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1 **Hydrological classification by clustering approach of time-integrated**  
2 **samples at the outlet of the Rhône River: application to  $\Delta^{14}\text{C}$ -POC**

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13

14 **Highlights**

- 15 • *The classification of the Rhône River hydrology was obtained by fuzzy C-mean logic*  
16 • *A 5-Cluster configuration is efficient to characterize Rhône River hydrology*  
17 •  *$\Delta^{14}\text{C}$ -POC distribution among each cluster confirms the main assessments in literature*  
18 • *This approach allows to identify the contribution of each hydrology to samples*

19

20

## 21 Abstract

22 Within the framework of the Rhône Sediment Observatory, monthly time-integrated  
23 samples have been collected by Particle Traps in the last decade to monitor particulate  
24 contaminants in the Rhône River and its main tributaries. In this watershed with a contrasted  
25 hydrology, a clustering approach is used to classify the samples according to the main  
26 hydrological events. This approach has been applied to riverine particulate organic  
27 radiocarbon signatures ( $\Delta^{14}\text{C}$ -POC) that are strongly affected by the origin of the material  
28 and the occurrence of nuclear power plant releases. Suspended Particulate Matter (SPM)  
29 samples were collected near the outlet of the Rhône River and analysed for  $^{14}\text{C}$  along with  
30 particulate organic carbon (POC), chlorophyll a and tritium contents to confirm  $\Delta^{14}\text{C}$ -POC  
31 origins. Cluster Analysis, coupled to Principal Component Analysis, were performed based on  
32 monthly average water discharges of the Upper Rhône River and the five main tributaries.  
33 The classification obtained by fuzzy C-mean logic of the Rhône River hydrology into 5 clusters  
34 is similar to that already observed in the literature with Mediterranean/Cevenol flood,  
35 oceanic pluvial flood, nival flood, low-water level and baseflow clusters. The contribution of  
36 each cluster among the  $\Delta^{14}\text{C}$ -POC values demonstrate the complexity of hydrological  
37 classification of time-integrated samples. First, the samples with a unique and significantly  
38 dominant cluster are easily explained with negative  $\Delta^{14}\text{C}$ -POC values observed in the flood  
39 clusters due to input of  $^{14}\text{C}$ -depleted material from soil or rock weathering, and positive  
40 values observed in the low-water level and baseflow clusters due to anthropogenic input by  
41 nuclear industry. Second, samples that present a homogeneous mixture between several  
42 clusters demonstrate the occurrence of different hydrological events during the sampling  
43 periods. This tool appears as a solution to estimate the contribution of each hydrological  
44 event classification in time-integrated samples.

45 **Keywords** : Hydrological distribution, Cluster Analysis, Radiocarbon, Particulate Organic  
46 Carbon.

## 47 1. Introduction

48 Rivers are unquestionably links between the Earth system reservoirs as they connect 87 % of  
49 the Earthland surface to the oceans (Meybeck, 1982). They are also the receptacle of  
50 pollutants such as organic and inorganic micropollutants due to agricultural, industrial,  
51 domestical and mining activities (Meybeck, 2003) but also artificial radionuclides that are  
52 released by nuclear industries (Eyrolle et al., 2020).

53 Suspended Particulate Matter (SPM) is one of the aquatic fractions and belongs to  
54 sedimentary systems with processes of particles burying and remobilisation within river  
55 systems entering in the long-term cycle (Leithold et al., 2016). Photosynthesis, microbial  
56 oxidation, floodplain sediment remobilisation, sediment introduction are so many processes  
57 that can affect pollutant composition across the river (Meybeck et al., 2003; Walling et al.,  
58 2003). Thus, monitoring riverine SPM dynamic is of a great challenge in the perspective of  
59 health risk assessment, ecological restauration or river management (Walling et al., 2003).  
60 The development of network monitoring of SPM and pollutant fluxes has been performed  
61 over these last decades using SPM discrete sampling (Horowitz et al., 2001) but their  
62 frequencies of acquisition are still be constrained to event with a fixed periodicity, such as  
63 flood, and variations of SPM concentration ( $C_{SPM}$ ) that can occur between samples are often  
64 omitted (Misset et al., 2019) .

65 The deployment of Particle Traps (PT) has been described as a serious alternative from direct  
66 sample as they are time-integrative, low cost and easily handled (Phillips et al., 2000; Schulze  
67 et al., 2007). However, they can cover periods that might integrate several hydrological

68 events and affect our knowledge on contaminant dynamic (Poulier et al., 2019). Thus,  
69 constraining hydrosedimentary behaviours of river systems using time-integrated sample is  
70 challenging. Multivariate analysis and clustering to characterize catchment seasonal  
71 hydrology could be linked with time-integrated sample. The Principal Component Analysis  
72 (PCA) coupled to Clustering Analysis (CA) has been widely used in Earth and Environmental  
73 sciences (e.g., Delaval et al., 2021, Raux et al., 2011). It is also an usual method for data  
74 mining when it comes to identify groups and classify individuals. However, many algorithms  
75 exist and present different results and convergence speeds (Jain et al., 1999). Fuzzy c-mean  
76 algorithms are usually considered as reliable algorithms in environmental sciences (Delaval  
77 et al., 2021, Kim et al., 2011). Their success is due to their simple geometric criteria and their  
78 robustness without any prior information on the cluster structure such as possible overlap or  
79 sphericity (Kamel and Selim, 1994). In addition, the fuzzy approach provides cluster  
80 membership degrees (probability for an observation to belong to a cluster) instead of sharp  
81 cluster boundaries. As a result, the ambiguity of the data can be preserved and these  
82 probabilities can be used later for post treatments or deeper interpretations (Kim et al.,  
83 2011).

84 The Rhône River is one of the major sources of freshwater and SPM to the Mediterranean  
85 Sea (Milliman and Farnsworth, 2011). It is also a strongly anthropized catchment where  
86 inorganic and organic pollutants are monitored for several decades (e.g., Delile et al., 2020;  
87 Eyrolle et al., 2018; Launay et al., 2019; Ollivier et al., 2011; Poulier et al., 2019; Radakovitch  
88 et al., 2008). Within the Rhône Sediment Observatory (OSR) framework, SPM are collected  
89 every month on the Rhône River and its main tributaries using PT (Lepage et al., 2022). While  
90 the results demonstrate a strong link between the contaminant concentrations and the  
91 hydroclimatic heterogeneities of this catchment including different tributary regimes (e.g.,

92 [Delile et al., 2020; Poulhier et al., 2019](#)), the occurrence of different events in a same time-  
93 integrated sample may lead to a bias in interpretation.

94 In this study, we propose to classify time-integrated samples according to hydrological  
95 events using a clustering approach and to investigate the distribution of the clusters among  
96 the concentrations of  $\Delta^{14}\text{C}$  (Carbon 14 reported to 1950 standard) in Particulate Organic  
97 Carbon (POC). Here, the challenge is that while the hydrology of the Rhône River was already  
98 classified based on hourly or daily water discharge values by previous studies (e.g., [Mourier](#)  
99 [et al., 2014](#); [Ollivier et al., 2011](#); [Poulhier et al., 2019](#); [Radakovitch et al., 2008](#); [Zebracki et al.,](#)  
100 [2015](#)), time-integrated samples, that can cover periods from two weeks to one month, might  
101 integrate several hydrological events ([Delile et al., 2020; Poulhier et al., 2019](#)). The hydrology  
102 of the Rhône River main tributaries during time-integrated sampling (164 samples) has been  
103 classified with a fuzzy-C mean algorithm. Carbon-14 ( $^{14}\text{C}$ ), expressed as  $\Delta^{14}\text{C}$ , in riverine POC,  
104 is a radioisotope occurring naturally in the upper parts of the atmosphere and from  
105 anthropogenic sources such as atmospheric nuclear weapon tests (1945-1990) or releases of  
106 nuclear industries ([Eyrolle et al., 2018](#)). The  $^{14}\text{C}$ -POC is selected here because its dynamic in  
107 the Rhône River is well documented:  $^{14}\text{C}$ -labelled POC by nuclear industry releases during  
108 low-water level is opposite to depleting  $^{14}\text{C}$ -POC by introduction of  $^{14}\text{C}$ -dead Carbon, during  
109 floods, coming from rock or soil weathering ([Copard et al., 2018](#) ; [Eyrolle et al., 2018](#); in  
110 [review](#)). Geochemical indicator distributions have been then discussed such as POC content  
111 in SPM (%POC) and Chlorophyll a content in POC (%Chl.a) to study the distribution of the  
112 clusters among the  $\Delta^{14}\text{C}$ -POC. To identify potential artificial  $^{14}\text{C}$  releases, tritium  
113 concentrations collected in water masses were also investigated.

