tub</b>	<b>Alluvial environment</b>	<b>Average daily temperature</b>	<b>Daily temperature standard deviation</b>	<b>Maximum temperature</b>	<b>Minimum temperature</b>
<b>BB1</b>	Highly connected to the active channel buried by sediment	1.3 °C	1.4 °C	15.1 °C	1.0 °C
<b>BB2 + BB3</b>	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
<b>BB4 + BB5</b>	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).

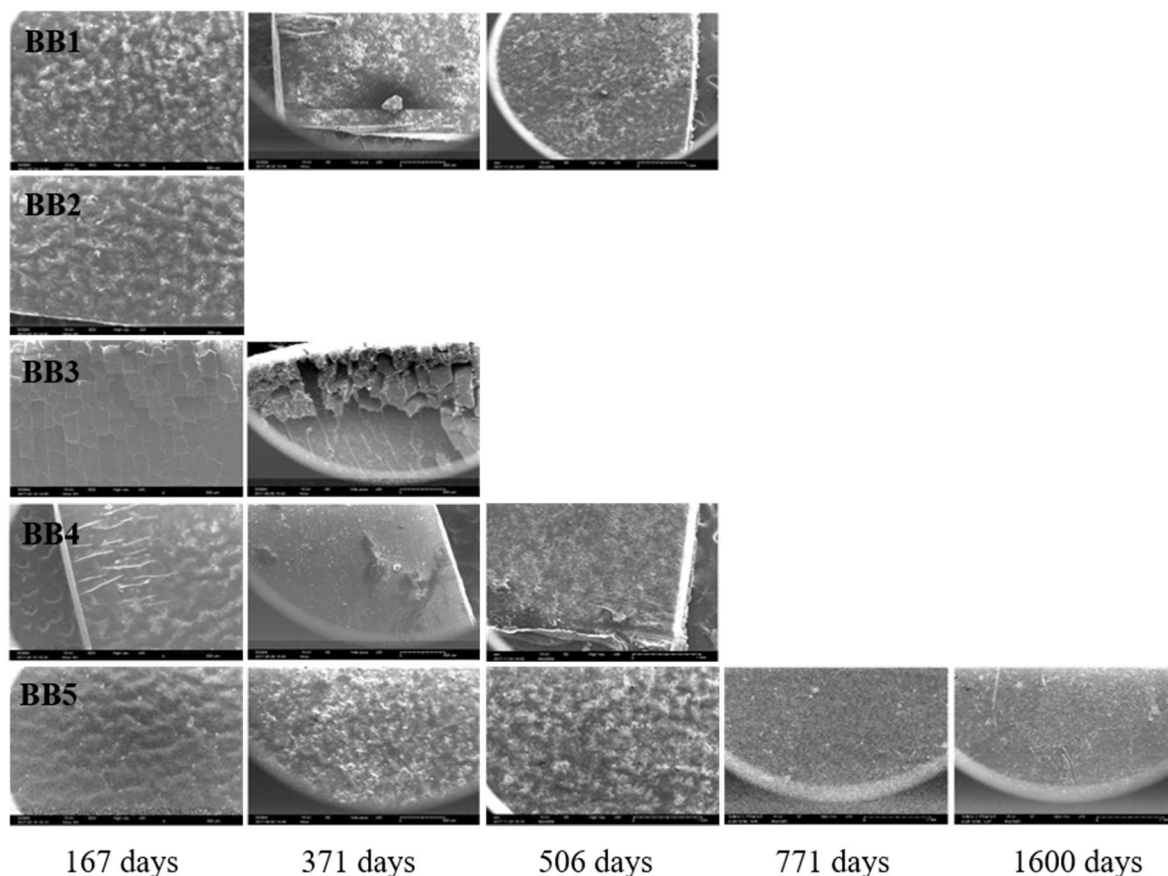
302 Samples of the tubs were taken for laboratory analysis after 167 days (17<sup>th</sup> of  
303 November 2016), 371 days (10<sup>th</sup> of March 2017), 506 days (11<sup>th</sup> of October 2017) and 1600  
304 days (9<sup>th</sup> of October 2020) of being placed on the Mariol point bar. After 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.



