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1 Occurrence of α , ω -dicarboxylic acids and ω -oxoacids in surface waters of the Rhone River and fluxes
2 into the Mediterranean Sea

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32 **Abstract**

33

34 The Mediterranean Sea is a semi-enclosed marine environment surrounded by densely
35 populated areas. This ecosystem is under strong anthropogenic pressure at present. Riverine waters are
36 important input pathways of water-soluble organic compounds that potentially contribute to the
37 dissolved organic carbon (DOC) pool. Here, we report the first ever measurements of bi-functional
38 carboxylic acids such as α , ω -dicarboxylic acids (or diacids) and related polar compounds ω -oxoacids
39 (or ketoacids) (BCAs = α , ω -dicarboxylic acids + ω -oxoacids), along with the DOC levels in Rhone
40 River waters. Surface water samples were collected from February 2006 to June 2009 approximately
41 50 km above the Rhone River mouth, which is the main supplier of freshwater to the Mediterranean
42 Sea. The BCA concentrations averaged $32.4 \pm 15.3 \mu\text{g l}^{-1}$, and exhibited a wide range of values from
43 $13.2 \mu\text{g l}^{-1}$ (Spring 2008) to $71.2 \mu\text{g l}^{-1}$ (winter 2007). The contribution of carbon from BCAs to the
44 DOC pool (BCA-C) accounted for 0.28 to 1.42% of the DOC. Although no seasonal trend was evident
45 in the studied period, our results showed that the highest BCA concentrations did not always follow
46 high water discharges. α , ω -dicarboxylic acids are the most abundant compound class ($20.7 \pm 10.6 \mu\text{g l}^{-1}$),
47 which is followed by ω -oxoacids ($11.7 \pm 6.2 \mu\text{g l}^{-1}$). The Rhone River was estimated to deliver
48 between 1.37 and 16.4 t d⁻¹ of BCA to the Gulf of Lions. Assuming a mean water discharge of ~ 1790
49 m³ s⁻¹, a broad estimate suggests a loading of 750-4000 t yr⁻¹ BCAs to the northwestern Mediterranean
50 Sea. Our results indicated that glyoxylic acid (ωC_2) was the most abundant BCA followed by oxalic
51 acid (C₂di) and fumaric acid (*trans* configuration of unsaturated C₄ diacid). This result indicates that
52 there is a different molecular distribution between the aquatic and atmospheric compartments,
53 including rainwaters and aerosols, for which previous studies highlighted a predominance of oxalic
54 acid, which was followed by malonic and/or succinic acid. Runoff and riverine biological process
55 (rather than photochemical oxidation reactions) are hypothesized to control the BCA occurrence and
56 molecular distribution in the Rhone River and thus their inputs to the coastal NW Mediterranean Sea,
57 although the environmental implications of this stock of BCA are still unknown.

58

59 1. Introduction

60

61 Low-molecular-weight (LMW: C₂-C₉) α , ω -dicarboxylic acids (diacids) and related polar
62 compounds such as ω -oxoacids (or ketoacids) hereafter called BCAs (bi-functional carboxylic acids
63 =diacids + ketoacids) are ubiquitous water-soluble organic compounds. These chemicals have been
64 detected in a variety of environmental compartments and regions, including atmospheric aerosols and
65 precipitation (Sempéré and Kawamura, 1996; Kawamura and Bikina, 2016), snowpacks and ice cores
66 (Narukawa et al., 2002; Kawamura et al., 2001), marine sediments (Gogou et al., 2000), lakes
67 (Bertilsson et al., 2000; Brinkmann et al., 2003) and seawaters (Goldstone et al., 2002; Tedetti et al.,
68 2006). BCAs can originate in the atmosphere from several natural processes, such as direct biogenic
69 emission (Kawamura and Gagosian, 1990), ozonolysis, as well as photooxidation of precursor organic
70 compounds (Sempéré, and Kawamura, 2003; Kawamura et al., 2005, Rinaldi et al., 2011). These
71 chemicals can also be released to the atmospheric compartment at important levels by several
72 anthropogenic sources, such as incomplete combustion of fossil fuels and biomass burning
73 (Kawamura et al., 2016). In streams and seawater, BCAs may be produced by phytoplankton
74 photorespiration (Steinberg and Bada, 1984) photochemical degradation of dissolved organic matter
75 (DOM) (Kirk, 1994; Pullin et al., 2004) and microbial degradation of long-chain lipids (Kester, 1963).
76 BCAs can also reach to seawater by diffusion from surface sediments (especially for oxalic acid)
77 (Peltzer and Bada., 1981), inputs of terrigenous material from rivers (Pullin et al., 2004) and wet and
78 dry depositions processes (Sempéré and Kawamura, 2003).