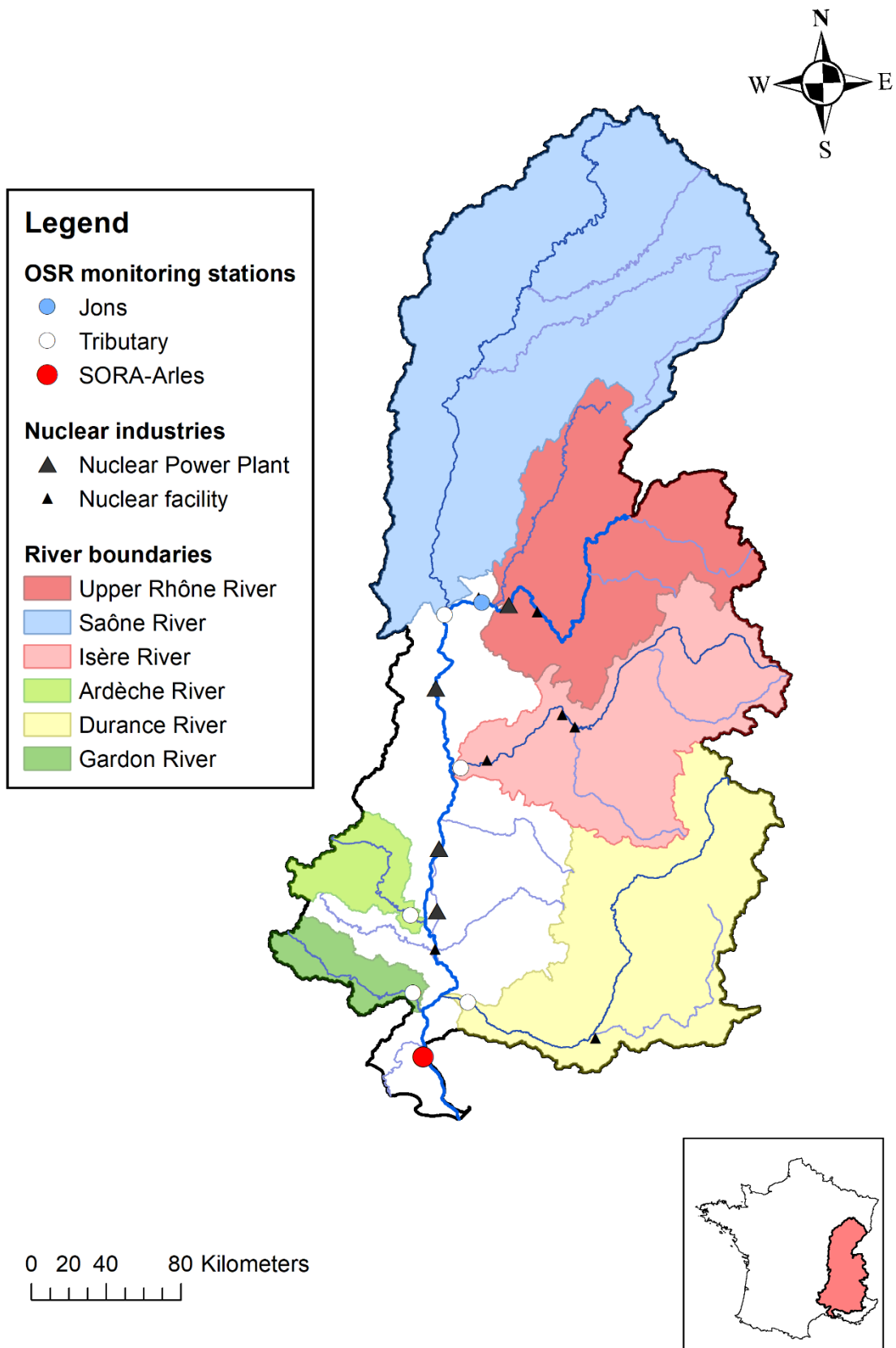
## 114 2. Material and methods

### 115 2.1. Study area

116 The Rhône River basin covers a 98 500 km<sup>2</sup> area (**Figure 1**), with a river stream length of 816  
117 km. The watershed boundaries are delimited with the presence of the Alps, Jura, Cevennes  
118 and Vosges mountains leading to a strong topographic gradient and hydroclimatic  
119 heterogeneities (Olivier et al., 2009). It encompasses tributaries with contrasted hydrologies  
120 :

121 i) oceanic pluvial regime observed at the North of the watershed in winter (Saône and Ain  
122 rivers);

123



124

125 Figure 1 – Map of the Rhône watershed with the delimitations of main tributary basins discussed in this study.

126 The locations of SORA and Jons stations, the tributary stations and the nuclear industries are also added.



127

128 ii) flash Mediterranean rainfalls, coming from Mediterranean Sea, and generally observed in  
129 autumn, that occur in the Southeastern part of the watershed (Durance, Drôme and Ouvèze  
130 rivers);

131 iii) flash Cevenol rainfalls that conduct to the same sharp flow variation than Mediterranean  
132 floods but occur early in fall season and are more located around the Cevennes mountains  
133 (Ardèche, Cèze and Gardon rivers);

134 iv) alpine regimes linked to the snow melt and generally occurring in Alps tributaries (Arve,  
135 Fier, Isère and Durance rivers) during spring;

136 v) generalized floods that encompass all flood events ([Delile et al., 2020](#), [Pont et al., 2002](#),  
137 [Sadaoui et al., 2016](#)).

138 In addition, fourteen nuclear reactors and various nuclear industries are distributed along  
139 the Rhône River making it as one of the most nuclearized river in the world ([Eyrolle et al.,](#)  
140 [2020](#)).

## 141 2.2. Sampling methodology

142 Samples were collected at the SORA monitoring station that is located at the outlet of the  
143 Rhône River, 47 km upstream from the mouth, and has been designed to monitor river  
144 inputs into the Mediterranean Sea ([Lepage et al., 2022](#)). It is located on the “Grand Rhône”  
145 branches where 90% of the water and sediment fluxes of the Rhône River are transiting,  
146 while the remaining 10% transit through the “Petit Rhône” ([Pont et al., 2002](#)). Water intake  
147 is performed on a floatable structure at 7 m from the bank and 0.5 m under the surface

148 regardless the water discharge and continuously supplies the sampling devices (Lepage et  
149 al., 2022).

150 The SPM are collected over a two-week to one-month period in PT, designed with the same  
151 characteristics as described by Schulze et al. (2007), deep-frozen (-18°C), freeze-dried, and  
152 finally homogenized by grinding in an agate mortar. SPM samples are stored in the dark and  
153 at ambient temperature before analysis (Lepage et al., 2022). A total of 164 samples were  
154 collected at SORA from 2007 to 2020 and  $\Delta^{14}\text{C}$ -POC was measured among 54 of them.

155 POC and Chlorophyll a are separately measured in SPM filtered in daily composite water  
156 samples. Sampling is achieved using a cooled automatic water sampler that fills a daily bottle  
157 with 150 mL every 90 minutes to constitute a composite sample each day (Eyrolle et al.,  
158 2020). The sampling frequency is reduced to every 30 minutes to constitute a composite  
159 sample every 4 hours when water discharge is greater than  $3000 \text{ m}^3 \text{ s}^{-1}$ . Samples are  
160 poisoned with  $\text{HgCl}_2$  and kept at 5°C until they are filtered on a 0.7 Whatman pre-  
161 conditioned glass fiber filters GF/F (dried at 500°C for 4 hours). The samples are then frozen,  
162 respectively, until laboratory analysis (Lepage et al., 2022). For tritium analysis, a few  
163 millimeters of water is collected per 80 minutes to obtain a monthly composite sample.  
164 Water is then filtered through  $0.22 \mu\text{m}$  GF/F before analysis (Eyrolle et al., 2020).