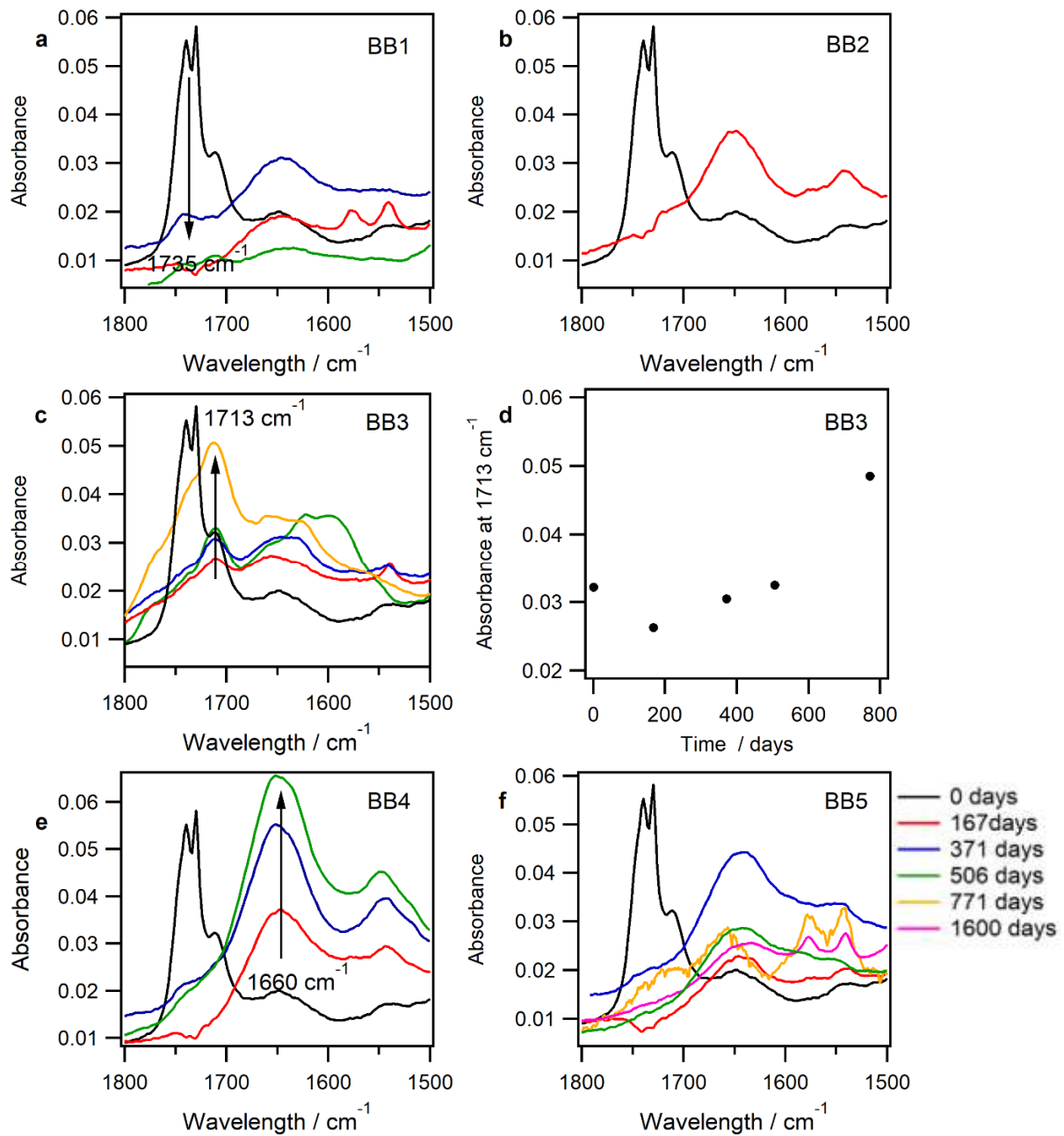
342

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  $1735\text{ cm}^{-1}$  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  $1735\text{ cm}^{-1}$  showed the most significant change in their spectra, however for  
357 BB3 a broad peak at  $1713\text{ cm}^{-1}$  in the carbonyl region ( $1700\text{ cm}^{-1}$  and  $1800\text{ cm}^{-1}$ ) appeared  
358 after 371 days, see figure 4c. The increase in the peak at  $1713\text{ cm}^{-1}$  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  $1700\text{ cm}^{-1}$  and  $1800\text{ cm}^{-1}$  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  $1660\text{ cm}^{-1}$  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  $3400\text{ cm}^{-1}$  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.