79 Aerosol particles enriched with BCAs can play important roles in several biogeochemical and
80 physical processes, contributing to the radiative forcing at the Earth's surface. The BCA hygroscopic
81 properties make these chemicals capable of acting as cloud condensation nuclei (Kerminen et al.,
82 2000). BCAs also participate in many biological processes in aquatic systems, such as by serving as
83 important intermediates in the tricarboxylic acid and glyoxylate cycles as well the catabolism and
84 anabolism of amino acids (Steinberg and Bada, 1982). In addition, BCAs could represent a non-
85 negligible fraction of LMW DOM and have a potential role in the organic carbon cycle in the natural
86 environment (Tedetti et al., 2006). However, because of analytical difficulties, studies on the BCA

87 occurrence in seawaters are limited to a few measurements performed in coastal waters from the
88 Pacific Ocean where one dicarboxylic acid, i.e., oxalic acid, and two ketocarboxylic acids (glyoxylic
89 and pyruvic) were detected (Steinberg and Bada 1982, and 1984) and the Sargasso Sea and coastal
90 waters off Florida, where ketocarboxylic acids (glyoxylic and pyruvic) and dicarbonyls
91 (methylglyoxal and glyoxal) were measured (Mopper and Stahovec, 1986; Kieber and Mopper, 1987;
92 Zhou, and Mopper, K., 1997). Even fewer data exist for semi-enclosed marine environments, such as
93 the Mediterranean Sea. Only one study reported the surface water concentrations of a homologous
94 series of BCA from samples collected in 2005 at levels of approximately $50 \mu\text{g l}^{-1}$ in the northwestern
95 (NW) Mediterranean Sea (Tedetti et al., 2006).

96 The Mediterranean Sea is under strong anthropogenic pressure (e.g. industrial, urban,
97 agriculture, and intense maritime traffic (The MERMEX group, 2011 and references therein,
98 UNEP/MAP, 2012) and it has been reported to be largely impacted by persistent organic pollutants
99 (POPs) and related anthropogenic contaminants, some of which have similar atmospheric sources as
100 BCA, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and
101 dibenzofurans (PCDD/Fs) (The MERMEX group, 2011; Berrojalbiz et al., 2011; Guigue et al., 2011,
102 2014; Castro-Jiménez et al., 2008, 2010, 2012). For example, common anthropogenic sources of BCA
103 and PAHs to the atmosphere are direct combustion processes such as fossil fuels and biomass burning
104 (Kawamura et al., 2013; Castro-Jiménez et al., 2012), as well as photochemical oxidation of precursor
105 aromatic hydrocarbons during long range transport in the atmosphere (Kawamura and Bikkina, 2016
106 and references therein). In addition to atmospheric deposition processes, riverine inputs are major
107 entry pathways for organic species to the Mediterranean coastal areas, especially the Gulf of Lions
108 (the NW Mediterranean Sea), which is under the influence of the Rhone River (Sempéré et al. 2000;
109 Panagiotopoulos et al., 2012). Although little is known about its chemical composition, riverine DOM
110 influences the bacterioplankton community structure and function (Crump et al., 2009). At a global
111 scale, previous studies showed that riverine DOC, that contains both degraded remains of aged and
112 recent vascular plant materials (Hedges et al., 1997), is modern and younger than particular organic
113 carbon (POC) (Raymond et al., 2007; Spencer et al., 2012). Such apparent degraded biochemical
114 signature of riverine DOM, along with modern radiocarbon ages of the DOC, has been reported in

115 systems from the Arctic to the Equator (Raymond et al., 2007; Spencer et al., 2012). Compared to the
116 rest of global ocean, the flux of riverine DOM to the Mediterranean Sea constitutes a major source of
117 reduced carbon to the Mediterranean Sea (Sempéré et al., 2000). The occurrence of BCA in riverine
118 surface waters and relative inputs of BCA to Mediterranean waters are poorly characterized, and to
119 best of our knowledge no data exist for the Rhone River which is the main supplier of organic carbon
120 to the whole Mediterranean Sea.

121 The objectives of this study are: (1) to provide the first assessment on the concentrations of
122 α,ω -dicarboxylic acids and ω -oxoacids in surface waters from the Rhone River as well as their relative
123 abundance within the dissolved organic carbon (DOC) pool, (2) to estimate the fluxes of
124 α,ω -dicarboxylic acids and ω -oxoacids from the Rhone River into the Mediterranean Sea and (3) to
125 investigate the possible organic matter and BCA sources in relation to the degradation mechanisms
126 occurring in the area.