165

## 166 2.3. Principal Component Analysis (PCA) and Cluster Analysis (CA)

### 167 2.3.1. Input data

168 With the perspective to trigger all hydrologic regimes occurring on the Rhône according to  
169 the literature, the water discharges (Q) of the five main tributaries (Saône, Isère, Ardèche,  
170 Durance and Gardon rivers) as well as the measures conducted at the Jons monitoring

171 station, considered as the reference station to evaluate water discharge from the Upper  
172 Rhône River, were used to define the clusters (**Figure 1**). For those stations, daily averaged  
173 water discharge data are continuously measured ([Thollet et al., 2021](#)) at the exception of the  
174 Upper Rhône station (Jons) where Q is estimated from a 1D hydrodynamic model with water  
175 discharges of upstream main tributaries as input data ([Launay et al., 2019](#)).

176 Mean water discharge values ( $Q_{\text{mean}}$ ) for each tributary and Jons monitoring stations were  
177 estimated from the start to the end of each 164 PT samples and submitted in PCA. We  
178 assumed that this is enough to characterized tributary hydrograph shapes for each period of  
179 acquisition ([Hannah et al., 2000](#), [Ouyang et al., 2010](#)).

180 In order to better interpret the results of the PCA and the clustering, hydrological data (Q  
181 and  $C_{\text{SPM}}$ ) at the SORA station was also used so as the  $C_{\text{SPM}}$  of the tributary stations if  
182 available. At SORA, daily averaged water discharge data are continuously measured ([Thollet  
183 et al., 2021](#)) while the SPM concentration ( $C_{\text{SPM}}$ ) at SORA station is measured by time-  
184 integrating weighing of daily automatic samples ([AFNOR, 2005](#)). At tributaries, averaged  
185 daily  $C_{\text{SPM}}$  is estimated from turbidity and  $C_{\text{SPM}}$  rating curves with 10-minute frequency of  
186 acquisition and monthly automatic water samples ([Lepage et al., 2022](#)). A mean value ( $C_{\text{SPM-}}$   
187  $\text{mean}$ ) was calculated for each PT sample.

### 188 2.3.2. PCA and CA algorithms

189 The PCA has been performed using R programming language including the R packages  
190 “FactoMineR” for PCA ([Husson et al., 2010](#)), “e1071” ([Meyer et al., 2021](#)) and “fclust” for  
191 fuzzy c-mean algorithms ([Ferraro et al., 2019](#)). The goal of PCA is to describe a data set using  
192 a smaller number of uncorrelated variables, while retaining as much information (variance)  
193 as possible. The reduction is achieved by transforming the data into a new set of continuous

194 variables named the principal components. The reduction of dimensionality provides a  
195 framework to visualize the Rhône hydrology. The essential of the information being on the  
196 first components ([Husson et al., 2010](#)), PCA is usually used as a pre-processing tool before  
197 clustering analysis ([Delaval et al., 2021](#)).

198 Then, clustering algorithms such as c-mean algorithms (crisp or fuzzy) classify individuals  
199 according to their variable similarities and allows to identify scenarios and trends in river  
200 hydrology and hydrochemistry. This is done by randomly defining  $i$  centroids in the same  
201 coordinate systems as the individuals. Each individual  $x$  (total of  $k$ ) is assigned to the closest  
202 centroid center  $C_i$ . The barycenter of each subgroup is then calculated and becomes the new  
203 centroid. This procedure converges when the centroids are no longer moving. In addition,  
204 the fuzzy alternative introduces two new parameters. The first one is the membership  
205 coefficient. This membership represents how closely the  $k_{th}$  data object ( $x_k$ ) is located from  
206 the  $i_{th}$  Cluster center. Membership score indicates the degree (in %) to which a sample  
207 belongs to each cluster. Each sample is assigned to the cluster with the highest membership  
208 among the others.

209 The second parameter  $m$  is the fuzzifier. It is greater than 1 and usually dependent on the  
210 dataset structure because it represents the degree of overlap of the clusters ([Klawonn and  
211 Höppner, 2003](#)). When  $m$  is close to one, the solution of the fuzzy c-means algorithm is  
212 similar to the one of c-means. Elements are simply assigned to only the nearest cluster and  
213 membership to other clusters is nearly existent. When  $m$  is large, fuzziness is also large and  
214 clusters are blurred which can be a more accurate description of the system. More details  
215 about c-mean algorithms are provided in [Bezdek et al., \(1988\)](#).

216 The best combination of  $\{C, m\}$  parameters is not determined by the algorithm. One  
217 approach is to run different simulations with different  $\{C,m\}$  pairs and to check the efficiency  
218 of clustering with a quality criteria (Ramze Rezaee et al., 1998). River hydrology related to  
219 clustering studies have a number of clusters falling in the interval  $[2,8]$  (Delaval et al., 2021;  
220 Javed et al., 2021; Ouyang et al., 2010). Our number of  $\Delta^{14}\text{C}$ -POC observations being limited  
221 ( $n=54$ ), we are expecting 8 clusters at most (Chaimontree et al., 2010) and we will set the  
222 test interval for the number of clusters to  $[2,8]$ .

223 The fuzzifier  $m$  can be in theory any real number between 1 and  $\infty$ .  $m$  is usually set to 2 by  
224 default but can be any real number between 1 and  $\infty$  usually decreasing with dataset size  
225 (Klawonn and Höppner, 2003). In our tests, we will take 1 as the lower limit for  $m$ . The upper  
226 limit is  $m=3$  according to the empirical threshold equation based on the length and  
227 dimensions of the dataset proposed by Schwämmle and Jensen (2010). As a result, we will  
228 perform clustering on the interval  $[2,8]$  for  $C$ , the number of clusters and on the interval  $]1,3]$   
229 for  $m$  the fuzzifier.

## 230 2.4. Analyses

### 231 2.4.1. Carbon-14 measurement

232 The  $^{14}\text{C}$  measurement in SPM are performed using a 3 MV NEC PELLOTRON Accelerator Mass  
233 Spectrometry (Artemis AMS facility, Dumoulin et al., 2017). Briefly, SPM samples are firstly  
234 decarbonated with 0.5 M HCl, placed in Pyrex sealed tubes and calcined ( $850^\circ\text{C}$  for 5 hours).  
235  $\text{CO}_2$  is collected into a glass line under vacuum ( $< 10^{-5}$  mbar) and cryogenically trapped via  
236 liquid nitrogen. The sample  $\text{CO}_2$  is reduced with hydrogen and iron powder as a catalyser  
237 following the protocol of Voegel et al., (1984) and pressed into an aluminium cathode (1 mm  
238 hole diameter) to form a graphite target.

239 In the AMS, the target is submitted to high bombing with Caesium sputter ion sources and  
240 sequentially sent, through a 90° magnet, to an accelerator tube. Here, Carbon isotopes are  
241 stripped in an argon gas and distinguished through a 45° analyser according to their weight.  
242 <sup>14</sup>C ions are counted in an ionization chambers (Cottureau et al., 2007).

243 After AMS counting, the <sup>14</sup>C/<sup>12</sup>C ratio R is normalized (R<sub>n</sub>) to a δ<sup>13</sup>C of -25‰ in order to take  
244 into account carbon isotopic fractionation (Stuiver and Polach, 1977) . A 1950 standard R<sub>s</sub>  
245 (i.e., oxalic acid II, a crop of sugar beet) is also incorporated in the sample batch and  
246 normalized as R<sub>sn</sub>. Following Stuiver and Polach (1977) formulation, Δ<sup>14</sup>C is privileged in  
247 order to take into account radiodecay (**Equation 1**) with y, the year of measurement and the  
248 Godwin's mean life (8267) estimated from soil and water samples (Godwin et al., 1962).