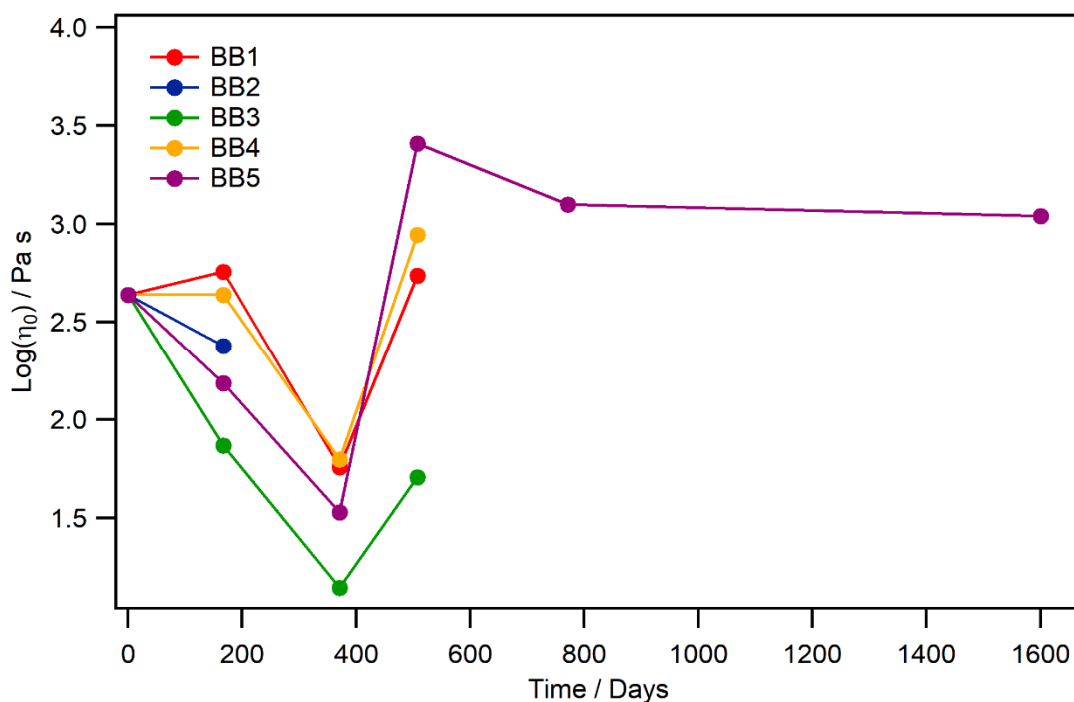
380

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<sup>-1</sup> 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<sup>-1</sup> in  
 385 the carbonyl region of BB3 is demonstrated in **d.** The peaks at 1660 cm<sup>-1</sup> 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<sup>-1</sup> 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,  $\eta_0$ , of the butter tub samples.  
403 The  $\eta_0$  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  $\eta_0$  of all the plastic butter tubs as a function of the time exposed to the  
407 environment.



408

409 **Fig. 5. Changes of  $\eta_0$  of plastic butter tubs.**  $\eta_0$  of aged plastic butter tubs obtained through  
 410 extrapolation of cole-cole plots.

411 Any alteration in  $\eta_0$  of a polymeric material from its initial  $\eta_0$  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  $\eta_0$  until 371 days (and until 167 days for BB2) of exposure in the environment, this is then  
 416 followed by an increase in  $\eta_0$ . The initial drop in  $\eta_0$  suggests that there is a chain scission  
 417 mechanism occurring within the polymer in the first year in the environment. The drop in  $\eta_0$  is  
 418 the most pronounced in BB3. The increase in  $\eta_0$  indicates a chain recombination process  
 419 (Commereuc et al., 2013; Commereuc et al., 2010), and the increase in  $\eta_0$  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  $\eta_0$  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
<b>BB1</b>	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 <sup>-1</sup> . 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
<b>BB2</b>	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 <sup>-1</sup> .	Decrease in Newtonian viscosity.
<b>BB3</b>	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 <sup>-1</sup> . A small peak appeared in carbonyl region at 1660 cm <sup>-1</sup> 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.
<b>BB4</b>	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 <sup>-1</sup> . Very little changes in the carbonyl and hydroxyl region.	Initial decrease in Newtonian viscosity, then followed by an increase in viscosity
<b>BB5</b>	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 <sup>-1</sup> . 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

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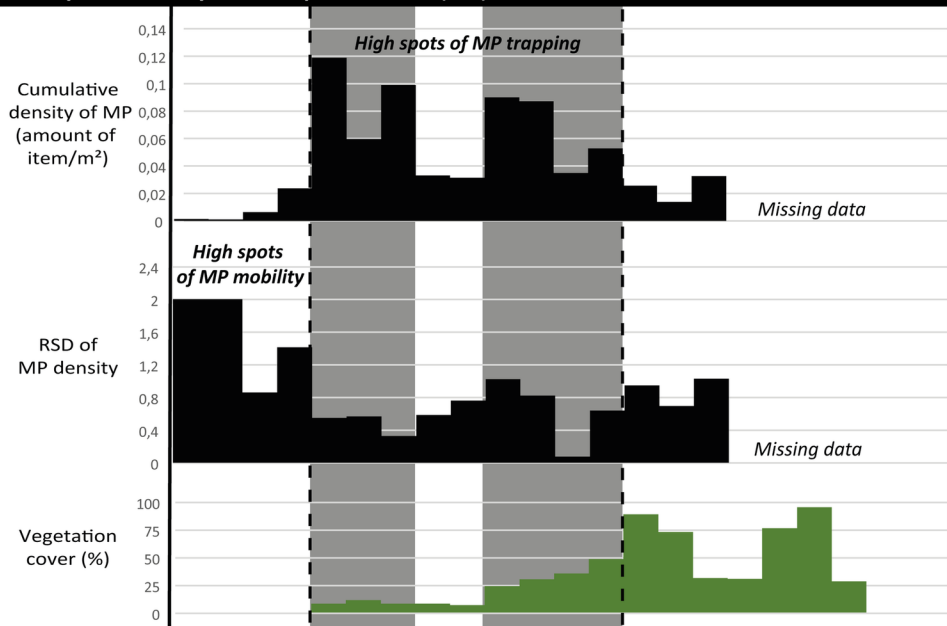
#### 692 **Author contributions.**

693 A. E. D. conceptualization, data curation, formal analysis, investigation, methodology,  
694 writing- original draft, review & editing. G. B. K. conceptualization, data curation, formal  
695 analysis, investigation, methodology. E. R., F. D.-J., J.-L. P., O. V., A. G., H. A. and V. V.  
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