127

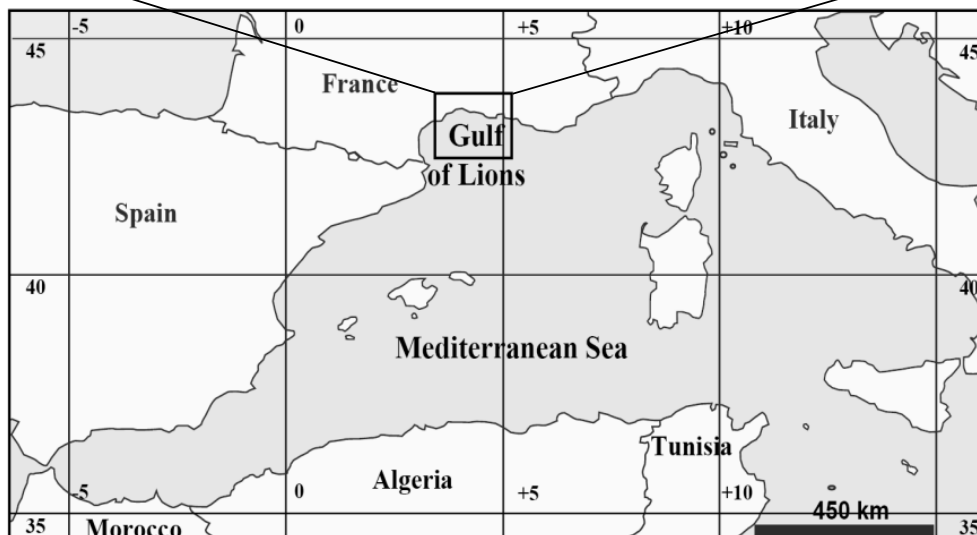
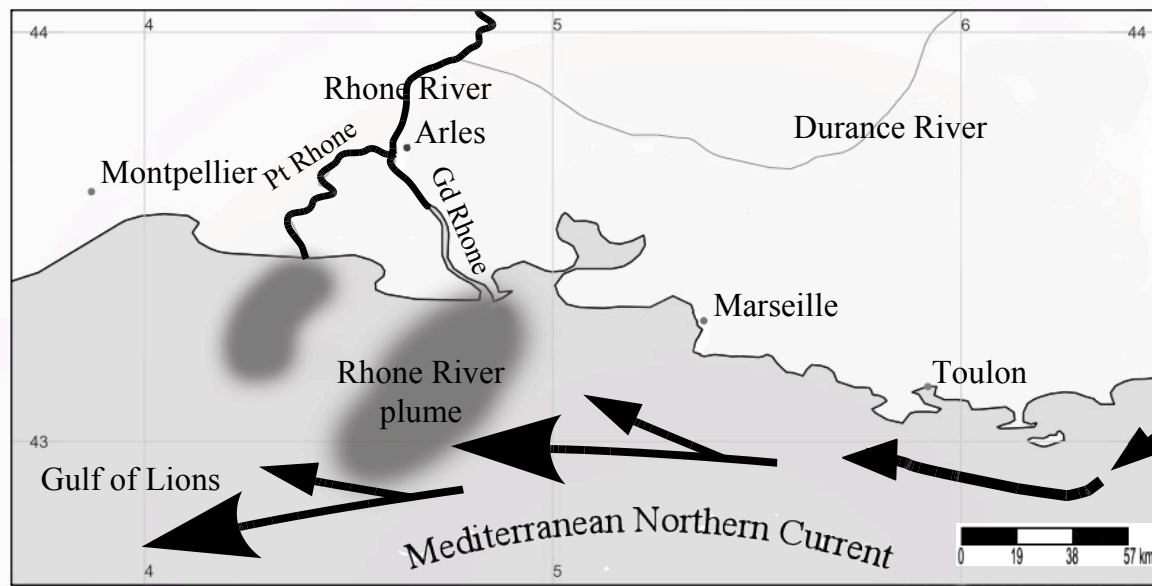
128 **2. Experimental**

129 **2.1. Sampling area description**

130 The Rhone River is 816 km long with a drainage basin area of $100 \times 10^3 \text{ km}^2$ and average
131 annual discharge of $53 \times 10^9 \text{ m}^3$ of water and 2-10 Mt of sediments (Ibanez et al., 1997; Sempéré et
132 al., 2000; Pont et al., 2002; Durrieu de Madron et al., 2003; Rabouille et al., 2008, Eyrolle et al., 2012,
133 Sadaoui et al., 2016). The river stage fluctuates by 2 to 6 m annually, and it has a peak discharge in
134 early spring and late autumn and a minimum in the summer (Pont et al., 2002). The Rhone Delta is
135 divided into two outlets, the Petit Rhone and the Grand Rhone, corresponding to 20% and 80% of the
136 water flow, respectively (Ibanez et al., 1997). The water samples analyzed in this study were collected
137 between June 2006 and June 2009 at the town of Arles (Fig. 1), which is located on the Grand Rhone
138 (47.5 km upstream of the Mediterranean Sea). The collection site was chosen from routinely studied
139 sites over the last two decades by French scientific community (Sempéré et al., 2000; Pont et al., 2002;
140 Sicre et al., 2008; Ollivier et al., 2010; Panagiotopoulos et al., 2012). Water samples were collected at
141 the SORA observatory station near the Compagnie Nationale du Rhone (CNR;
142 <http://www.cnr.tm.fr/fr/>) gauging station in Arles at 7 m from the right bank and 0.5 m under the

143 surface. During the sampling period, the Rhone water discharge varied from 450 to 3821 m³ s⁻¹ (mean
144 = 1787 ± 835 m³ s⁻¹).