249

$$250 \quad \Delta^{14}\text{C} = \left( \frac{R_n}{R_{sn}} \times e^{\left(\frac{y-1950}{8267}\right)} - 1 \right) \times 1\,000 \quad \text{Equation 1}$$

251 Carbon, after the 1950 standard, has a Δ<sup>14</sup>C up to 0 ‰ and could integrate the contribution  
252 of anthropogenic sources such as the effects of thermonuclear weapon tests (1945-1990) or  
253 releases of nuclear industries. Values reaching -1000‰ are linked to material old of up  
254 50 000 years BP (Trumbore et al., 2016).

#### 255 2.4.2. Particulate nutrient and tritium analyses

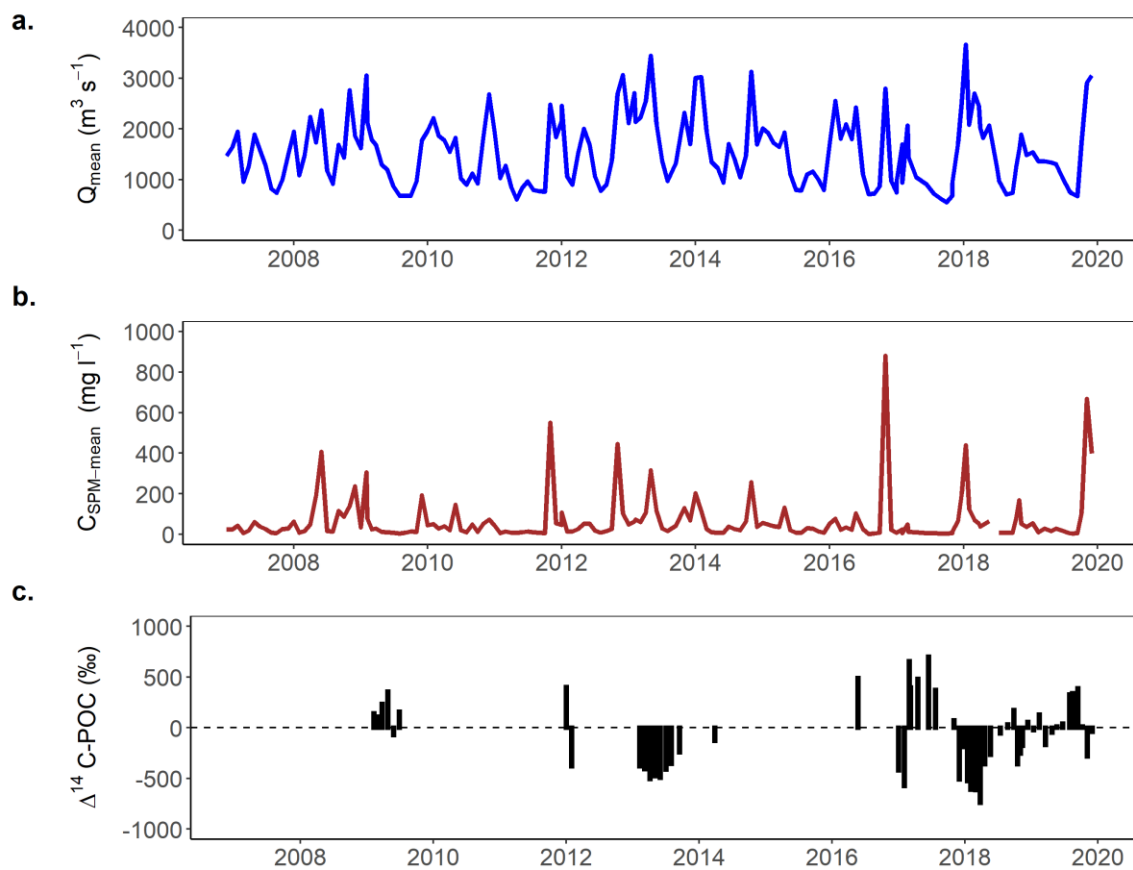
256 The POC concentration measurements were carried out at the Mediterranean Institute of  
257 Oceanography (M.I.O.) and were performed on daily decarbonated SPM by using high  
258 combustion procedure (950°C) on a Carbon Nitrogen (CN) Integra mass spectrometer  
259 (serCon Ltd, Crewe, UK) as described in Raimbault et al. (2008). Chlorophyll a measurement  
260 is conducted through fluorimetry methodology after its extraction with methanol according

261 to Raimbault et al. (2004). Tritium analyses ( $\text{Bq l}^{-1}$ ) were carried out at the LMRE/IRSN by  
262 liquid scintillation counting (AFNOR, 2015).

### 263 3. Results

#### 264 3.1. Data description

265 The distributions of environmental data treated by CA are available in *Dataset S1*. The  $Q_{\text{mean}}$   
266 and  $C_{\text{SPM-mean}}$  histories are respectively presented in **Figures 2.a.** and **2.b.** and  $\Delta^{14}\text{C-POC}$   
267 values in **Figure 2.c.**



268  
269 Figure 2 - Distribution of a.)  $Q_{\text{mean}}$  ( $n = 164$ ), b.)  $C_{\text{SPM-mean}}$  ( $n = 163$ ) and c.)  $\Delta^{14}\text{C-POC}$  values ( $n = 54$ ) over the  
270 2007-2020 period.

271

272

273

274

275 During the whole 2007-2020 period, for all 164 samples,  $Q_{\text{mean}}$ , at Arles varied between 558  
276 and  $3\,668\text{ m}^3\text{ s}^{-1}$  (mean=  $1\,565\text{ m}^3\text{ s}^{-1}$ , s.d. =  $687\text{ m}^3\text{ s}^{-1}$ ) while  $C_{\text{SPM-mean}}$  varied between 2.9 mg  
277  $\text{l}^{-1}$  and  $879.7\text{ mg l}^{-1}$  (mean=  $68.3\text{ mg l}^{-1}$ , s.d. =  $117.4\text{ mg l}^{-1}$ ).  $\Delta^{14}\text{C-POC}$  signatures are ranged  
278 from -742 to 699 ‰ (mean =  $-84.5\text{ ‰}$ , s.d. =  $346\text{ ‰}$ ). The signatures are unequally  
279 distributed over the period (**Figure 2.c.**) because  $\Delta^{14}\text{C-POC}$  analyses in SPM have been  
280 continuously performed since 2014 despite some exceptional measurements performed  
281 around 2009 and 2012 (Eyrolle et al., 2018).

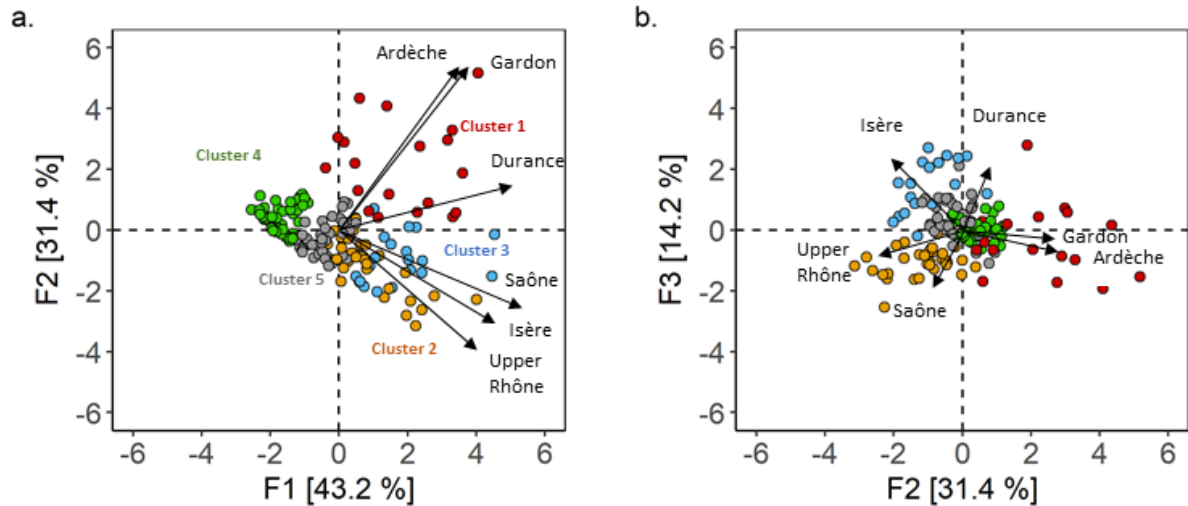
282 The average POC content in SPM (%POC) is estimated between 1.03% and 10.37% (mean=  
283 3.95 %, s.d. = 1.73 %). The average chlorophyll a content in POC (%Chl.a) is varying between  
284 0.01% and 2.15 % (mean = 0.34 %, s.d. = 0.42 %), while tritium concentrations in water  
285 between 0.4 and  $20.7\text{ Bq l}^{-1}$  (mean =  $6.1\text{ Bq l}^{-1}$ ).

