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1 **Hydro-climatic drivers of land-based organic and inorganic particulate-**
2 **bound micropollutant fluxes: the regime of the largest river water inflow of**
3 **the Mediterranean Sea**

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10

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12 **Abstract**

13 Land-based micropollutants are the largest pollution source of the marine environment acting
14 as the major large-scale chemical sink. Despite this, there are few comprehensive datasets for
15 estimating micropollutant fluxes released to the sea from river mouths. Hence, their dynamics
16 and drivers remain poorly understood. Here, we address this issue by continuous
17 measurements throughout the Rhône River basin (~ 100,000 km²) of 1) particulate-bound
18 micropollutant concentrations (persistent organic micropollutants: polychlorobiphenyls
19 [PCBi] and polycyclic aromatic hydrocarbons [PAHs]; emerging compounds: glyphosate and
20 AMPA; and trace metal elements [TME]), 2) suspended particulate matter [SPM], and 3)
21 water discharge. From these data, we computed daily fluxes for a wide range of
22 micropollutants ($n = 29$) over a long-term period (2008-2018). We argue that almost two third
23 of annual micropollutant fluxes is released to the Mediterranean Sea during three short-term
24 periods over the year. The watershed hydro-climatic heterogeneity determines this dynamic

25 by triggering seasonal floods. Unexpectedly, the large deficit of the inter-annual monthly
26 micropollutant fluxes inputs (tributaries and the Upper Rhône River) compared to the output
27 (Beaucaire station) claims for highly contaminated missing sources of micropollutants in the
28 Rhône River watershed. Based on a SPM-flux-averaged micropollutant concentrations mass
29 balance of the system and the estimates of the relative uncertainty of the missing source
30 concentration, we assessed their location within the Rhône River catchment. We assume that
31 the potential missing sources of PAHs, PCBi and TME (only for Pb, Cd and Hg) would be,
32 respectively, the metropolitan areas and the alluvial margins of the Rhône River valley, and
33 the unmonitored Cevenol tributaries.

34 **Keywords:** Particulate micropollutant fluxes, Suspended particulate matter, Rhône River,
35 Mediterranean Sea, Hydrological dynamic, Land-based pollution

36 **1. Introduction**

37 Identified as one of the nine processes that regulate the stability and resilience of the Earth
38 system, chemical pollution and its control variables, and interactions with other biophysical
39 processes, remains poorly quantified (Rockström et al., 2009; Steffen et al., 2015; Lade et al.,
40 2019). Such quantification is all the more critical as the large-scale ubiquity of chemical
41 pollution threats at least half of European freshwater bodies (Malaj et al., 2014). Organic
42 micropollutants and trace metal elements (TME) are released into the hydrographic networks
43 from agricultural, industrial, domestic and mining activities, and urban areas (Meybeck et al.,
44 2003). They are largely transferred downstream and finally trapped into the marine
45 environment. As a result, land-based human activities are known to be the largest source of
46 pollution to the marine environment, which act as the major chemical sink at the regional and
47 global scales (Dachs et al., 2002; Gioia et al., 2011). Source-to-sink transport of
48 micropollutants are river mouths for the coastal environments and atmosphere for the open

49 ocean (Gioia et al., 2011; Gómez-Gutiérrez et al., 2006; Wang et al., 2007; Liu et al., 2008).

50 In fact, an undetermined amount of the micropollutants discharged into the coastal
51 environments is then transferred through unknown routes to open seawaters, thus acting as an
52 additional source of contamination to the remote marine environment (Gioia et al., 2011).

53 Persistent organic pollutants (POPs), such as indicator polychlorobiphenyls (PCBi) and
54 polycyclic aromatic hydrocarbons (PAHs), and most TME are preferentially transported on
55 suspended particulate matter (SPM) (Meyer et al., 2009; Schwientek et al., 2013). In rivers,
56 SPM are (i) providing an integrated signal of particle-bound micropollutant concentrations
57 (Schwientek et al., 2013; Masson et al., 2018; Rügner et al., 2019), and (ii) acting as the main
58 transfer driver of such micropollutants into the river networks (UNEP/MAP, 2003; Horowitz
59 et al., 2009). Therefore, the accurate assessment of SPM-bound micropollutant transported
60 and discharged by rivers is critical to appraise the environmental and health risks they pose, as
61 well as to develop suitable management programs for limiting them (Gómez-Gutiérrez et al.,
62 2006; Walling et al., 2003). Unfortunately, our current knowledge on micropollutant fluxes
63 transferred to the sea via the main rivers of the globe is insufficient, as is their seasonal
64 dynamics (i.e., Gómez-Gutiérrez et al., 2006; Qi et al., 2014; Parajulee et al., 2017; Launay et
65 al., 2019; Poulier et al., 2019). This is largely due to the difficulty to obtain, over a large
66 period of time, all the data required to calculate micropollutant fluxes, including
67 comprehensive datasets on water discharge, SPM and particulate micropollutant
68 concentrations (Ollivier et al., 2011; Poulier et al., 2019). Actually, the assessment of the total
69 sediment fluxes delivery to the sea, for which the suspended sediment load largely prevails
70 compared to the bedload load (Syvitski and Saito, 2007), is not widespread since less than
71 10% of the river mouths worldwide have been monitored for their sediment delivery (Syvitski
72 et al., 2005; Bravard, 2018). Such a monitoring within the river catchments is even rarer
73 (Bravard, 2018). Moreover, available SPM concentration data are generally focused on a

74 particular event (typically flood) or over a limited period of time (typically one year), leading
75 also to large uncertainties on the inter-annual average SPM and micropollutant fluxes
76 estimations (Gómez-Gutiérrez et al., 2006; Wang et al., 2007; UNEP/MAP, 2003; Qi et al.,
77 2014; Launay et al., 2019; Bravard, 2018). Finally, most studies lack representative dataset on
78 micropollutant concentrations in SPM to calculate inter-annual average micropollutant fluxes
79 in rivers, as this is a sampling and analytical challenge that remains expensive and labour
80 intensive (Poulier et al., 2019).

81 The targeted hydrophobic organic micropollutants (PCBi and PAHs) are POPs (Tables
82 S1 and S2), legacy contaminants, listed for PCBi in the Stockholm Convention (UNEP, 2001)
83 and for PAHs in the Aarhus Protocol on Persistent Organic Pollutants (United Nations, 1998),
84 because of their toxic, persistent, bioaccumulative, ubiquitous and lipophilic properties. We
85 also focused on glyphosate and its degradation product aminomethylphosphonic acid
86 (AMPA), as these emerging and absorbable organic micropollutants recently raised great
87 concerns in our societies (e.g., Beckie et al., 2020). Indeed, the ubiquity of glyphosate and
88 AMPA in the environment, and particularly in surface waters and sediments (Grandcoin et al.,
89 2016), results from the extensively resort of the parent compound as the most effective
90 herbicide used worldwide (e.g., Baylis, 2000; Grandcoin et al., 2016; Beckie et al., 2020).
91 Because glyphosate and AMPA are strongly adsorbed to soil particles (hydrogen and cationic
92 interactions; Al Rajab, 2007) (e.g., Grandcoin et al., 2016), they reach water streams through
93 rainfall-induced runoff (e.g., Yang et al., 2015). This is all the more important to focus on
94 these two compounds that there are very few studies dealing with the concentrations of
95 glyphosate and AMPA in river sediments and even rarer on river fluxes. Finally, because this
96 study aims to include a wide range of micropollutants, we spread our investigations to 9
97 TME. All these micropollutants are priority substances within the scope of European
98 regulations (i.e., Water Framework Directive, E.C., 2000). For the first time, to our

99 knowledge, the present study investigated simultaneously the SPM-bound micropollutant
100 concentrations and fluxes of 20 organic and 9 inorganic priority pollutants over ten years
101 (2008-2018) at the Rhône River mouth, and on its main tributaries, covering 80% of the
102 watershed area (~ 96,500 km²) (Fig. 1).

103 The main goal of this study is to decipher the major drivers controlling the transport and
104 export of the micropollutant fluxes and concentrations from a large river basin into the sea. In
105 this aim, we took into account the long-term character of our data set by calculating 10-years
106 yearly and monthly averages. This investigation is based on time-integrative micropollutant
107 concentrations, and continuous SPM and water discharge data acquired throughout the Rhône
108 River catchment. This implies to (i) accurately quantify the inter-annual average fluxes of a
109 large range of organic and inorganic micropollutants ($n = 29$) released into the Mediterranean
110 Sea, (ii) identify the specific contributions of the main Rhône River tributaries, (iii) explore
111 the seasonal dynamics of the micropollutant fluxes within the Rhône River catchment and at
112 its outlet, and (iv) determine the land-based chemical pollution sources.

113 2. Materials and Methods

114 2.1. Study area

115 We chose to focus specifically on the Rhône River based on the main features of this
116 large river catchment (Fig. 1), which naturally places it as a reference for the assessment of
117 SPM-bound micropollutant fluxes that are discharged into the Mediterranean Sea:

118 - The Rhône River is the largest single source of freshwater (~ 18% of the total inputs)
119 (e.g., UNEP/MAP, 2003; Antonelli et al., 2008; Ludwig et al., 2009) and particulate matter
120 (e.g., Qi et al., 2014; Antonelli et al., 2008; Syvitski et al., 2007) of the Mediterranean Sea;

121 - The Rhône River catchment is characterized by a land-use diversity (Fig. S1) and a
122 high population density with ~ 180 inh/km² (one-third higher than the French average);

123 - The Rhône River catchment is characterized by a striking climatic and geological
124 heterogeneity (e.g., [Bethemont and Bravard, 2016](#); [Launay et al., 2019](#)). The northern part of
125 the watershed is characterized by oceanic influences and the southern part by Mediterranean
126 climatic conditions. The geological contrast of the Rhône River basin stretches from west to
127 east, since its western edge corresponds to the old Hercynian crustal segments (240 Ma and
128 older) of the Massif Central, and its eastern fringe is marked by the young Alpine mountains
129 (30–120 Ma) ([Blichert-Toft et al., 2016](#));

130 - The Rhône River is composed of three distinct hydrological regimes including snow
131 and glacier melting (Isère River and the Upper Rhône), an oceanic pluvial regime (Saône
132 River), and a Mediterranean component (Durance River).