145



146

147 **Figure 1.** Rhone River mouth area and sampling location (Arles). Gd Rhone and Pt Rhone indicate “Grand
 148 Rhone” and “Petit Rhone”, respectively, which are the two functional arms of the river.

149

150

151 **2.2. Sample collection**

152 Rhone River water (1-2 L) samples were collected between February 2006 and June 2009
 153 (Table 1) using pre-cleaned glass bottles (rinsed with a 2% HCl solution and baked for 6h at 450°C).

154 The bottles were rinsed three times with the sample, closed with Teflon-lined screw caps, and kept in
 155 the dark at 4°C until filtration. The samples were brought to the laboratory on dry ice (< 24 h) and

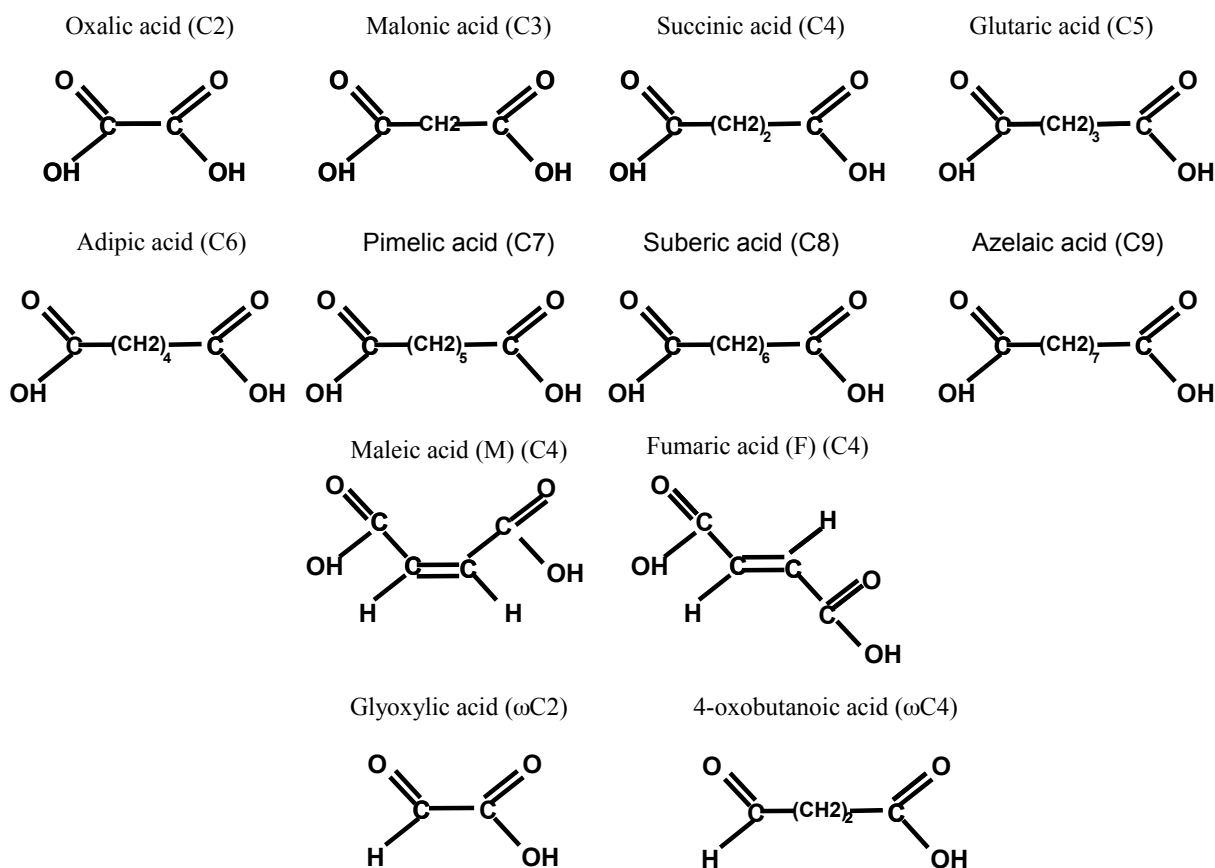
156 filtered through 0.7-µm filters (GF/F-47 mm precombusted for 6h at 500°C; P<50 mm Hg) to remove

157 the water particulate phase. Prior to filtration, the 0.7- μm GF/F filters were flushed with (100 ml)
158 Milli-Q water and a small volume of the sample to minimize contamination (Yoro et al., 1999).
159 Triplicate sub-samples were collected for DOC analyses and transferred into 10-ml glass ampoules
160 (Wheaton®), which were previously precombusted for 6h at 450°C and rinsed 3 times with sample.
161 Then, 20 μL of H_3PO_4 acid was added as a preservative (final pH~ 2), and the ampoules were flame-
162 sealed. The ampoules were stored in darkness at 4°C until further analyses. The remaining sample was
163 used for dissolved BCA analyses and stored in precombusted (6 h, 450°C) Pyrex bottles with a
164 bactericide HgCl_2 (10 mg l^{-1}), in dark at -4°C.