### 286 3.2. Principal Component Analysis

287 The PCA transformed the variables (mean Q for the five tributaries and Jons) into six vectors  
288 (**Figures 3a and b**).

289





290  
 291 Figure 3 – Principal component analyses 1 and 2 of the dataset. The PCA were conducted on the mean of the  
 292 water discharge of the five main tributaries of the Rhône River (Saône, Isère, Ardèche, Gardon and Durance  
 293 rivers) and the station of Jons that monitors the Upper Rhône River. Clusters are highlighted by colours.

294  
 295

296 The F1 axis explains 43.2 % of the variance of the dataset and all tributary vectors are  
 297 oriented toward the right side of the PCA. The F2 axis, explaining 31.4% of the variance,  
 298 distinguishes, from the top to the bottom, southern tributaries (Ardèche, Gardon and  
 299 Durance rivers) and northern ones (Saône, Isère and Upper Rhône rivers) (**Figure 3.a.**).

300 Through the F1 × F2 axis configuration (PCA1), the observations are concentrated around the  
 301 0 axis on the left side of F2 while they are scattered on the right side. Through the F2 × F3  
 302 axis (14.2% of the variance) configuration (PCA2), the Isère and Durance vectors are located  
 303 on the top side of the PCA whereas other vectors are located on the bottom side. As  
 304 observed for PCA1, Ardèche and Gardon vectors are grouped. The F4 axis explains 6.6 % of  
 305 the variability and separates Durance and Saône rivers from other tributaries (*Supplementary*  
 306 *information, Figure S1*). Through F3 × F4 axis configuration (PCA3), samples are centred and  
 307 staggered across the F4 axis.

308

### 309 3.3. Cluster number assessment

310 The fuzzy clustering was performed with the first four components of the PCA in order to  
311 cumulate an explained variance of up to 95 % (*Figure S2*). The performances were estimated  
312 through Xie and Beni index (XB) (to minimize) according to different {C,m} simulations (*Table*  
313 *S1*). The five-cluster configuration showed the lowest score ( $m = 13$ ,  $XB = 0.296$ ) and will be  
314 retained for the remainder of this work.

### 315 3.4. Hydrodynamic distribution for each cluster

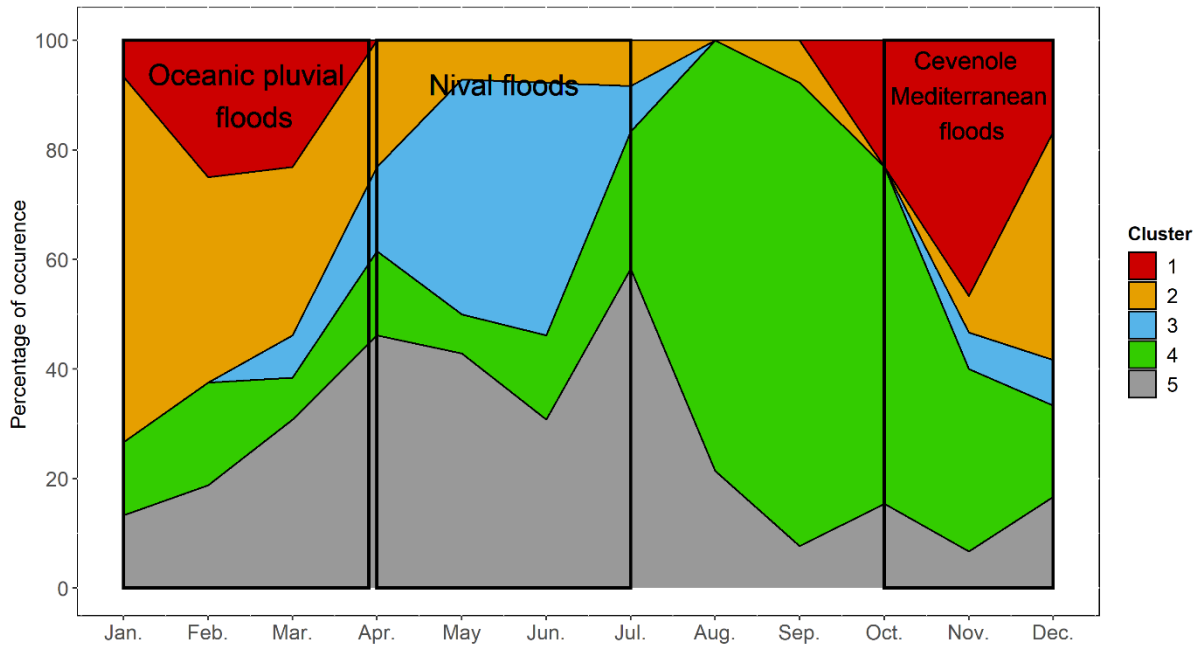
316 Respectively, 12.1 %, 20.1 %, 11.6 %, 31.2 % and 25.0 % of  $Q_{\text{mean}}$  are distributed among  
317 clusters 1, 2, 3, 4 and 5. The  $Q_{\text{mean}}$  and  $C_{\text{SPM-mean}}$  distributions at Arles, Jons and tributaries  
318 are respectively available in *Tables S2 and S3*. In both PCA1 and PCA2, Cluster 1 includes  
319 Ardèche and Gardon vectors (**Figures 3a and 3b**). For clusters 2 and 3, the results are  
320 contrasted. In PCA1, Cluster 2 integrates the three northern stations while in PCA2 the Isère  
321 vector is excluded. For Cluster 3, only the Isère vector is included in PCA2 while the Saône  
322 vector is included in PCA1. Finally, in both configurations, the Durance vector is located  
323 between clusters 1 and 3.

324 Clusters 1, 2 and 3 are characterized by a maximum  $Q_{\text{mean}}$  above the daily flood threshold at  
325 Arles ( $3000 \text{ m}^3 \text{ s}^{-1}$ ) with high standard deviations (up to  $400 \text{ m}^3 \text{ s}^{-1}$ ). For clusters 1 and 3,  
326 similar results were observed for the  $C_{\text{SPM-mean}}$  with average concentrations close to  $200 \text{ mg l}^{-1}$   
327 at Arles and high values in the Ardèche (mean  $C_{\text{SPM-mean}} = 27 \text{ mg l}^{-1}$ ), Durance (mean  $C_{\text{SPM-}}$   
328  $\text{mean} = 661 \text{ mg l}^{-1}$ ) and Gardon (mean  $C_{\text{SPM-mean}} = 58 \text{ mg l}^{-1}$ ) rivers for Cluster 1 and Isère (mean  
329  $C_{\text{SPM-mean}} = 333 \text{ mg l}^{-1}$ ) and Durance (mean  $C_{\text{SPM-mean}} = 498 \text{ mg l}^{-1}$ ) rivers for Cluster 3. For

330 Cluster 2, while the  $C_{SPM-mean}$  observed at Arles (mean  $C_{SPM-mean} = 77 \text{ mg l}^{-1}$ ) are lower than  
331 clusters 1 and 3 (mean  $C_{SPM-mean} > 150 \text{ mg l}^{-1}$ ).

332 Located on the left side of the PCA1, Cluster 4 presents lowest values of  $Q_{mean}$  with a mean  
333 at Arles of  $849 \text{ m}^3 \cdot \text{s}^{-1}$ . Cluster 4 is also characterized by the lowest  $C_{SPM-mean}$  at Arles and for  
334 all tributaries. Cluster 5 is centred between F1 and F2 with a predominance of the Isère and  
335 Durance rivers (**Figure 3b**) and also of the Saône River but their discharges remain lower  
336 than those observed in clusters 2 and 3. Cluster 5 presents moderate  $C_{SPM-mean}$  at Arles  
337 (mean=  $33 \text{ mg l}^{-1}$ ) with low variability and moderate increases of the Durance and Isère  
338 rivers  $C_{SPM-mean}$  ( $77$  and  $54 \text{ mg l}^{-1}$  respectively).