133

134 **2.2. SPM sampling**

135 Except for the Rhône River at Beaucaire station, SPM samples were collected using
136 particle traps designed with the same characteristics of those described in [Schulze et al.](#)
137 [\(2007\)](#). The related technical features are detailed in [Schulze et al. \(2007\)](#), [Masson et al.](#)
138 [\(2018\)](#), and [Poulier et al. \(2019\)](#). Particle traps were immersed near the riverbank in the water
139 column at a depth of 0.5-1 m at cross-section with fairly homogeneous SPM concentrations
140 ([Launay, 2014](#)). At each station, SPM sampling is done every month, but for the Upper Rhône
141 River (Jons station) the particle trap was emptied every two weeks. Particulate traps
142 accumulate a volume of suspended matter proportional to the SPM concentration in the water,
143 which is the most variable parameter that makes the SPM flux (discharge varies over a much
144 narrower range). Therefore, samples from particle traps are nearly proportional to SPM flux
145 variations, not just time-averaged concentrations. They are therefore suitable for
146 micropollutants fluxes assessment ([Schulze et al., 2007](#); [Masson et al., 2018](#)). The use of
147 particle traps allowed continuous sampling of SPM over the exposure time, as well as

148 recovering sufficient amounts of particles for micropollutant analysis. At the Beaucaire
149 station, SPM samples for micropollutant analysis were collected every two weeks by a high
150 speed continuous flow centrifuge (Masson et al., 2018; Poulhier et al., 2019). The comparative
151 study conducted by Masson et al. (2018) on the SPM sampling between particle traps and a
152 continuous flow centrifuge did not show significant differences in Hg and PCB concentrations
153 testifying that these SPM sampling systems are comparable. The particle size distributions of
154 the SPM samples collected in the present study (i.e., for the six river stations investigated) are
155 mainly multimodal. Indeed, between 2 and 4 (3 in most cases) Gaussian distributions were
156 generally observed: mode 1 between 1 and 10 μm (average 4 μm particle size; clays and very
157 fine silts), mode 2 between 10 and 27 μm (average 14 μm ; fine silts), mode 3 between 27 and
158 80 μm (average 39 μm ; coarse silts), and mode 4 between 80 and 2000 μm (average 136 μm ;
159 fine to coarse sands) (Launay, 2014; Masson et al., 2018; Lepage et al., 2019). The SPM
160 samples were sorted depending on the hydrological conditions during SPM sampling, and the
161 median micropollutants concentrations was calculated for low flow and flood conditions.
162 These low flow or flood site-specific median concentrations were used to fill the gaps in the
163 measurement time series, which resulted from field material vandalism, or technical and
164 logistical glitches. In this respect, thresholds were defined at each station to distinguish
165 hydrological regimes with potentially differing contamination levels. The rule is as follows: if
166 more than 50% of the SPM cumulative flux over the exposure period of the particle trap
167 corresponds to a water discharge higher than the flood threshold (defined as half of the 2-year
168 flood peak discharge), then the SPM samples are considered under flood conditions. By doing
169 so, we obtained low flow and flood median concentrations for all micropollutants at each
170 station (Table S2).

171 2.3. Water discharges

172 Hourly averaged water discharge data at each station, except for the Rhône River at Jons
173 station for which no hydrometric station exists, were provided by the “*Compagnie Nationale*
174 *du Rhône*” (CNR), the main operator of hydropower plant on the Rhône River. At the Jons
175 station, hourly water discharge was computed using a 1-D hydrodynamical model (Launay et
176 al., 2019), requiring the discharge data of the Rhône River at Lagnieu, and those from the Ain
177 and the Bourbre tributaries.

178 **2.4. SPM concentrations**

179 The method for the estimation of SPM concentrations is described in detail in Poulier et al.
180 (2019), and the main steps are summarized here. Except for the Rhône River at Arles, SPM
181 concentrations are derived from *in situ* turbidity measurements every 10 min, and
182 reconstituted via site-specific turbidity-SPM rating curves calibrated using water sampling
183 and filtration (i.e., by manual water sample collection at the time of SPM sampling, and by
184 automated hourly sampling during flood events). At Arles solely, daily time-integrated SPM
185 concentrations were measured, and used for the fluxes computed at Beaucaire. We considered
186 that it was representative for both branches of the Rhône River, as fine particle inputs are
187 negligible between the two stations (Pont et al., 2002). For low flow conditions,
188 concentrations of SPM were obtained by analysis of daily composite water samples collected
189 automatically, whereas during floods the sampling frequency was increased to every 4 h for a
190 better temporal resolution. Data are freely available from the online database of the Rhône
191 Sediment Observatory (Thollet et al., 2018).

192 **2.5. Micropollutant concentrations**

193 **2.5.1. Polychlorobiphenyls (PCBi) analysis**

194 The concentrations of 7 indicator PCBi (congeners 28, 52, 101, 118, 138, 153, and 180) in
195 SPM were analyzed by IRSTEA laboratory according to the French Standard XP X33-012

196 (AFNOR, 2000). Approximately 1.0 g dry weight (d.w.) of sample was extracted with a
197 cyclohexane/acetone 90:10 v/v mixture, concentrated by evaporation and purified on a 1 g
198 Florisil SPE cartridge. A small amount of copper powder (10 mg mL^{-1}) was finally added in
199 order to avoid sulfur interferences prior to gas chromatography analysis with a ^{63}Ni electron
200 capture detector (GC-ECD). Samples were analyzed on two different columns (RTX®-5, 30
201 $\text{m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ for quantification and RTX®-PCB, 30 $\text{m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ for
202 confirmation of the compound identity) to confirm the results. Procedural blanks and control
203 standard solutions were systematically checked. The accuracy of measurements was checked
204 via intercomparison exercises and the analysis of a certified reference material (BCR 536). A
205 sediment sample from the Bourbre River, a tributary of the Rhône River, was used to
206 determine analytical uncertainties, as no certified reference material exists for such low levels
207 of PCB_i in equivalent matrix. Analytical uncertainties were estimated to be 60% ($k = 2$) for
208 concentrations lower than 3-times the limit of quantification (LOQ) and to be 30% ($k = 2$) for
209 concentrations higher than 3-times the LOQ. The LOQs were estimated between 0.5 and 1 μg
210 kg^{-1} (d.w.) depending on the congeners. PCB_i 28 and 52 were mostly below the LOQ
211 (average quantification frequency around 35%), and were not used in this study. The
212 quantification frequency (QF) of the other congeners was on average 72%. Data are freely
213 available from the online database of the Rhône Sediment Observatory (Thollet et al., 2018).

214

215 **2.5.2. Polycyclic aromatic hydrocarbons (PAHs) analysis**

216 A total of 15 priority PAHs (2-methylfluoranthene, anthracene, benz[a]anthracene,
217 benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene,
218 dibenz[a,h]anthracene, fluoranthene, indeno[1,2,3-cd]pyrene, phenanthrene, pyrene,
219 naphthalene and 2-methylnaphthalene) were analyzed by the accredited Laboratory of Hygiene
220 and Environment (Alpha group, Rouen, France) according to the XP X33-012 Standard

221 (AFNOR, 2000). Samples were extracted with a hexane/acetone 50:50 v/v mixture,
222 concentrated by evaporation and purified on silica, then analyzed by capillary gas
223 chromatography coupled to a mass spectrometer (GC-MS). Analytical uncertainties were
224 estimated to be 60% ($k = 2$) for concentrations lower than 3-times the LOQ and to be 30% (k
225 $= 2$) for concentrations higher than 3-times the LOQ. The LOQ ranged from 1 to 2 $\mu\text{g kg}^{-1}$
226 (d.w.) for most of the PAHs, except for dibenz[a,h]anthracene and phenanthrene (up to 5 μg
227 kg^{-1}). Naphtalene and 2-methynaphtalene were mostly below the LOQ (average QF around
228 50%) and were not used in this study. The QF of the other PAHs was on average 96%. The
229 laboratory was accredited by the French Committee for Accreditation (Cofrac) (accreditation
230 n° 1-1351) for measuring PAHs in sediments and fulfils the requirements of the standard NF
231 EN ISO/IEC 17025 (2017).

232 **2.5.3. Glyphosate and AMPA analysis**

233 Glyphosate and AMPA were analyzed by the accredited Laboratory of Hygiene and
234 Environment (Alpa group, Rouen, France). Extraction was performed by agitation with an
235 alkaline solution of 0.5M KOH. Then, a SPE purification step was carried out using an Oasis
236 HLB cartridge. Before analysis, a derivation step was achieved (with 9-
237 fluorenylmethylchloroformate). The analysis was done by capillary liquid chromatography
238 coupled to a mass spectrometer (LC-MS). The LOQ of glyphosate and AMPA for a 5 g (d.w.)
239 sample) was 10 $\mu\text{g kg}^{-1}$ (d.w.). The QF was on average 55% for glyphosate and 86% for
240 AMPA. The laboratory was accredited by the French Committee for Accreditation (Cofrac)
241 (accreditation n° 1-1351) for measuring glyphosate and AMPA in sediments and fulfils the
242 requirements of the standard NF EN ISO/IEC 17025 (2017).

243 **2.5.4. Trace Metal Elements (TME) and mercury (Hg) analysis**

244 The TME (As, Cd, Co, Cr, Cu, Ni, Pb, Zn) in the SPM were measured by CEREGE
245 laboratory. Aliquots of 40-mg dry SPM were weighed out into acid-cleaned Teflon beakers.
246 All reagents were ultrapure grade compounds. Then, aliquots were dissolved in a mixture of 3
247 mL of HCl (34%), 4 mL HNO₃ (67%), 20 drops of H₂O₂ (35%) and 0.5 mL of HF (47-51%).
248 The mixtures were digested on a hotplate at 170°C (10 min), and then 250°C (10 min; P=100
249 bar) in an UltraWAVE Single Reaction Chamber (Milestone, Thermo-Scientific). The
250 samples in solution were all clear, attesting the complete breakdown of the SPM samples. The
251 solutions were diluted with ultrapure Milli-Q water (Merck) and measured by ICP-MS
252 (Perkin-Elmer, Nexlon 300X) against calibration curves and rhodium solution as internal
253 standard. The procedural blanks and reference sediments STSD-3 and MESS-4 (Canadian
254 Certified Reference Materials Project) were analyzed repeatedly. Uncertainties for Cd, Co, Cr,
255 Cu, Ni, Pb, Zn and As concentration measurements were 14%, 3.6%, 1.2%, 5.0%, 2.3%,
256 3.2%, 3.0% and 6.7%, respectively. The LOQ of Cd, Co, Cr, Cu, Ni, Pb, Zn and As in SPM
257 were 0.1 mg kg⁻¹ (d.w.), 0.05 mg kg⁻¹ (d.w.), 0.1 mg kg⁻¹ (d.w.), 0.1 mg kg⁻¹ (d.w.), 1 mg kg⁻¹
258 (d.w.), 1 mg kg⁻¹ (d.w.), 5 mg kg⁻¹ (d.w.) and 0.5 mg kg⁻¹ (d.w.), respectively. The QF of all
259 TME was 100%.