165

166 **2.3. Diacids and ketoacids determination**

167 α , ω -dicarboxylic acids (or diacids) and ω -oxoacids (or ketoacids) (Fig. 2) were determined by
168 the method of Tedetti et al. (2006). Briefly, 100 ml of the sample was first concentrated to 3-4 ml
169 using a rotary evaporator under vacuum. The sample was then transferred into a 25-ml pear-shaped
170 flask, further concentrated by the rotary evaporator, and finally concentrated to almost dryness under a
171 nitrogen stream. A total of 0.25 ml of 14% BF_3 /1-butanol was immediately added to the sample, and
172 the flask was sealed with a glass stopper, Teflon tape, and clamp. The organic acids and reagent were
173 mixed under ultrasonication for 1 min and then heated at 100°C for 30 min to derive dibutyl esters for
174 the carboxyl group and dibutoxy acetal for the aldehyde group. The derivatives were extracted with 5
175 mL of *n*-hexane after adding 3 ml of Milli-Q water and 0.2 ml of acetonitrile. The hexane layer was
176 further washed with Milli-Q water (3x3 ml). The derivatives were dried using a rotary evaporator, and
177 a nitrogen stream, and were finally dissolved in 100 μl of *n*-hexane.



178
 179 **Figure 2.** Chemical structure of dicarboxylic acids and ketoacids detected in the Rhone River water. C_n means
 180 dicarboxylic acid, and M and F are abbreviations for the unsaturated diacids maleic and fumaric acids,
 181 respectively. C_nω indicates ω-oxocarboxylic acid with n carbons and Gly means glyoxylic acid.
 182

183 A volume of 1 μl of the n-hexane solution containing the derivatives was injected onto an
 184 Agilent 6850 gas chromatograph equipped with a 7683B split/splitless auto-injector that was used in
 185 the pulsed splitless mode. The GC was interfaced with an Agilent 5975C mass spectrometer that was
 186 configured in the electron impact (EI) mode. Chromatographic separation of dibutyl esters was
 187 accomplished with a fused-silica capillary Agilent J&W GC HP-5MS column (Agilent Technologies,
 188 30 m, phase: (5%-phenyl-methylpolysiloxane). Compounds were identified by comparison of the
 189 retention times and mass spectra with those of standards and quantified using a spike experiment of
 190 diacids in a natural Rhone sample by GC-MS selected ion monitoring mode (SIM) (Tedetti et al.,
 191 2006). Samples were analyzed in duplicate, and all identified compounds showed good
 192 reproducibility, with relative standard deviation (RSD) less than 10%. Blanks had Milli-Q water as the
 193 sample; the blanks for oxalic acid were < 5% of real samples. The blank values were subtracted for all
 194 samples. Concentrations of BCAs in water samples were determined using spike experiments.

195 For each spike experiment, a standard solution containing a known amount of the targeted
196 compounds was added to one Rhône sample. From these five experiments we established a linear
197 regression between spikes concentration of BCAs and the measured peak areas. The method responds
198 linearly to the increasing concentrations of BCAs in Rhône water for all the compounds. The slopes of
199 these linear regressions, that are significantly different from zero ($r^2 = 0.95$ and their slopes and y-
200 intercepts are significantly ($p < 0.01$) different from zero (t-test), were used to determine the
201 concentrations of the targeted compounds in unknown water samples. Different ranges of spiked
202 concentrations were used depending on the initial concentration of the compound in seawater.

203

204 **2. 4. DOC determination**

205 The DOC was measured using a Shimadzu (Model TOC-V total) carbon analyzer with a quartz
206 combustion column filled with 1.2% Pt on silica pillows (Sempéré et al., 2008). Prior to analysis,
207 samples were sparged for 10 min by CO₂-free pure air to remove inorganic carbon. A four-point
208 calibration curve was conducted daily using standards prepared by diluting a stock solution of
209 potassium hydrogen phthalate in Milli-Q water. Then, 100 µl of sample was injected 3–4 times for
210 each sample and standard; the analytical precision of the procedure was an average of 2%. Low carbon
211 water (LCW) and deep sea water reference (DSR) were kindly provided by the Bermuda Biological
212 station and were measured daily to monitor the accuracy and stability of the TOC analysis. The
213 precision of the TOC analysis was determined by the standard deviation of triple or quadruple analysis
214 of the same sample. The accuracy of the instrument and the system blank were determined by
215 analyzing reference materials (D. Hansell, Rosenstiel School of Marine and Atmospheric Science,
216 Miami, USA), including the Deep Atlantic Water (DAW) and low carbon water (LCW) reference
217 materials. The average DOC concentrations in the DAW and LCW reference standards were 45 ± 2
218 $\mu\text{M C}$, $n=24$ and $1 \pm 0.3\mu\text{M C}$, $n = 24$, respectively. The nominal analytical precision of the procedure
219 was within 1%.