339 Percentages of occurrence for calendar months are presented in **Figure 4**. The samples for  
340 Cluster 1 are generally centred in from October to December (maximum of 47%), February  
341 (25%) and March (23%). Cluster 2 samples are mainly centred from December to April  
342 (maximum of 67%). Cluster 3 is mainly observed from April to June (up to 46%). Cluster 4  
343 samples are generally observed from July to November (up to 85%). Finally, Cluster 5 mainly  
344 occurs from March to August with a peak in July (58%).



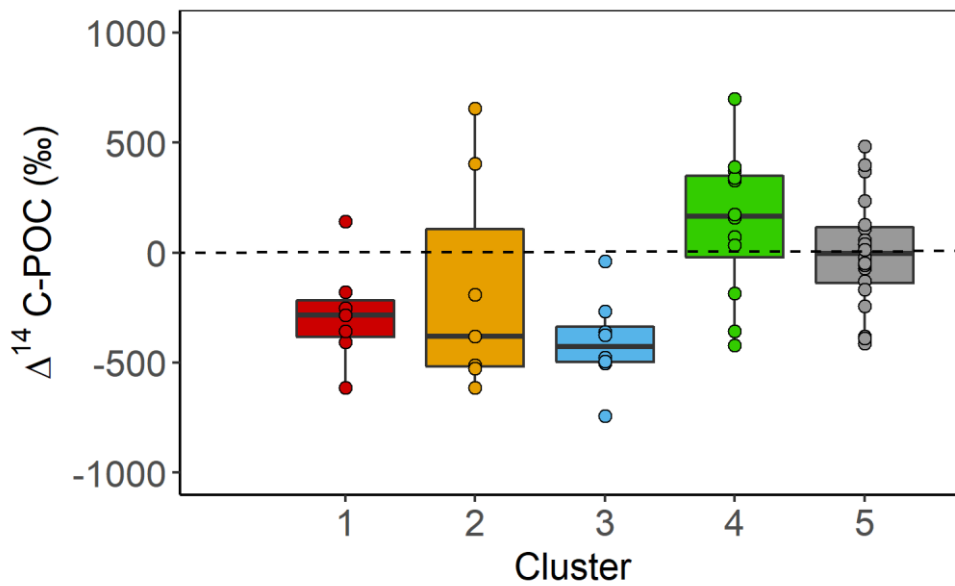
345 Figure 4 – Inter-annual occurrences of each cluster among the 164 samples. Flood delimitations were estimated from [Delile](#)  
 346 [et al., 2020](#).

347

348 3.5.  $\Delta^{14}\text{C}$ -POC distribution among the clusters

349 Distribution of  $\Delta^{14}\text{C}$ -POC among the clusters are presented in **Figure 5** where each value was  
 350 associated to the cluster with the highest contribution (**Figure 6**). While  $\Delta^{14}\text{C}$ -POC values  
 351 cover all hydrological events, the number of  $\Delta^{14}\text{C}$ -POC data is unequally distributed among  
 352 clusters (7, 7, 8, 12 and 20 respectively).

353



354

355 Figure 5 –  $\Delta^{14}\text{C-POC}$  (n=54) distribution among the 5 clusters over the 2007-2020 period. Each value was associated to the  
 356 cluster with the highest membership score. Dotted horizontal line represents the year 1950 for which the value is 0 ‰ (cf.  
 357 equation 1).

358

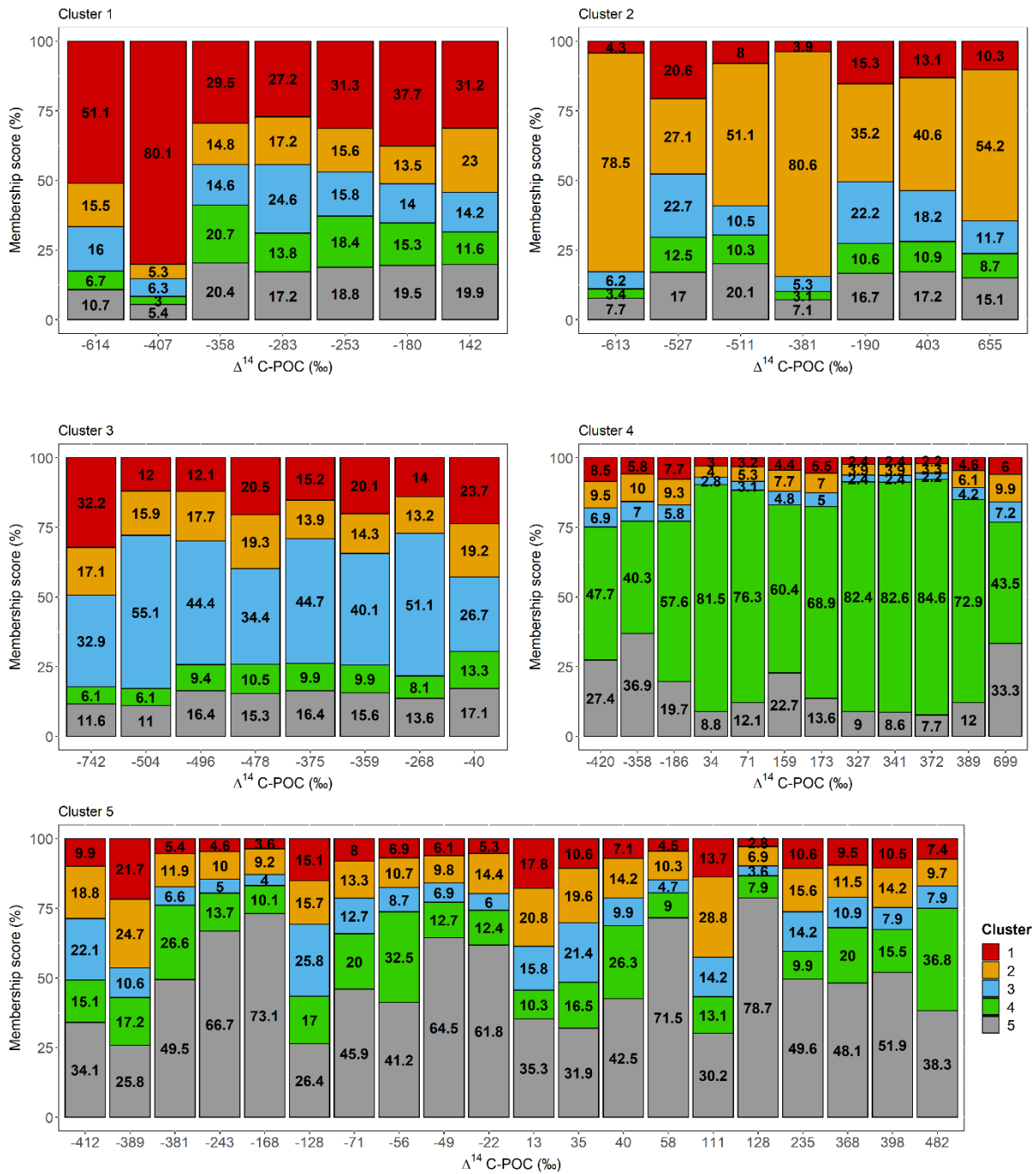
359

360 Cluster 1, Cluster 2 and Cluster 3 include the lowest values with a median of -223, -367 and -  
 361 487‰. Cluster 2 includes the largest distribution of  $\Delta^{14}\text{C-POC}$  signatures from - 613 to 655 ‰  
 362 while clusters 1 and 3 are concentrated between -614 and 142 ‰ and -742 and -40‰. Most  
 363 of the values of the Cluster 4 are above 0‰ with a median of 174 ‰, excepted for three  
 364 negative values (-420, -354 and -185 ‰). The Cluster 5 is equally centred around 0‰ with a  
 365 median of -24 ‰.