260 The determination of total Hg in SPM was performed by IRSTEA laboratory using an
261 automated atomic absorption spectrophotometer, DMA 80 (Milestone), according to EPA
262 method 7473 (U.S. EPA, 1998). Blanks and certified reference materials (IAEA 433, marine
263 sediment; IAEA 457, coastal sediment; LGC 6187, river sediment) were systematically used
264 to control analytical accuracy (94%) and uncertainty (14%; k=2). The LOQ of Hg in SPM
265 was 10 µg kg⁻¹ (d.w.). Mercury was always quantified.

266 In the present paper, TME (including Hg) concentrations and fluxes were summed as
267 Σ₉TME to simplify the description of results, and thus facilitate the comparison of the TME
268 group with the other micropollutant families. Obviously, each TME or group of TME is

269 discussed apart since Zn and Cr weigh around two thirds of $\Sigma_9\text{TME}$ (Table S1 and S2). Data
270 are freely available from the online database of the Rhône Sediment Observatory (Thollet et
271 al., 2018).

272 2.6. SPM and micropollutant fluxes

273 The calculation of SPM and micropollutant fluxes is based on the method developed in
274 Poulhier et al. (2019), and the main steps are summarized below. To appraise micropollutant
275 fluxes at an inter-annual and inter-annual monthly resolution over the 2008-2018 exposure
276 period, we calculated firstly SPM fluxes as the product of hourly measured data of both water
277 discharges and SPM concentrations at each station. When missing values of SPM
278 concentrations occurred (non-monitored periods or gaps in the measurement time series),
279 SPM values were reconstructed on the basis of the empirical known relation involving water
280 discharges (Q), and SPM concentrations (C_s) called C_s - Q rating curves (i.e., Poulhier et al.,
281 2019; Horowitz, 2003; Sadaoui et al., 2016). Secondly, micropollutant fluxes were calculated
282 by multiplying the SPM fluxes to the monthly time-integrated particulate micropollutant
283 concentrations obtained from particle traps, or by a continuous flow centrifuge only at the
284 Rhône at Beaucaire station. Data for micropollutants with a $QF < 50\%$ were not considered in
285 this study (2 PCBi and 2 PAHs). For some other organic micropollutants (other PCBi and
286 PAHs), below LOQ data were changed to LOQ/2 for calculation.

287 Non-monitored periods or gaps in the measurement time series, which resulted from
288 field material vandalism, or technical and logistical glitches, were filled by low flow or flood
289 site-specific median concentrations for all micropollutants (Poulhier et al., 2019). Because no
290 micropollutant concentrations-water discharge relationships were found (Pearson's r between
291 averaged water discharge and Hg, Pb, $\Sigma_{13}\text{PAH}$, $\Sigma_5\text{PCB}$, glyphosate and AMPA concentrations
292 of -0.25, -0.16, 0.37, -0.15, 0.19 and -0.40, respectively at the Rhône River outlet) (Fig. S2),

293 we chose to fill gaps by the median of low flow or flood site-specific concentrations in order
294 to be as close as possible to the field sampling condition based on time-integrated particle
295 traps. In other words, this gap-filling technique provides the convenience of filling monthly
296 average concentrations, rather than the detailed dynamics of instantaneous concentrations.
297 Moreover, it is not useful to resort to continuous relationships, which do not really exist with
298 respect to [figure S2](#).

299 Accordingly, we distinguished the measured and the estimated micropollutant
300 concentrations, depending on the availability of measurements from sediment-trap samples
301 for the considered period. The total micropollutant flux ($F_{i,j}$) is the sum of the measured flux
302 ($F_{i,j,\text{measured}}$) and the estimated flux ($F_{i,j,\text{estimated}}$) for which the micropollutant
303 concentrations ($C_{i,j}$) are estimated (i.e., as the low flow and flood site-specific median
304 concentrations). The total uncertainties of the inter-annual and inter-annual monthly
305 micropollutant fluxes were estimated (distinguishing measured and estimated fluxes) using
306 95% level of uncertainty, which corresponds to 2 standard deviations for a Gaussian
307 distribution; they are shown in absolute and relative values in [Table S1](#) (see details on
308 uncertainty computation in [the supplementary text](#)). We also computed the weight (in
309 variance) of the estimated concentration uncertainty in the total flux uncertainty
310 ($W_{i,j,\text{estimate}}$) ([Table S1](#)) ([see the supplementary text](#)). The uncertainty analysis we introduce
311 in this paper, although via a simplified approach, proves to be an interesting exercise to assess
312 the significance of our flux estimates.

313

314 **3. Results and Discussion**

315 **3.1. Decadal assessment of inter-annual SPM and particulate micropollutant fluxes**

316 For the period 2008-2018, we obtained an inter-annual average for Σ_{13} PAH, Σ_5 PCB, Σ_9 TME,
317 glyphosate and AMPA fluxes of about, respectively, 3.0 ± 0.7 t yr⁻¹, 61 ± 8 kg yr⁻¹, $1,802\pm 152$ t
318 yr⁻¹, 97 ± 20 kg yr⁻¹, 220 ± 45 kg yr⁻¹ at the Rhône River mouth (Beaucaire station) (Table S1).
319 The average of the total inter-annual fluxes uncertainty of the micropollutant families at the
320 same station is about 16% (ranging from 8 to 22% for, respectively, TME and PAHs) (Table
321 S1) for which the weight of the estimated concentration uncertainty accounts for about 46%
322 on average (ranging from 10 to 82% for, respectively, TME and glyphosate/AMPA) (Table
323 S1). The uncertainty analysis we introduce in this study proves to be an interesting way to
324 assess the reliability of our flux estimates. However, the total flux uncertainty and the weight
325 of the estimated concentration uncertainty in the total flux uncertainty show a high variability
326 according to the tributaries and the micropollutants considered (Table S1).

327 These estimates of the inter-annual average micropollutant fluxes are substantially
328 different from those found in the literature about organic and inorganic micropollutant fluxes
329 discharged by the Rhône River to the Mediterranean Sea. For instance, based on standard
330 values of annual SPM flux of 4-5 M t yr⁻¹, Lipiatou and Albaiges (Lipiatou and Albaigés,
331 1994) estimated ~14-18 t yr⁻¹ for the annual Σ_{14} PAH flux of the Rhône River. In the same
332 way, Lipiatou et al. (Lipiatou et al., 1997) evaluated the annual Σ_{11} PAH flux to ~5-33 t yr⁻¹
333 using standard SPM flux values between 2-10 t yr⁻¹. These values are coherent with the
334 Σ_{14} PAH flux of 14 t yr⁻¹ assessed by Sicre et al. (2008), using by an annual SPM flux of 13.9
335 M t yr⁻¹ for the year 1994-1995. These assessments of HAPs fluxes are between 2- and 11-
336 fold higher than our measurements due in part to the high annual SPM flux values used in
337 these studies. They are up to 2.5-fold higher than our inter-annual average SPM flux (5.5 M t
338 yr⁻¹). Similarly, the annual Σ_5 PCB flux estimated by Tronczyński and Héas-Moisán (1996)
339 during the year 1994-1995 is four-fold higher than our estimate. In this case, the Σ_5 PCB flux
340 difference is explained both by the high values of the annual SPM flux (15.8 M t yr⁻¹ vs. 5.5

341 M t yr⁻¹ in this study) and the Σ_5 PCB concentrations (35.5 $\mu\text{g kg}^{-1}$ vs. 12.7 $\mu\text{g kg}^{-1}$ in this
342 study) measured by the authors. Always about PCB, the recent study of Dendievel et al
343 (2019) evaluated the inter-annual Σ_5 PCBi budget (2007-2017) of about 97 kg yr⁻¹. This
344 overestimation of about 60% higher than our estimate could be attributed to the use of a
345 standard mean Σ_5 PCBi concentration value, rather than a continuous measure of PCBi
346 concentrations during the span of time. Finally, annual TME fluxes are also concerned by
347 such differences in assessment due to the SPM flux estimates. According to Radakovitch et al.
348 (2008) and Ollivier et al. (2011), which calculated an inter-annual SPM flux ~ 7 M t yr⁻¹, the
349 sum of Cr, Co, Ni, Cu, Zn, Cd and Pb fluxes between 2001 and 2003 was about 3,182 t yr⁻¹ on
350 average, against 1,720 t yr⁻¹ for Σ_7 TME in the present study (Table S1).

351 At the Rhône river mouth, these studies carried out since the mid-1990s assessing
352 organic and inorganic micropollutant fluxes discharged to the Mediterranean Sea were usually
353 based on limited grab sampling surveys over a full year at best. Such short monitoring periods
354 lead to significant disparities in annual micropollutant fluxes, because they induce an
355 overestimation of the annual SPM flux. Indeed, beyond the different methods used to
356 calculate SPM fluxes discharged to the sea, the high inter-annual variability of SPM fluxes
357 rules out any attempt to assess representative micropollutant fluxes inferred from a single year
358 of SPM monitoring.

359
360 A comparison of these micropollutant fluxes at the Rhône River outlet with those
361 discharged to the sea by other large rivers shows significant differences, since PAHs and
362 PCBi fluxes were estimated for the Yangtze River (watershed surface area 1.8 M km²), the
363 Mississippi River (3.3 M km²) and the Saint-Laurent River (1.3 M km²) around, respectively,
364 365 and 73 t yr⁻¹ (~ 120 - and 1200-fold higher, respectively), 160 and 32 t yr⁻¹ (~ 50 - and 500-
365 fold higher, respectively), and 25 and 5 t yr⁻¹ (~ 8 - and 80-fold higher, respectively) (Liu et al.,

366 2008). These annual micropollutants fluxes have to be weighted by the catchment size of
367 these rivers to estimate specific fluxes and thus assess their differences of contamination. In
368 this regard, PAHs and PCBi specific fluxes are, respectively, around 73-329 g km² yr⁻¹ and 7-
369 73 g km² yr⁻¹ (highly above the Rhône River) for the Yangtze River, 17-78 g km² yr⁻¹ (similar
370 to the Rhône River) and 1.8-17 g km² yr⁻¹ (highly above the Rhône River) for the Mississippi
371 River, and 7-32 g km² yr⁻¹ (slightly below the Rhône River) and 0.7-7 g km² yr⁻¹ (highly
372 above the Rhône River) for the Saint-Lawrence River.