220

221

222

223 3. Results and discussion

224 3.1. Water discharge and DOC concentrations in the Rhone River

225 General information regarding the Rhone River annual discharge as well as the bulk parameter
226 features (water discharge, total suspended matter, organic carbon content of particles, and POM
227 concentrations) during the sampling period (Feb. 2006-June 2009) are described in detail in
228 Panagiotopoulos et al. (2012). Briefly, during the sampling period, water discharges ranged from 450
229 to 3820 m³ s⁻¹, with peak values occurring during the “flood” events of April 2008 (3244 m³ s⁻¹), May
230 2008 (3821 m³ s⁻¹), September 2008 (2983 m³ s⁻¹), and October 2008 (3817 m³ s⁻¹) (Table 1). It is
231 worth noting that the events that occurred in May and September 2008 were not related to physical
232 phenomena resulting in floods (i.e., artificial water release from dam); therefore, they were not
233 considered in the annual fluxes estimates (Panagiotopoulos et al., 2012). The DOC concentrations
234 were generally > 1000 µg l⁻¹, averaging 1640±372 µg l⁻¹; however, their maximum values did not
235 always coincide with the high water discharge values, as one would expect (Table 1). Such DOC
236 values are slightly lower, but in good agreement with previous studies carried out in the Rhone River
237 (Sempéré et al., 2000).

238 **Table 1:** The Rhone River water discharge (Q); dissolved organic carbon (DOC); bi-functional
 239 carboxylic acids, including the sum of the dicarboxylic acid and ketoacid (BCA) concentrations and
 240 fluxes; the fraction of carbon in BCAs (BCA-C) concentrations and the BCA-C/DOC ratios measured in
 241 the Rhone River during the period from February 2006 to June 2009.

Date	Q (m ³ s ⁻¹)	DOC (μg l ⁻¹)	BCAs (μg l ⁻¹)	BCA's Fluxes (t d ⁻¹)	BCA-C (μg l ⁻¹)	BCA-C/DOC (%)
02/12/2006	450	1596	35.19	1.37	11.8	0.74
04/20/2006	2200	2172	34.68	6.59	11.1	0.51
05/05/2007	750	1752	40.95	2.65	13.1	0.75
06/26/2007	1910	1404	26.86	4.43	8.8	0.63
12/11/2007	2660	2016	71.21	16.36	22.3	1.11
01/17/2008	2823	2388	64.87	15.82	20.1	0.84
02/05/2008	1835	1620	42.57	6.75	13.3	0.82
03/11/2008	1233	1440	32.49	3.46	10.5	0.73
03/25/2008	1852	1488	13.26	2.12	4.1	0.28
04/08/2008	1458	2028	37.85	4.77	28.9	1.42
04/22/2008 *	3244	2028	54.02	15.14	16.8	0.83
05/30/2008 *	3821	1440	25.19	8.32	8.2	0.57
07/01/2008	1366	960	20.93	2.47	6.9	0.72
09/08/2008 *	2983	2592	41.69	10.74	13.8	0.53
10/22/2008	932	1536	23.33	1.88	7.2	0.47
11/18/2008	1341	1692	25.65	2.97	8.1	0.48
12/03/2008	1444	1644	20.12	2.51	6.1	0.37
03/10/2009	1950	1464	38.36	6.46	11.9	0.81
03/24/2009	1400	1440	25.31	3.06	8.1	0.56
04/07/2009	1600	1392	14.49	2.00	4.6	0.33
04/22/2009	1600	1284	17.37	2.40	5.4	0.42
05/05/2009	1000	1320	16.26	1.40	5.2	0.39
06/08/2009	1250	1560	22.87	2.47	7.0	0.45
Mean	1787	1663	32.41	5.48	11.0	0.64
SD	835	381	15.34	4.72	6.2	0.27