366 The dominant or attributed cluster in each sample is characterized by its membership degree  
 367 ranging from 25.8% to 84.6% (**Figure 6**). A few samples show a homogeneous cluster  
 368 membership score distribution highlighting that they could belong to another cluster than  
 369 the attributed one. For example, the sample with the highest  $\Delta^{14}\text{C-POC}$  in Cluster 3 (-40‰)  
 370 presents membership degrees ranging from 13.3 to 26.7 %. Respectively 29%, 57%, 25%,

371 75% and 35% of the samples have an appartenance degree to their attributed cluster higher  
 372 than 50% in Cluster 1 to 5.

373



374

375 Figure 6 – Distribution of cluster memberships for  $\Delta^{14}\text{C-POC}$  values ( $n = 54$ ) among the classification. Each  
 376 membership score is expressed in %.

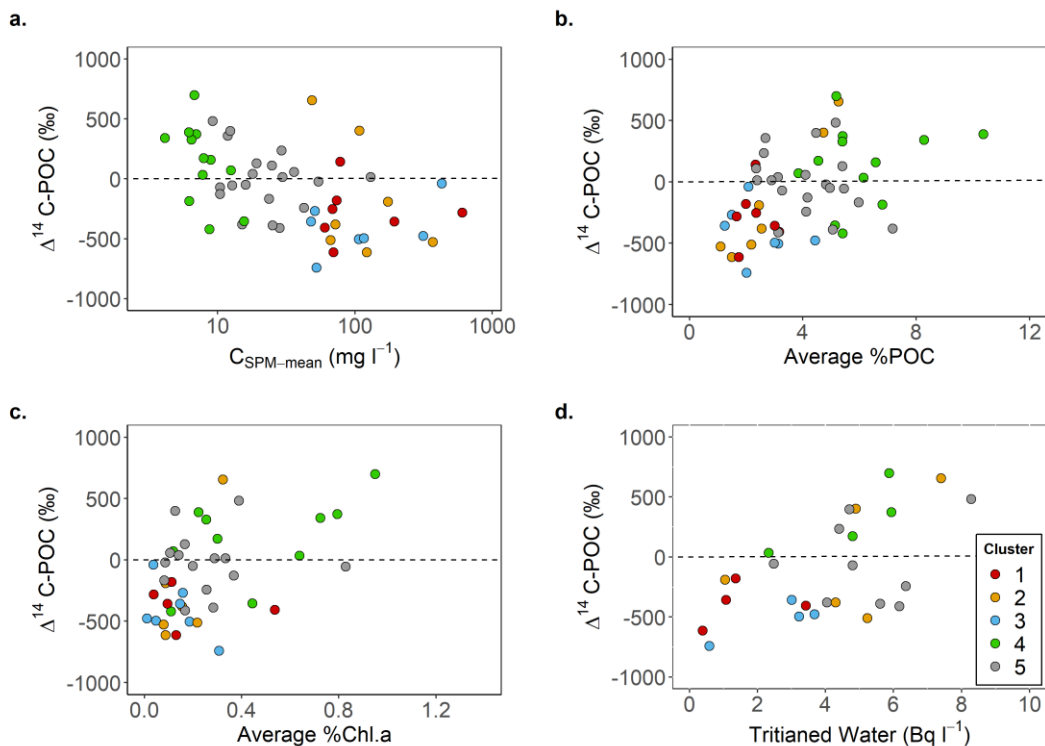
377

378

379

### 380 3.6. Geochemistry distribution

381 The  $\Delta^{14}\text{C}$ -POC relationships with  $C_{\text{SPM-mean}}$ , average %POC, %Chl.a and tritium concentrations,  
382 among the 5 clusters, are presented in **Figure 7** . Overall,  $\Delta^{14}\text{C}$ -POC shows positive  
383 relationships with %POC and a negative relationship with  $C_{\text{SPM-mean}}$ . High  $\Delta^{14}\text{C}$ -POC are  
384 correlated with high %Chl.a (up to 0.6 %) and high tritium concentrations (up to 5 Bq l<sup>-1</sup>).  
385 Cluster 1, 2 and 3 gather low %POC while clusters 4 and 5 present higher and more variable  
386 records. Highest %POC, %Chl.a. and tritium records are observed for Cluster 4 and Cluster 5  
387 and some exceptions in Cluster 2.



388

389 Figure 7 –  $\Delta^{14}\text{C}$ -POC relationships with a.)  $C_{\text{SPM-mean}}$ , b.) average %POC, c.) average %Chl.a. and d.) tritium  
390 concentrations according to the cluster.

391  
392  
393  
394

## 395 4. Discussion

### 396 4.1. Characterisation of the clusters

#### 397 4.1.1. PCA interpretation

398 The PCA1 made with time-integrated samples is similar to the one given by Sadaoui et al.,  
399 (2016) with daily water discharge (**Figure 3a**). The F1 axis contains the information of water  
400 discharge variation for all tributaries while F2 axis separates the northern tributaries from  
401 the southern tributaries that have contrasted hydrologies in accordance with Pont et al.,  
402 (2002). In PCA 2, F3 axis explains the temporal variability (spring vs autumn) and opposes  
403 alpine tributary hydrology to other hydrologies (**Figure 3b**).

#### 404 4.1.2. Cluster hydrodynamic characterisation

405 Despite the use of integrated samples (and associated hydrological data) in this study that  
406 may aggregate several hydrological events, the five clusters defined are similar to the  
407 hydrological classification of the Rhône River made from daily water discharge (Pont et al.,  
408 2002, Sadaoui et al., 2016).

409 Cluster 1 is linked to southern tributary vectors (**Figure 3a**) and gathers southern flash-flood  
410 events (Pont et al., 2012, Eyrolle et al., 2012, Delile et al., 2020). No distinction between  
411 Cevenol and Mediterranean floods are proposed by the algorithm. The high standard  
412 deviations of average  $Q_{\text{mean}}$  and  $C_{\text{SPM-mean}}$  highlight sharp variabilities. In the literature,  
413 southern events contribute the most on large export of SPM at the Rhône River scale. Eyrolle



414 [et al., \(2012\)](#) or [Copard et al., \(2018\)](#) demonstrated that, the Durance River could contribute  
415 to sediment load from < 1% to 80% during Mediterranean flood events. However, numerous  
416 studies have also estimated sediment budgets using geochemical methods and agree on the  
417 exceptional but non-negligible contribution of the Cevenol floods, that could occasionally  
418 reach more than 40% ([Ollivier et al., 2011](#); [Radakovitch et al., 2008](#); [Zebracki et al., 2015](#)).

419 Cluster 2 gathers oceanic regime with  $Q_{\text{mean}}$  distribution at Arles occurring during winter and  
420 the activation of the Saône and Upper Rhône rivers. The contrast between average  $C_{\text{SPM-mean}}$   
421 and  $Q_{\text{mean}}$  is explained by the main roles of these two tributaries as water suppliers. At the  
422 interannual scale, their contribution on water fluxes reaches more than 60% while their  
423 contribution in term of SPM (11 and 6 % respectively) are lower ([Delile et al., 2020](#); [Poulier](#)  
424 [et al., 2019](#); [Sadaoui et al., 2016](#)).

425 Cluster 3 observations occur during the end of spring season (**Figure 4**) and gather nival  
426 flood regime with net predominance of alpine rivers (Isère and Durance rivers) (**Figure 3b**).  
427 Their contribution can exceed 80 % in water fluxes and over 100% in SPM fluxes ([Delile et al.,](#)  
428 [2020](#), [Poulier et al., 2019](#)).

429 Cluster 4 observations gather low-water level, during summer (**Figure 4**), with lowest  $Q_{\text{mean}}$   
430 and  $C_{\text{SPM-mean}}$ . During such period, the production of autochthonous organic matter is  
431 increased as observed with the increase of %POC and %Chl.a (**Figure 4**).

432 Cluster 5, located at the center of the PCA1 (**Figure 3.a.**), gathers baseflow regime with  
433 medium  $Q_{\text{mean}}$  and  $C_{\text{SPM-mean}}$  values. It occurs over spring and summer seasons (**Figure 4**) and  
434 the slight increases of  $Q_{\text{mean}}$  and  $C_{\text{SPM-mean}}$  in the Durance and Isère rivers indicate nival  
435 episodes that might happen during these periods. As for Cluster 4, high values of %POC and  
436 %Chl.a indicate a production of autochthonous POC.