373 As consequence, it appears more suitable to compare these fluxes with rivers showing
374 features, such as the size of catchment and numbers of inhabitants, analogous to the Rhône
375 River basin (75,900 km² and 15.5 M inhab). For instance, the inter-annual average Σ_7 PCBi
376 and Σ_{16} PAH fluxes assessed at the Seine River outlet (78,600 km² and 17.5 M inhab) between
377 the period 2000-2014, with 90 kg yr⁻¹ (i.e., around 1 g km² yr⁻¹) (Briand et al., 2016) and 2.3 t
378 yr⁻¹ (i.e., around 30 g km² yr⁻¹) (Fisson et al., 2015), respectively, are similar to those of the
379 Rhône River at Beaucaire (i.e., respectively, about 0.8 g km² yr⁻¹ and 40 g km² yr⁻¹) estimated
380 in the present study (Table S2). These results strengthen the fact that these micropollutants
381 track rather well urbanization and population (i.e., Schwientek et al., 2013; Rügner et al.,
382 2019). In contrast, glyphosate (870 kg yr⁻¹ or 11 g km² yr⁻¹), AMPA (4,700 kg yr⁻¹ or 60 g km²
383 yr⁻¹), and Σ_9 TME (323 t yr⁻¹ or 4 kg km² yr⁻¹) fluxes (Fisson et al., 2015) delivered at the Seine
384 estuary are wholly different from those of the Rhône River at its outlet, with about 97±20 kg
385 yr⁻¹ (1.3 g km² yr⁻¹), 220±45 kg yr⁻¹ (2.9 g km² yr⁻¹) and 1,802±152 t yr⁻¹ (24 kg km² yr⁻¹),
386 respectively (Table S1). Regarding glyphosate and AMPA, such differences could be explain
387 by agricultural activities since they are highly developed in the Seine River basin (Schott et
388 al., 2009), and largely prevailed by cereal cultivation, which is known to resort on glyphosate
389 (Grandcoin et al., 2017). Finally, the geological basements of the Rhône and Seine watersheds

390 involve contrasting mineralogical compositions that could explain their distinct TME fluxes
391 (Rügner et al., 2019).

392

393 **3.2. Hydro-climatic control of the micropollutant fluxes dynamic: floods as seasonal** 394 **trigger**

395 The inter-annual and inter-annual monthly SPM and particulate micropollutant fluxes were
396 calculated over the entire period 2008-2018 for the five tributaries monitored, and at the
397 catchment scale (Rhône River at Beaucaire station) (Figs 2, S3 and Table S2). The mean
398 inter-annual SPM flux contributions of the tributaries to the total flux at Beaucaire station are
399 as follows: 31% for the Isère and Durance Rivers, 11% for the Upper Rhône (Jons station),
400 6% for the Saône River and 0.1% for the Gier River. For the total inter-annual
401 micropollutants flux (all micropollutant families together) released at the Rhône River outlet,
402 the average contributions of the tributaries are the following: 21% for the Isère River, 12% for
403 the Saône River, 10% for the Durance River, 9% for the Upper Rhône (Jons station) and 1%
404 for the Gier River; but these values fluctuate from one micropollutant family to another. Such
405 variability in micropollutant contributions between tributaries is explained by the station-
406 specific chemical fingerprint and SPM flux.

407 At the Rhône River outlet (Beaucaire station), the evolution of the mean inter-annual
408 monthly micropollutant fluxes is characterized by a tri-modal distribution over the year with
409 maxima centered in (1) November, (2) January, and (3) May-June (Fig. 3). The sum of the
410 micropollutant fluxes exported to the sea during these periods (one third of a year) represents
411 nearly two thirds of the mean inter-annual micropollutant budget of the Rhône River at its
412 outlet. Such a dynamic of the micropollutant fluxes over the year appears to be driven by the
413 hydrological regime of the Rhône River, given the strong positive correlation between water,
414 SPM, and micropollutant (average value used of the Pearson's r computed for all the

415 micropollutants) fluxes at the Rhône River mouth (Pearson's $r = 0.98$ for SPM vs.
416 micropollutant fluxes (ranging from 0.95 to 1 according to the micropollutants); $r = 0.70$ for
417 water vs. micropollutant fluxes (ranging from 0.64 to 0.78 according to the micropollutants),
418 and $r = 0.70$ for SPM vs. water fluxes). The three-mode profile of the inter-annual monthly
419 micropollutant fluxes closely follows the modes of the complex hydrological regime of the
420 Rhône River combining (Fig. 3):

- 421 - a first Mediterranean component in November accounting for 24% of the mean
422 inter-annual budget of particulate micropollutant fluxes;
- 423 - a second oceanic pluvial component in January accounting for 15% of the mean
424 inter-annual budget of particulate micropollutant fluxes;
- 425 - a third nival component in May-June accounting for 24% of the mean inter-annual
426 budget of particulate micropollutant fluxes.

427

428 Such a seasonal behavior of the micropollutant fluxes dynamic of the Rhône River over
429 the year suggests a decisive hydro-climatic control. In this respect, the daily time-series of the
430 water and micropollutant fluxes calculated over the 2008-2018 period show that 70% of the
431 particulate micropollutant fluxes released to the Mediterranean Sea occurred during flood
432 events (defined as half of the 2-year flood peak discharge at Beaucaire; i.e., $Q > 2,900 \text{ m}^3 \text{ s}^{-1}$)
433 accounting for 11% of the time. These figures are similar to the estimates assessed by
434 Radakovitch et al. (2008) and Ollivier et al. (2011) since they considered ~ 80% of the inter-
435 annual average TME fluxes delivered into the Mediterranean Sea occurs in less than 12% of
436 the time. In comparison, Sicre et al (2008) assessed that 90% of the inter-annual average flux
437 of $\Sigma_{14}\text{PAH}$ reach the Mediterranean Sea during flood events. Still based on the daily time-
438 series of the micropollutant fluxes, this large micropollutant flux carried by the Rhône River
439 during floods evolves exponentially according to the flood power:

- 440 - the last decile of the most powerful floods ($Q > 4,500 \text{ m}^3 \text{ s}^{-1}$), integrating 1% of time
441 spent, accounts for 28% on average of the total micropollutant fluxes discharged to
442 the sea during the time range of the study (2008-2018);
- 443 - floods exceeding the 2-year flood peak discharge ($Q > 6,000 \text{ m}^3 \text{ s}^{-1}$) (Pont et al.,
444 2002), integrating 0.2% of time spent, account for 11% on average of the total
445 micropollutant fluxes discharged to the sea during the time range of the study (2008-
446 2018).

447 Based on the mean inter-annual monthly profiles of the micropollutant fluxes of the
448 Rhône River tributaries (Fig. 3), the identification of the sources of the three seasonal modes
449 occurring at the river mouth are easily resolved. In this way, the first Mediterranean
450 component appears to be largely triggered by the micropollutant fluxes coming from the
451 Durance River, which supplies about 19% (ranging from 9% to 40% according to the
452 micropollutant families) of the total micropollutant fluxes released into the sea in November.
453 In comparison, the other tributaries inputs fluctuate between 1.5% (Gier River) and 7%
454 (Saône River) during this period. The second seasonal mode of the micropollutant fluxes
455 observed in January at the Rhône River outlet implies an oceanic pluvial component
456 regulating part of the hydrology of the Saône, Isère and Upper-Rhône basins, which,
457 respectively, provide 18%, 14%, and 10% of the micropollutant fluxes exported to the sea at
458 this time. Finally, the nival component of the micropollutant fluxes, arising in May and June,
459 integrates a further significant contribution from the Isère River accounting for 84 and 34%,
460 respectively. In addition, the Durance River and the Upper Rhône River basin provide each an
461 average of 10% of the micropollutant fluxes delivered to the Mediterranean Sea in May and
462 June (Fig. 3).

463 This hydro-climatic control of the seasonal micropollutant fluxes dynamic in the Rhône
464 River basin raises the issue of the climate change impacts on the future trends of these fluxes.

465 Since floods act as the main transport vector of the micropollutant fluxes towards the
466 Mediterranean Sea, it appears essential to focus on the regional patterns of the climatic-
467 change signal in flood discharges (Blöschl et al., 2019). In this end, data from the Explore
468 2070 project (Chauveau et al., 2013), which estimated the possible impacts of climate change
469 on surface water until the end of the twenty-first century for the whole French hydrographic
470 network, provide insights on the probable evolution of the three periods of micropollutant
471 fluxes discharges into the Mediterranean Sea. At the scale of the Rhône River watershed, but
472 also for the main Rhône River tributaries, the oceanic pluvial component should progress
473 (increasing floods) with the increasing winter discharges (Blöschl et al., 2019; Madsen et al.,
474 2014; Bethemont and Bravard, 2016; Dayon et al., 2018) caused by increasing rainfall
475 between January and March (Chauveau et al., 2013). Conversely, the spring nival component
476 is expected to decrease (decreasing floods) at the Rhône River outlet, and more specifically
477 for the major Alpine tributaries (Upper Rhône River basin and Durance and Isère Rivers), due
478 to the warmer temperatures resulting in earlier and decreasing spring snowmelt floods
479 (Blöschl et al., 2019; Chauveau et al., 2013; Madsen et al., 2014; Bethemont and Bravard,
480 2016; Dayon et al., 2018). Finally, the Mediterranean component is defined by high-intensity
481 floods following intense precipitation events and affecting especially the small “Cevenol”
482 rivers (right bank, southern tributaries of the Rhône River) (Fig. 1). Recently, Blöschl et al.
483 (2019) estimated that, in a warmer climate, local convective storms might increase in southern
484 Europe and could lead to an increase of the floods magnitude in small watersheds. Typically,
485 we could expect an increase in the fall moisture flux originating from warmer Mediterranean
486 temperatures that would result in increasing Cevenol rivers floods. This assumption is
487 supported by the projection of the 10-year return period flood quantile, using multi-models of
488 changes, which could increase for the Cevenol rivers in the next decades (Sauquet and Lang,
489 2017). As a result, the Mediterranean component weight would increase. These potential

490 responses of the seasonal behavior of micropollutant fluxes due to the changing climate
491 would result in particulate micropollutant fluxes released into the Mediterranean Sea over a
492 shorter period of time, which would be centered in autumn and winter. As a result, the
493 chemical pollution on the receiving coastal waters would be more intense at this time of year
494 than it currently is.

495

496 **3.3. Defining the chemical cocktails and the overall pollution level to track the spatial** 497 **heterogeneity of large watersheds**

498 In order to define the spatial trends and ranking of the overall contamination level of the
499 six stations studied, a Principal Component Analysis (PCA) was performed on flood versus
500 low flow median concentrations of the 29 quantified substances (Fig. 4A and B). Based on
501 114 tests of Pearson's correlation coefficient performed between the content of particulate
502 organic carbon (POC in g kg^{-1} dry weight) and the 5 PCBi, 13 PAHs and Hg concentrations
503 (mg kg^{-1} dry weight) (micropollutants for which there is an affinity for organic carbon) at the
504 six stations, no micropollutant concentrations-organic content relationship was found. For
505 ~75% of the cases (87 of 114) $r < 0.2$ and $p\text{-value} > 0.05$. As a result, the micropollutant
506 concentrations are expressed only on a dry weight (d.w.) basis.