242

243 *Flood event

244

245 3.2. BCA concentrations, BCA/DOC ratios, and fluxes

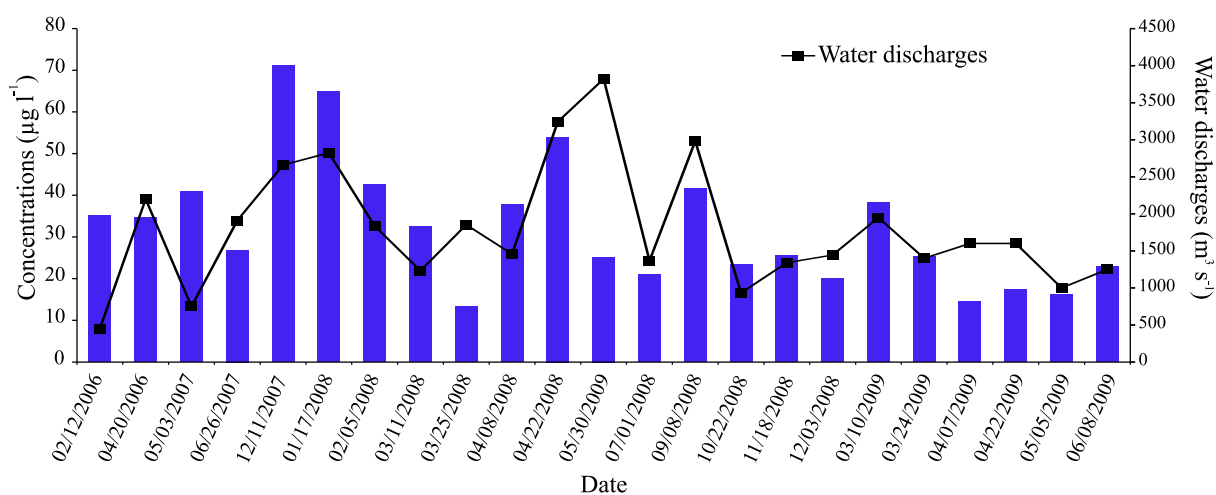
246 The BCA concentrations (as sum of compounds) exhibited a wide range of values from 13.2 μg
 247 l⁻¹ (March 2008) to 71.2 μg l⁻¹ (December 2007) (Fig. 3). The arithmetic mean concentration is 32.4 μg
 248 l⁻¹ (sum of concentrations $C_i/n=23$) while the weighted mean concentration ($\sum Q_i C_i/\sum Q_i$) would be
 249 35.5 μg l⁻¹. The contribution of carbon from BCAs to the DOC pool (BCA-C) accounted for 0.28 to
 250 1.42 % of DOC (Table 1, Fig. 4). Individual BCA concentrations are presented in Table 2. The α, ω-
 251 dicarboxylic acids (C₂-C₉), and two ω-oxocarboxylic (C₂ and C₄) acids concentrations averaged (20.7

252 $\pm 10.6 \mu\text{g l}^{-1}$) and ($11.7 \pm 6.2 \mu\text{g l}^{-1}$), respectively and they were detected for the first time in the Rhone
253 River (Table 2). Although no seasonal trend was evident during the study period, the results showed,
254 as for the DOC, that the highest BCA concentrations did not always follow high water discharges
255 (flood events). The highest values were found in winter 2007 and, to a lower extent by the end of
256 winter 2008 (Fig. 3). This is the first study to report a complete series of homologous dicarboxylic and
257 ketoacids in River waters. The Rhone River BCA levels are close to those reported for Mediterranean
258 coastal seawaters (15.9 to $58.3 \mu\text{g l}^{-1}$; 1-2.5% DOC; Tedetti et al. 2006) and wet deposition (22.6 - 1040
259 $\mu\text{g l}^{-1}$; 1-5% of DOC; Sempéré and Kawamura, 1994; Sempéré and Kawamura, 1996). It is worth
260 noting that our BCA-C/DOC values are comparable to those recorded for the water- soluble fraction of
261 marine aerosol particles (2-15% WSOC; Sempéré and Kawamura, 2003). A comparison with other
262 identified organic compounds within the DOC pool for the Rhone River indicated that our BCA
263 concentrations are two to three orders of magnitude higher than the reported values of dissolved water
264 phase PAHs ($0.003 - 0.12 \mu\text{g l}^{-1}$), one of the most abundant classes of organic contaminant in the
265 marine environment (Bouloubassi and Saliot, 1993, Sicre et al. 2008), and/or the sum of dissolved
266 water phase phthalates ($0.61 \mu\text{g l}^{-1}$; Paluselli et al., 2017, this issue). Our BCA values are on the same
267 order of magnitude as natural compounds, such as polysaccharides (180 - $558 \mu\text{g l}^{-1}$; Panagiotopoulos et
268 al., 2012) measured in the Rhone River or glycolic acid in the western Mediterranean Sea (24 to $89 \mu\text{g}$
269 l^{-1} ; Leboulanger et al., 1994). These BCA levels are close to the concentration of the sum of some
270 mono- (acetic, formic) and dicarboxylic/ketoacids acids (pyruvic, oxalic, malonic and succinic acids:
271 equal to $34 \mu\text{g l}^{-1}$) recorded in Bog Lake drain in Germany (Brinkmann et al., 2003), and they fall
272 within the lower range of values reported for pyruvic (75 - $6680 \mu\text{g l}^{-1}$) and oxalic (50 - $1510 \mu\text{g l}^{-1}$)
273 acids in sediment pore waters (Xiao et al., 2010). These compounds accounted for 6.4% and 0.7-18%
274 of the DOC, respectively in Bog Lake drain, Germany (Xiao et al., 2010), and in sediment pore waters
275 in Bosten Lac, China (Xiao et al., 2010), and they agree with the present study.