## 437 4.2. Classification of $\Delta^{14}\text{C}$ -POC

438 The  $\Delta^{14}\text{C}$ -POC depletion observed for clusters 1 and 3 confirms the main knowledge  
439 presented in the literature about  $^{14}\text{C}$  dynamic in the Rhône (Copard et al., 2018, Eyrolle et  
440 al., 2018; Eyrolle et al., in review). Indeed, the increase of  $C_{\text{SPM-mean}}$  and the decrease of  
441 %POC (**Figure 7**) confirm the organic matter dilution with particulate mineral fractions by the  
442 weathering of carbonate rocks (Higuera et al., 2014). Then, rocks such as i) Black Marls,  
443 composed bare Mesozoic Badlands located among the French alps arc (Graz et al., 2011) or  
444 ii) Coal mines observed in slag heaps of Cevennes or mining operation sites in Briançonnais  
445 area of Alps, containing high contents of organic matter old of up 50 000 years BP. Because  
446 they are characterized by low vegetation density and violent hydroclimatic conditions, they  
447 could be considered as main sediment hotspots and could release consequent amount of  
448 organic matter (Eyrolle et al., in review). However, their contribution in sediment budget at  
449 the Rhône scale still poorly documented, excepted for the Durance River (Copard et al.,  
450 2018). Another source of such  $^{14}\text{C}$ -depleted material might be the remobilisation of aging  
451 sediment POC trapped in flood plain across the main network (e.g., Leithold et al., 2016).

452 The case of Cluster 2 is different as the oceanic floods (Saône and Upper Rhône rivers) are  
453 characterized by a low level of  $C_{\text{SPM-mean}}$ . The range of  $\Delta^{14}\text{C}$ -POC values and their disparity  
454 around 0 (**Figure 5**) can be explained by the fact that the SPM sampled for the measurement  
455 of  $\Delta^{14}\text{C}$ -POC do not specifically come from these two tributaries. Since the samples are  
456 integrated over a period of about one month, they are very sensitive to floods that generate  
457 a lot of material or to anthropogenic inputs (e.g., dam flushing).

458 Cluster 4 and Cluster 5 present more enriched  $\Delta^{14}\text{C}$ -POC (**Figure 5**), displaying a privileged  
459 autochthonous origin, related to high %Chl.a, for positive signatures (after 1950) showing

460 aquatic plants development preferentially higher when water flow and turbidity are low  
461 **(Figure 7)** (Higuera et al., 2014). High tritium concentrations, combined to high  $\Delta^{14}\text{C}$ -POC  
462 values in clusters 4 and 5 might be related to the releases from the nuclear facilities **(Figure**  
463 **7)**. At the outlet of the Rhône River, the possibility of nuclear release increasing  $\Delta^{14}\text{C}$ -POC is  
464 significant when %Chl.a is high suggesting a contamination of POC when primary  
465 productivity is important. Several studies have highlighted that  $^{14}\text{C}$  is released as dissolved  
466 inorganic forms (DIC) because of oxidation processes applied in effluents before releases  
467 (e.g., Kang et al., 2019) and it could integrate POC through photosynthesis. However  
468 additional investigations might be conducted as the sampling methods were not the same  
469 for these two parameters and could lead to bias in the interpretation.

#### 470 4.3. Relevance of Cluster analyses for classification of $\Delta^{14}\text{C}$ -POC signatures.

471 **Figure 6** displays the complexity of hydrological classification of time-integrated sampling as  
472 a few samples are characterized by a mixture of clusters including several hydrological  
473 events and  $\Delta^{14}\text{C}$ -POC signatures including different origins. Moreover, for the outliers **(Figure**  
474 **5)**, the relationship between the cluster classification and the  $\Delta^{14}\text{C}$ -POC values is complex to  
475 explain and requires looking at the hydrograph during the sampling periods. For example,  
476 southern quick flood events have been registered in samples of low-water level related  
477 clusters (4 and 5) with depleted values of  $\Delta^{14}\text{C}$ -POC. For Cluster 1, the positive value of  $\Delta^{14}\text{C}$ -  
478 POC is observed in a sample with a southern flash flood occurring at the beginning of the  
479 sampling period but followed by a low-water level period favourable of  $\Delta^{14}\text{C}$ -artificial POC.  
480 Cluster 1 samples also have consequent appartenances to clusters 2 and 3. The sum of the  
481 membership degrees for the flood-related clusters (1, 2 and 3) is always higher than 58% and  
482 highlights that i) northern floods could also simultaneously occur than southern floods in  
483 autumn and ii) some southern floods could be observed during spring season as the same

484 time than nival flood events (**Figure 4**). The complex relationship of Cluster 2 with  $\Delta^{14}\text{C}$ -POC  
485 values is due to the low  $C_{\text{SPM}}$  load of the Saône and Upper Rhône river floods and the  
486 consequent sensitivity to other events such as the Durance river floods or industrial  
487 discharges. The main solution to reduce the disparity of the values would have been to use  
488 the flux of SPM instead of the water discharge as the input data to determine the clusters.  
489 Therefore, this would improve the classification of  $\Delta^{14}\text{C}$ -POC values measured on SPM.  
490 Unfortunately, such data was not available from all the tributaries and for the entire period  
491 of study (starting since 2011), while clustering using water discharge was already commonly  
492 used (Delaval et al., 2021). Finally, samples in the Cluster 5 seem to be a mix between the  
493 Cluster 4 (low-water level cluster) and the flood-related clusters (1, 2 and 3). For this cluster,  
494 centred in the PCA (**Figure 3**), the absence of relationship with the  $\Delta^{14}\text{C}$ -POC values is directly  
495 related to the complexity to categorize samples collected during baseflow.

## 496 5. Conclusion

497 This study presents a first classification of time-integrated samples by clustering approach  
498 according to the Rhône hydrology. Principal Component Analysis (PCA) followed by fuzzy-C  
499 mean Cluster Analysis have been performed using time average of Q among the five major  
500 water tributaries and the Upper Rhône River monitored at Jons. We used  $\Delta^{14}\text{C}$ -POC data  
501 collected in Particle Traps (PT) over a two-week to one-month sampling period as a  
502 candidate to validate the classification. The classification exhibited 5 groups of hydrology  
503 similar to that described in the literature: southern floods with Mediterranean and Cevenol  
504 hydrologies confounded (Cluster 1), northern oceanic pluvial floods (Cluster 2), nival floods  
505 (Cluster 3), but also baseflows (Cluster 5) and low-water levels (Cluster 4). Overall,  $\Delta^{14}\text{C}$ -POC  
506 distribution in time-integrated sample confirms the clustering classification according to

507 flood-related, baseflow and low-water level clusters. High  $\Delta^{14}\text{C}$ -POC signatures, correlated to  
508 high tritium concentrations, are observed in clusters 4 and 5, incorporating nuclear releases,  
509 and are opposed against depleted signatures occurring during flood events observed in  
510 clusters 1 and 3 because of the  $\Delta^{14}\text{C}$ -depleted material mobilisation from tributaries (e.g.,  
511 black marls). The  $\Delta^{14}\text{C}$ -POC outliers observed at each cluster show the sensitivity of PT  
512 samples to short events remobilising high sedimentary material or nuclear releases during a  
513 long sampling period especially for clusters 2 and 4. Furthermore, the overlaps of different  
514 events making difficult the Cluster Analysis to attribute the origins of  $\Delta^{14}\text{C}$ -POC especially for  
515 flood clusters. Indeed, homogenous distribution of membership scores at some samples in  
516 clusters 1 to 3 shows a mixture of contrasted flood events over the sampling period. Because  
517 Cluster 5 is a mix of flood and low-water level events, some  $\Delta^{14}\text{C}$ -POC values are incorrectly  
518 attributed here. If this method of classification with  $Q_{\text{mean}}$  showed pertinent results for  $\Delta^{14}\text{C}$ -  
519 POC, applying SPM fluxes would improve the CA abilities to classify  $\Delta^{14}\text{C}$ -POC according to  
520 the Rhône River hydrology. For this purpose, other signatures are expected for the coming  
521 years.

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