507 The first principal component (F1 ~ 89%) was largely contributed from all
508 micropollutants, meaning that F1 tracks the overall pollution level. Consequently, the F1
509 scores of each station for low flow and flood conditions (Fig. 4A) allow to rank the stations
510 according to their overall contamination level. The resulting first ranking is presented on the
511 X-axis of Fig. 4A, in descending order from right to left, from the Gier River for low flow to
512 the Durance River for flood. In order to ensure the reliability of this classification, two Heat
513 Maps were performed using the same data set (Fig. 4C). The left panel of the figure 4C shows
514 a Heat Map run with all the stations, which are ranked from left to right on the x-axis in a

515 descending order according to their overall pollution level. The resulting classification is
516 similar to that provided by the PCA (Fig. 4A). A third ranking was performed, using land use
517 data for the catchments of the monitoring stations, by summing the anthropized-land use
518 categories (Fig. S1). This third ranking is similar to those obtained by the statistical
519 treatments, except for the Durance and Isère Rivers which are nevertheless very close: Gier
520 (64%) > Saône (63%) > Beaucaire (43%) > Jons (35%) > Durance (23%) > Isère (22%).

521 Based on these classifications of the overall pollution level, three coherent water
522 quality-related groups of stations arise (defined by the clustering analysis of the Heat Maps;
523 see section Statistical analysis of micropollutant concentrations of the Supplementary
524 Material) (Fig. 4C): considered as highly contaminated (Gier and Saône Rivers), intermediate
525 (Beaucaire and Jons stations on the Rhône River), and relatively clean (Isère and Durance
526 Rivers) (Fig. 4). The stations of Jons and Beaucaire display an intermediate level of
527 contamination suggesting the Rhône River waters homogenize efficiently the various
528 contributions of its tributaries. Moreover, the higher overall contamination level of the
529 Beaucaire station compared to the Jons station, both in low flow and flood conditions (Fig.
530 4A and C), demonstrates of a progressive downstream enrichment of the pollution of the
531 Rhône River's waters. Such a spatial trend, with increasing PCB concentrations downstream
532 the Rhône River, has recently been reported by Mourier et al. (2014) using sediment cores
533 from the alluvial plain. This downstream increasing trend of the chemical pollution of the
534 Rhône River's waters could result from the density of the metropolitan areas sheltered in the
535 Rhône Valley downstream to the Jons station (Lyon, Vienne, Valence, Montélimar, and
536 Avignon). This urban density probably act as many potential contamination sources.

537 The ranking of the monitoring stations also provides useful information on the influence
538 of the hydrological conditions on the overall pollution levels. Indeed, for low flow conditions,
539 the Rhône River tributaries are systematically more contaminated than in floods (Fig. 4A and

540 **C**), probably as a consequence of a dilution effect resulting from the introduction of “clean
541 SPM” during sustained hydrological events. For the Gier River, this dilution effect in floods is
542 significantly higher than for the other tributaries (**Fig. 4A**). A possible explanation is that the
543 widespread catchment areas of the main Rhône River tributaries (Saône, Isère and Durance)
544 are able to limit the dilution effect subsequent to the remobilization of contaminated
545 sediments by the erosion and leaching of the floodplain and bank deposits during flood events
546 (**Ciszewski and Grygar, 2016; Pavlowsky et al., 2017**). Such a flood-induced reworking of
547 inherited sediments is probably less relevant for the Gier River because of the narrowness of
548 its valley bottoms, and the numerous hydraulic facilities (dikes, ripraps, channelization and
549 covered sections) limiting floodplain sedimentation. Finally, the two Rhône River stations
550 show an opposite behavior with a general pollution (i.e., taking into account all
551 micropollutants) increasing in flood conditions (**Fig. 4A and C**). Therefore, we suppose
552 inherent processes to the Rhône Valley capable of triggering secondary pollution sources
553 occurring during sustained water discharge events and readable through chemical fingerprints.

554 In order to test this hypothesis, the second step consists to define sub-catchment-specific
555 chemical fingerprints to highlight the major anthropogenic and geographical sources of
556 micropollutant families in the Rhône River catchment, as well as to decipher the composition
557 of the micropollutant fluxes inputs (tributaries) and output (river mouth). The projection of
558 the 29 micropollutants in the factorial plan of the PCA defined by the principal components
559 F2 and F3 distinguishes efficiently the micropollutants families (panel right **Fig. 4B**). Indeed,
560 in the correlations circle, PAHs are located on the right side, PCB_i on the upper left quarter,
561 and TME, glyphosate and AMPA on the lower left quarter. This clustering of micropollutant
562 families is similar to that of the vertical cluster analysis inferred from the Heat Maps (see
563 panel left in **Fig. 4C**). To ensure the reliability of our conclusions inferred from of the
564 chemical fingerprints (**Figs. 4B and C**), we compared them to the station-specific chemical

565 spectrum (Fig. S4). Hence, for low flow conditions, the chemical cocktails recognized are as
566 follows:

- 567 - Beaucaire: PCB, TME and glyphosate/AMPA;
- 568 - Jons: PAH and TME (Cu, Cd, Zn);
- 569 - Saône: PAH and TME (As, Hg, Pb, Cd);
- 570 - Gier: PCB, TME and glyphosate/AMPA;
- 571 - Isère: TME and AMPA;
- 572 - Durance: no specific chemical fingerprint identified.

573 The chemical cocktails of the Gier, Beaucaire and Jons stations change towards
574 prevailing PAHs fingerprints during flood condition. This is especially striking for the
575 Beaucaire station experiencing mirror-shape chemical fingerprints (Fig. 4C-right and S4C).
576 Indeed, during floods the TME, glyphosate and AMPA concentrations decrease in favor of
577 PAHs (Fig. 4C-right and S4C). The activation of this secondary source of contamination
578 during floods is probably caused by runoff over artificial areas (Blanchard et al., 2001; Bigus
579 et al., 2014; Froger et al., 2019), which are more widespread in the three catchments involved
580 (Fig. S1). This diffuse source of PAHs is probably triggered when floods are combined with
581 intense precipitation events (David et al., 2012). For both Rhône River stations, this leaching
582 process over artificial surfaces could explain the higher PAHs contamination level during
583 flood periods (Fig. 4B and C-right, S4C and S4E). Indeed, $\Sigma_{13}\text{PAH}$ concentrations at the
584 Beaucaire and Jons stations increase, respectively, from 444 to 651 $\mu\text{g kg}^{-1}$ (+ 47%), and from
585 499 to 569 $\mu\text{g kg}^{-1}$ (+ 14%) (Tab. S1). This increase of $\Sigma_{13}\text{PAH}$ concentrations during floods
586 does not affect the Gier River (see the left Heat Map in Fig. 4C and Table S2) because the
587 dilution effect of this river is more effective than the PAHs inputs during floods.

588 In order to decipher the pollution source of PAHs in the Rhône River SPM, the most
589 frequently used PAHs molecular diagnostic ratios, i.e., Fla/(Fla+Pyr), BaA/(BaA+Chry) and
590 IndP/(IndP+BghiP) (e.g., Froger et al., 2019; Yunker et al., 2002; Ravindra et al., 2008), were
591 investigated (Fig. S5). Firstly, based on these PAHs ratios, all the monitoring stations show
592 similar fingerprints characterized by a restricted PAHs space implying a common-source of
593 PAHs for the Rhône River SPM. Secondly, these PAHs fingerprints fit that of the runoff
594 particles collected by Gaspéri et al. (2017, 2018) from a storm sewer of the densely urbanized
595 catchment of Sucy (south-east of Paris in France) (Fig. S5). In this respect, as recently
596 suggested by Froger et al. (2019) for the Orge River SPM (catchment located in the Seine
597 River basin), runoff particles would be the main direct PAHs source in the urbanized areas of
598 the Rhône River basin. Thirdly, while atmospheric particles are known to be sensitive to the
599 fossil fuel combustion (Froger et al., 2019) derived from vehicular emissions (Keyte et al.,
600 2016) or household heating (Motelay-Massei et al., 2003), runoff particles-derived pollution
601 source of the Rhône River SPM is mainly composed of mixed vehicular, and biomass
602 combustion emissions, as well as of a minor contribution from fossil fuel combustion (Fig.
603 S5). Finally, this investigation based on two levels of PAHs fingerprints (direct local sources
604 and general combustion origins) evidences that urban runoff is the main direct PAHs source
605 of the Rhône River SPM, which encompasses multiple origins including biomass and fossil
606 fuel combustion. These results are in good agreement with the general statement that urban
607 pressure, population density, and PAHs concentrations in SPM are positively correlated (i.e.,
608 Schwientek et al., 2013; Rügner et al., 2019; Parajulee et al., 2017; Poulier et al., 2019).

609 **3.4. Exploring the micropollutant missing sources**

610 The inter-annual and inter-annual monthly micropollutant budgets at the Rhône River
611 outlet (Beaucaire station) were computed and compared to the micropollutant fluxes inputs
612 from the tributaries (Figs. 2 and S3). We consider that the negative imbalance (i.e., deficit

613 budget) is related to the missing sources of micropollutants including non-monitored
614 tributaries, wastewater effluents, runoff over artificial areas, as well as remobilization of
615 highly contaminated sediments subsequent to the erosion and leaching of the floodplain, and
616 bank deposits during flood events (e.g., Ciszewski and Grygar, 2016; Pavlowsky et al., 2017;
617 Poulhier et al., 2019). These missing sources constitute about 47% on average, and more
618 specifically about 65% for Σ_5 PCB, 54% for Σ_{13} PAH, 60% for glyphosate, 24% for AMPA,
619 and 31% for Σ_9 TME of the total annual flux of micropollutants (Figs. 2 and S3). Because
620 these values are greater than the inter-annual SPM deficit (21%), this implies that the missing
621 sources have higher particulate micropollutant concentrations. In order to remove the
622 influence of SPM flux variations, SPM-flux-averaged micropollutant mean concentrations,
623 called thereafter “total concentration”, were calculated to improve the assessment of the
624 missing sources magnitude, as well as their identification. The total concentration $C_{total,j}$ of
625 a micropollutant j from n inputs (or tributaries) is the sum of the partial concentrations
626 $C_{partial,j}$ of the inputs to the system:

$$627 \quad C_{total,j} = \frac{\sum_{i=1}^n F_{i,j}}{\sum_{i=1}^n F_{i,SPM}} = \sum_{i=1}^n C_{partial,j} \quad (1)$$

$$628 \quad \text{with } C_{partial,j} = \frac{F_{i,j}}{\sum_{i=1}^n F_{i,SPM}} \quad (2)$$

629 $F_{i,j}$: flux of micropollutant j from input i

630 $F_{i,SPM}$: flux of SPM from input i

631 Analogous to partial pressures in a mixture of gases, the “partial concentration” of an
632 input is the notional concentration of that input if the micropollutants alone were diluted in
633 the entire SPM flux of all the inputs. Then, we compared the inter-annual and inter-annual

634 monthly $C_{total,j}$ of the inputs to that one output of the system at the Rhône River outlet
635 (Beaucaire station) for:

$$636 \quad C_{output,j} = \frac{F_{output,j}}{F_{output,SPM}} \quad (3)$$

637 with $F_{output,j}$: flux of micropollutant j from *output*

638 $F_{output,SPM}$: flux of SPM from *output*

639 Results of $C_{total,j}$, $C_{partial,j}$ and $C_{output,j}$ in figures 2 and S6 are expressed in terms of
640 tributaries contributions (%) to be consistent with SPM and micropollutant fluxes, as well as
641 to facilitate the comparison of the inputs micropollutant “total concentration” ($C_{total,j}$) vs.
642 output micropollutant concentration ($C_{output,j}$). By measuring the positive (excess) or the
643 negative (deficit) difference between $C_{output,j}$ and $C_{total,j}$, we can assess the presence and the
644 relative degree of contamination of the micropollutant missing sources. Regarding that, two
645 groups of micropollutants can be distinguished at the inter-annual scale (Figs 2 and S6). The
646 first one refers to the PCBi, PAHs and glyphosate, and shows a significant negative imbalance
647 (large deficit) because their inter-annual deficit is between 28% and 51%. The second one
648 encompasses AMPA and TME, which show a minor negative imbalance (small deficit),
649 because their inter-annual deficit is between 1% and 13%. Such low deficits highlight low
650 micropollutant concentrations of the missing sources.

651 In order to facilitate the identification of the missing sources of contamination, we
652 performed an inter-annual monthly decomposition of the $C_{partial,j}$ (tributaries inputs) relative
653 to the $C_{output,j}$ (Rhône River outlet, Beaucaire station) for all micropollutants (Fig. 5 and S7).
654 The inter-annual monthly distribution of the total Σ_{13} PAH concentrations relative to the
655 output Σ_{13} PAH concentrations shows an irregular trend over the year with the highest deficits
656 in April (36%), May (46%), June (50%), and November (58%). This temporal pattern is

657 consistent with the rainiest months of the Rhône Valley (Météo France), which shelter
658 numerous metropolitan areas (Lyon, Vienne, Valence, Montélimar, and Avignon). The main
659 missing sources of the total Σ_{13} PAH concentrations should be triggered by precipitation-
660 induced runoff, and leaching over artificial surfaces of the Rhône valley's urban areas. This
661 potential and non-exclusive missing urban source of PAHs concentrations is finding support
662 in Becouze-Lareure et al. (2019) showing that stormwater is the most important source of
663 PAHs at the outlet of two urban catchments in the Lyon metropolitan area. According to the
664 uncertainty analysis, the inter-annual deficit of the SPM-flux-averaged PAHs mean
665 concentrations of about 28% (Fig.5) is explained for 41% by the relative uncertainty of the
666 PAHs missing source concentration (see the supplementary text).

667 In contrast, the inter-annual monthly profile of the total Σ_5 PCB concentrations relative
668 to the output Σ_5 PCB concentrations (Figs 5 and S7) is steady over the year, with a mean
669 deficit of about 51%, except for October (only about 10%), due to a very high contribution
670 from the Upper-Rhône River (56%). This sudden increasing of the Upper-Rhône River
671 contribution has to be considered as an artefact resulting from a deliberate or accidental
672 isolated discharge of PCB_i into the Upper Rhône River waters. Indeed, an exceptionally high
673 value of PCB_i concentration measured (two-fold higher than the low flow median
674 concentration) was found in SPM collected in October 2013 (PCB_i concentrations were
675 measured two times on the same sample to check for the absence of analytical bias). The
676 unchanging profile of the total Σ_5 PCB concentrations over the year could express the presence
677 of a single, permanent, and relatively highly contaminated source of PCB_i. According to the
678 recent sediment-cores investigation led by Liber et al. (2019) on subsurface PCB-
679 contaminated sediments along the Rhône River's alluvial margins, surface sediments
680 deposited to a maximum depth of 25 cm from the topographic level (time window > 2005)
681 downstream of the city of Lyon show elevated PCB_i concentrations. The Σ_5 PCB

682 concentration is on average about $42 \pm 12 \mu\text{g kg}^{-1}$ ($76 \pm 29 \mu\text{g kg}^{-1}$ for the time window > 1968)
683 in these easiest remobilized sediments induced by floodplain surface leaching during flood
684 events (Ciszewski and Grygar, 2016).

685 In order to test the reliability of this potential missing source of PCB_i, the assessment of
686 the SPM flux released from the alluvial margins to fill alone the inter-annual PCB-flux deficit
687 was estimated. The SPM flux $F_{k,SPM}$ of a missing source k with assumed concentration $C_{k,j}$ in
688 micropollutant j can be computed as:

$$689 \quad F_{k,SPM} = \frac{F_{k,j}}{C_{k,j}} \quad (4)$$

$$690 \quad \text{with } F_{k,j} = F_{output,j} - \sum_{i=1}^n F_{i,j} \quad (5)$$

691 Therefore, considering an inter-annual PCB-flux deficit of about 40 kg (Table S1) and a
692 mean PCB concentration of $42 \mu\text{g kg}^{-1}$ in the subsurface stored sediments of the Rhône
693 River's alluvial margins (Liber et al., 2019), this potential missing source of contamination
694 should then supply a SPM flux of 0.95 Mt yr^{-1} to fill alone the inter-annual PCB-flux deficit.
695 Although such a value may appear high in view of the mean inter-annual SPM flux at
696 Beaucaire (about 17%) (Table S1), it falls within the range of errors of the inter-annual SPM
697 flux measurement at the Rhône River outlet commonly considered $< \pm 20\%$ (Horowitz, 2003).
698 As a result, this estimated figure of the SPM flux inputs required to fill alone the inter-annual
699 PCB-flux deficit shows that the alluvial margins are a convincing missing source of PCB_i in
700 the Rhône River basin. This missing source of PCB_i is all the more convincing that the inter-
701 annual deficit of the SPM-flux-averaged PCB_i mean concentrations of about 51% (Fig.5) is
702 explained for 21% by the relative uncertainty of the PCB_i concentration (see the
703 supplementary text) of the subsurface stored sediments of the Rhône River's alluvial margins.

704 The inter-annual monthly profiles of the total glyphosate and AMPA concentrations
705 relative to the output glyphosate and AMPA concentrations (Figs 5 and S7) exhibit significant
706 differences leading to distinct mean monthly deficits about 46% and 1%, respectively.
707 Because AMPA is, among other, a glyphosate degradation product, they usually co-occur in
708 the environment (Aparicio et al., 2013; Lupi et al., 2015), so it was expected to observe a
709 similar monthly co-evolution over the year. According to the literature reviewed by
710 Grandcoin et al. (2017) about glyphosate and AMPA in the streams, a few factors lead to
711 accelerate degradation rates of glyphosate. These include the sorption capacity of soils, which
712 depends in turn to clay, organic matter, and Al-Fe oxides and hydroxides contents, and the
713 total metal concentrations in soils and water. A particular focus on the partial glyphosate and
714 AMPA concentrations of the inputs reveals an overall similar proportion for these two
715 molecules for each tributary, except for the Isère River marked by a disproportionate mean
716 monthly partial concentration reaching 47% of the output AMPA concentration against 10%
717 for glyphosate (Fig 5). By removing this surplus of AMPA coming from the Isère River, the
718 general profiles of the total glyphosate and AMPA concentrations of inputs over the year is
719 similar to that of Σ_{13} PAH. Consequently, their highest deficits, recorded from May until
720 November (Fig 5), could result from the same urban missing sources located in the Rhône
721 valley downstream of the city of Lyon. Indeed, in addition to agricultural leachates, AMPA
722 and glyphosate have an urban wastewater effluents source (e.g., Grandcoin et al., 2017;
723 Kolpin et al., 2006; Botta et al., 2009), for which releases are particularly substantial during
724 heavy rainfall runoff (Botta et al., 2009; Hanke et al., 2010).

725 Finally, the inter-annual monthly mean deficit between the output TME concentrations
726 and their total concentrations of inputs is much lower than for the other micropollutant
727 families, since it is around 13%. This figure should be considered with caution as large
728 differences are observed between TME that could be sorted in two groups as follows (Fig. 5):

- 729 - Zn, Ni, Cu, Cr, Co, and As display a mean inter-annual monthly deficit of about
730 10% (ranging from 5 to 15%), which is explained for 36% on average (ranging from
731 27 to 48%) by the relative uncertainty of this TME cluster's missing source
732 concentration;
- 733 - Pb, Hg, and Cd display a mean inter-annual monthly deficit of about 26% (ranging
734 from 25 to 28%), which is explained for 25% on average (ranging from 21 to 31%)
735 by the relative uncertainty of this TME cluster's missing source concentration.

736 As expected, the largest partial TME concentrations of the inputs are coming from the
737 Isère River, with an average contribution to the total TME concentrations over the year of
738 about 36%. (Fig. 2). This figure is higher for the first TME group (40%), than the second
739 group (28%). In view of these differences, we assume that the main TME missing sources are
740 highly enriched in Pb, Hg, and Cd in the one hand, and slightly less for Zn, Ni, Cu, Cr, Co,
741 and As, on the other hand. In addition, the co-evolution of the total Pb, Cd and Hg
742 concentrations of the inputs over the year indicates a triggering of their main missing source
743 from September to November, since the greatest deficits of the TME concentrations inputs
744 occurred at this time (Figs. 5 and S6). This information builds a strong body of evidence
745 toward the non-monitored Cevenol tributaries (Eyrieux, Ardèche, Cèze and Gard rivers, Fig.
746 1), as the main sought missing source, because they are known to be highly enriched in TME
747 coming from the remobilization of former mining sites tailings (Pb/Zn mining districts, and
748 coal production districts) (Resongles et al., 2014, 2015). To ensure the reliability of this
749 missing source, we compared the Cevenol tributaries' SPM fluxes ($F_{k,SPM}$) needed to fill the
750 inter-annual TME-flux deficits ($F_{k,j}$), with the inter-annual SPM flux deficit ($\sim 1.1 \text{ Mt yr}^{-1}$)
751 (Table S1). We used a mean concentration of the Cevenol tributaries $C_{k,j}$ (Ardèche, Gard and
752 Cèze) (Fig. 1) of 93.3 mg kg^{-1} for Pb, 0.05 mg kg^{-1} for Hg, 0.82 mg kg^{-1} for Cd, 211.4 mg kg^{-1}
753 for Zn, 35.7 mg kg^{-1} for Ni, 46.4 mg kg^{-1} for Cu, 80.7 mg kg^{-1} for Cr, 14.9 mg kg^{-1} for Co, and

754 44.5 mg kg⁻¹ for As (data from the Rhône Sediment Observatory). The Cevenol tributaries'
755 SPM fluxes ($F_{k,SPM}$) were estimated at around 1.1 Mt yr⁻¹ (ranging from 0.5-1.5 Mt yr⁻¹
756 according to the TME considered and more specifically 0.9 Mt yr⁻¹ for Pb and Cd), with the
757 exception of Hg with 4 Mt yr⁻¹. Therefore, we suggest that the Cevenol tributaries constitute
758 the main missing source of TME fluxes, except for Hg, since the estimated SPM flux ($F_{k,SPM}$)
759 is equal to the inter-annual SPM flux deficit.

760 **4. Conclusions and perspectives**

761 Based on the Rhône Sediment Observatory, a one-of-a-kind monitoring network, we have
762 explored the seasonal dynamic of land-based organic and inorganic particulate-bound
763 micropollutant fluxes, which appears to be controlled by the complex hydrological regime of
764 the Rhône River. The inter-annual monthly distribution of the micropollutant fluxes released
765 into the Mediterranean Sea displays a three-mode profile related to the Mediterranean,
766 oceanic pluvial, and nival floods acting as the primary transport vector. Face to climate
767 change, the major part of micropollutants fluxes would reach the Mediterranean Sea during a
768 single shorter period centered in autumn and winter. Original multi-variate statistical analysis
769 methods integrating median concentrations of a large number of micropollutants highlighted
770 the spatial heterogeneity of watersheds in terms of the overall micropollutant concentrations,
771 land use and chemical cocktails. Finally, based on a SPM-flux-averaged micropollutant
772 concentrations mass balance of the system and the estimates of the relative uncertainty of the
773 missing source concentration, we tried to identify the missing sources of micropollutants in
774 the Rhône River watershed. We assume that the potential missing sources of PAHs, PCBi and
775 TME (only for Pb and Cd) would be, respectively, the metropolitan areas and the alluvial
776 margins of the Rhône River valley, and the unmonitored Cevenol tributaries.

777 From this research emerge perspectives relating to the potential interactions between the
778 micropollutant fluxes dynamic, climate change, river-floodplain connectivity, river restoration
779 programs and legacy contaminated sediments. For the past twenty years the river restoration
780 and management programs of the Rhône River include the reactivation of channel side arms,
781 and the removal of lateral embankments in order to reinstate lateral connectivity between the
782 channel and its alluvial margins (e.g., Provansal et al., 2012; Bravard and Gaydou, 2015;
783 Riquier et al., 2015). However, without an accurate assessment of the contamination levels of
784 the sedimentary volumes stored on the margins, these actions could lead to the reintroduction
785 into the system of inherited sediments highly contaminated because of their remobilization
786 (Provansal et al., 2012; Delile et al., 2014; Bravard and Gaydou, 2015; Eschbach et al., 2018).
787 This issue is even more sensitive that the river engineering could positively interact with the
788 climate change-enhanced flood magnitude. Indeed, improving the river-floodplain
789 connectivity would facilitate the propagation of the increased flood discharges towards the
790 alluvial margins and strengthening their ability to remobilize contaminated legacy deposits on
791 floodplains. To that purpose, it would be useful to resort to sediment cores to evaluate
792 micropollutant volumes stored, as well as their chemical composition. Still based on sediment
793 cores, they could be used as archives of past SPM and particulate micropollutant fluxes
794 (Ferrand et al., 2012; Cossa et al., 2018) able to fill the gap between recent measurements
795 from the monitoring station network and past fluxes. Such a perspective would provide a
796 pluri-secular historical depth to the spatial and temporal trajectories of the development of the
797 urban societies.

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1117 **Figure captions**

1120 **Fig. 1.** Map of the Rhône River basin with its main tributaries and the monitoring stations for
1121 water discharge, suspended particulate matter and associated micropollutants.

1122 **Fig. 2.** Inter-annual and inter-annual monthly water, SPM and micropollutant budgets (plain
1123 colors) and partial/total (sum of partial) micropollutant concentrations (pale colors) relative to
1124 the Rhône River outlet (orange line, Beaucaire station) (in %). The contributions of the
1125 monitored tributaries to the budgets and to the total concentrations are shown for each family
1126 of micropollutants.

1127 **Fig. 3.** Inter-annual monthly water, SPM and micropollutant fluxes over the 2008-2018
1128 period at each monitoring station. Organic and inorganic micropollutant fluxes are expressed

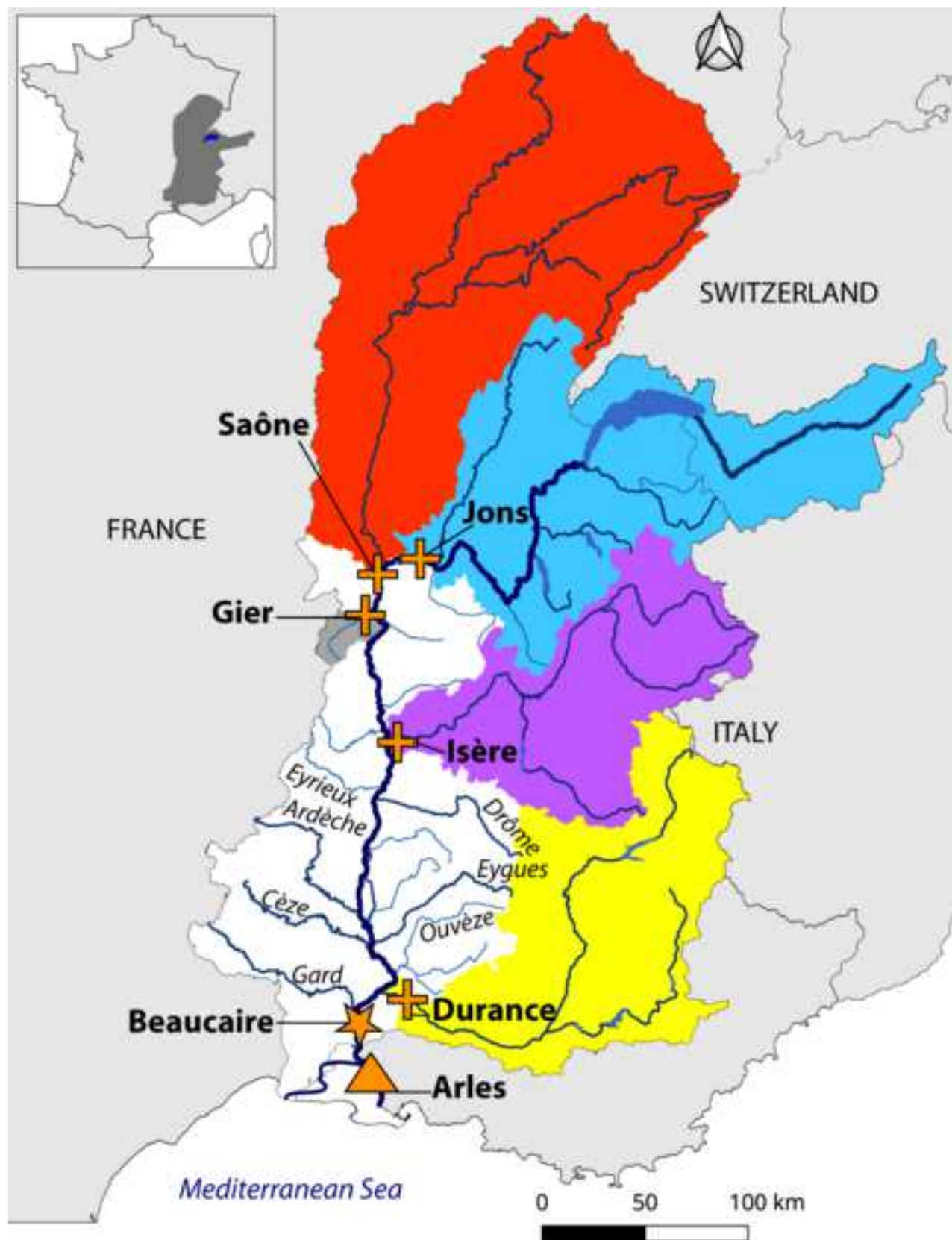
1129 in kilograms and tons by year, respectively. Listing of abbreviations of micropollutants
1130 detailed in **Table S1 and S2**.




1131 **Fig. 4.** Statistical analysis of the median concentrations for all the micropollutants at all the
1132 monitoring stations, for low flow and flood conditions: Principal Component Analysis (panels
1133 A and B for factors F1/F2 and F2/F3, respectively) and Heat Maps (panel C) whose columns
1134 and rows are arranged according to a hierarchical cluster analysis. The left Heat Map in the
1135 panel C includes all the monitoring stations, while the right one is performed without the Gier
1136 River to improve the readability of the results of the other stations. The arrows in the panel B
1137 depict the prevailing PAHs fingerprint during flood conditions for the Gier and Beaucaire
1138 stations. Listing of abbreviations of micropollutants detailed in **Table S1 and S2**.

1139 **Fig. 5.** Decomposition of the inter-annual monthly total micropollutant concentrations relative
1140 to the Rhône River outlet (orange line, Beaucaire station) (in %). The contributions of the
1141 partial micropollutant concentrations of the monitored tributaries are displayed for each
1142 family of micropollutants.

Figure

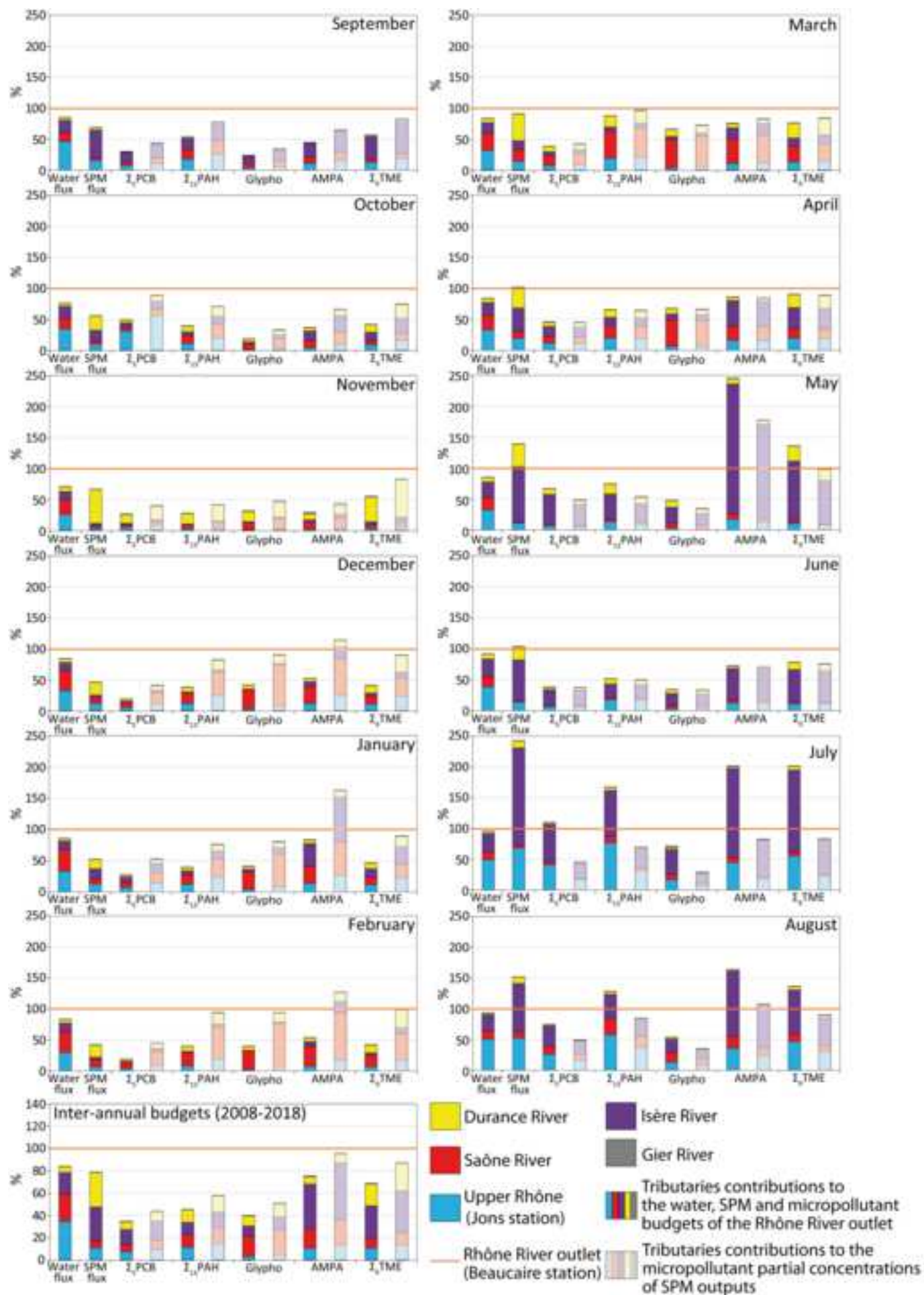
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-  Water discharge, turbidity monitoring and particle trap
-  Turbidity monitoring and continuous flow centrifuge
-  Water discharge monitoring

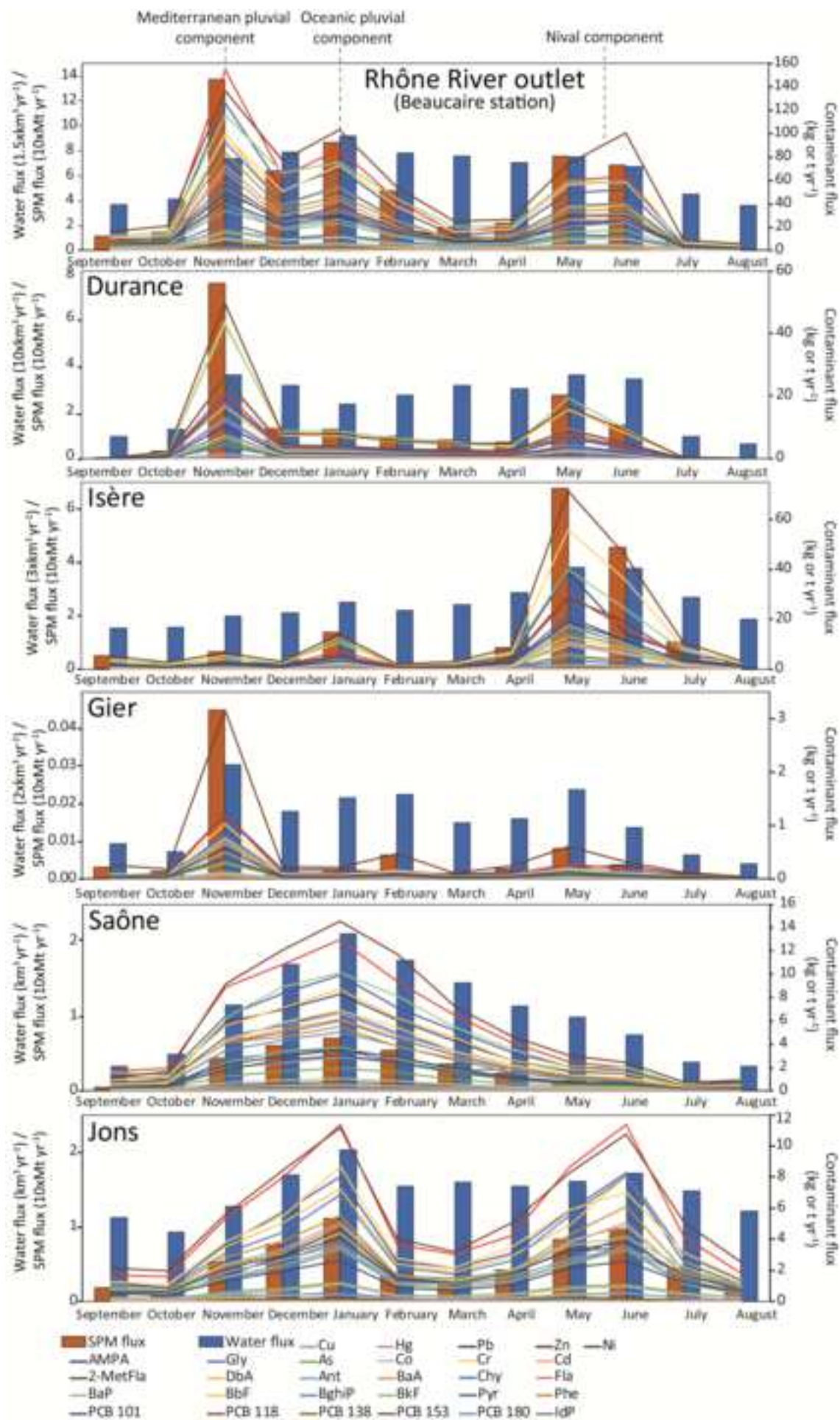
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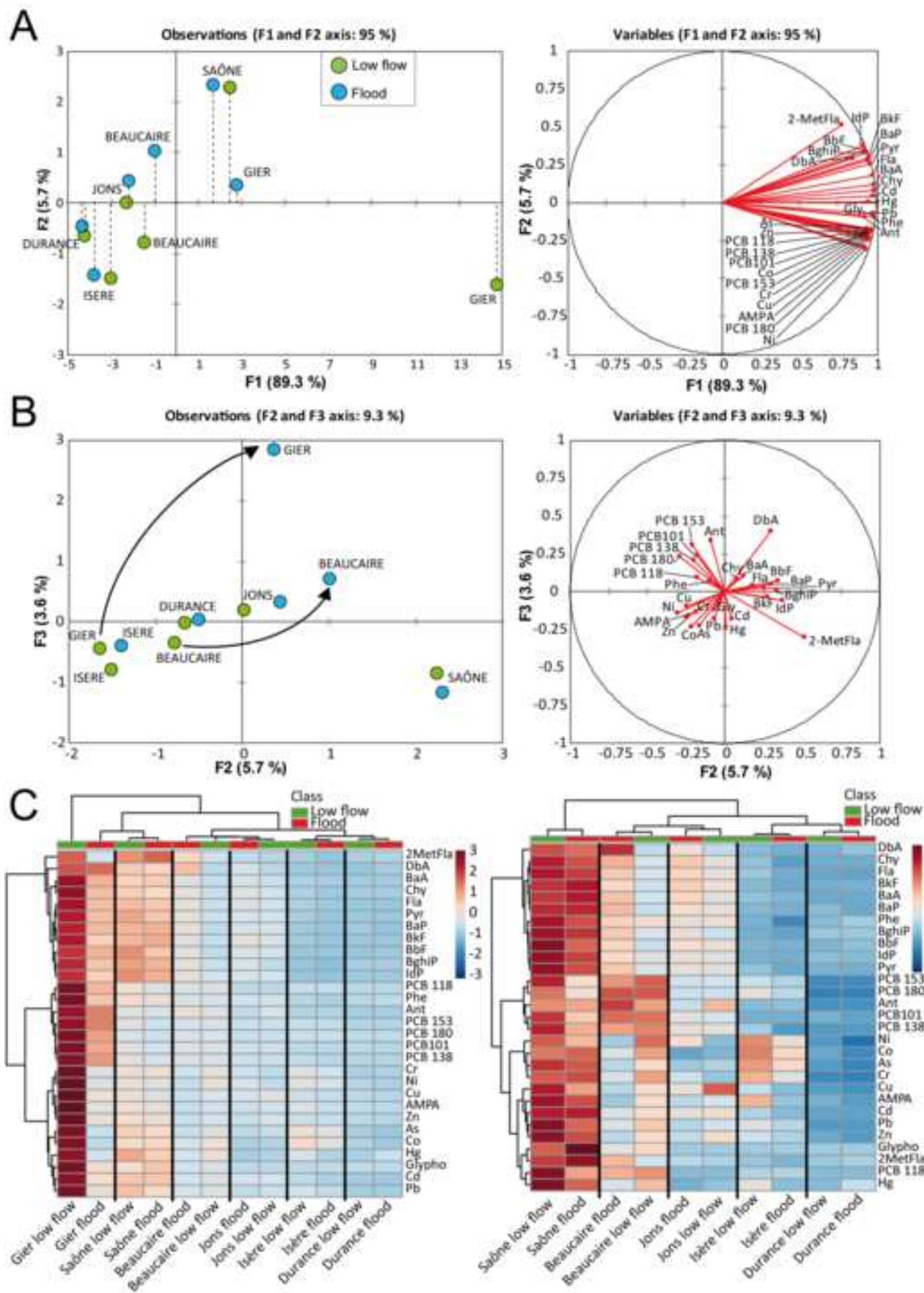
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