276

277 **Table 2.** Concentration ranges and average concentrations of individual dicarboxylic acids and ketoacids
 278 collected in the Rhone River (n = 23) during the period from February 2006 to June 2009.

	Concentrations ($\mu\text{g l}^{-1}$)		Relative abundance (%)	
	Range	Average	Range	Average
Oxalic acid (C ₂)	3.35-23.01	9.08±5.54	15.9-42.6	27.1±7.0
Malonic (C ₃)	1.05-5.98	2.56±1.50	4.0-16.2	8.0-3.2
Maleic acid (C ₃)	0.16-8.04	0.86±1.70	0.82-11.29	2.12±2.65
Succinic Acid (C ₄)	0.88-4.18	2.00±0.88	4.3-11.9	6.4±1.6
Fumaric acid (C ₄)	1.41-9.68	4.73±2.16	10.3-21.4	14.7±2.7
Glyoxylic acid (ω C ₂)	3.77-26.43	11.37-6.20	14.1-50.7	35.8±10.3
Glutaric acid (C ₅)	0.11-0.70	0.35±0.15	0.65-2.11	1.13±0.38
Adipic acid (C ₆)	0.15-3.00	0.62±0.57	0.89-7.33	1.98±1.44
4-oxobutanoic acid (ω C ₄)	0.10-2.98	0.31±0.58	0.29-7.16	0.95±1.37
Pimelic acid (C ₇)	0.00-0.23	0.07±0.08	0-0.81	0.19±0.25
Suberic acid (C ₈)	0.05-0.44	0.16±0.10	0.22-1.08	0.49±0.24
Azealic acid (C ₉)	0.08-0.79	0.32±0.18	0.46-3.77	1.06±0.71



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280

281 **Figure 3.** The total BCA concentrations ($\mu\text{g l}^{-1}$) and water discharge ($\text{m}^3 \text{s}^{-1}$) in the Rhone River during the
 282 period from February 2006 to June 2009.

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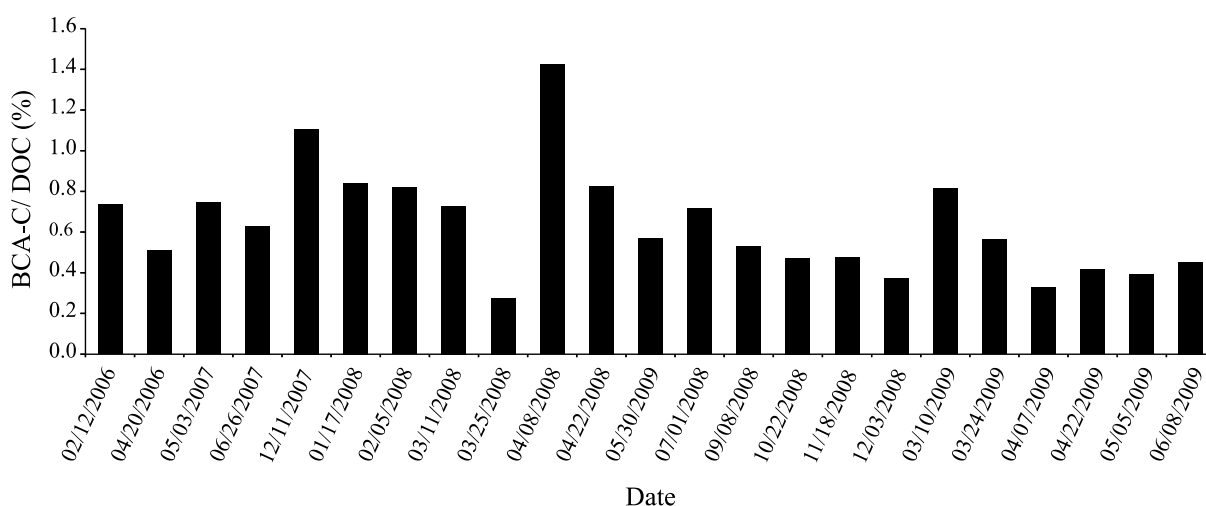
284

During the sampling period (Feb. 2006-June 2009), the Rhone River discharge varied from 450

285

to $3821 \text{ m}^3 \text{ s}^{-1}$, which corresponds to daily flux levels of the DOC and BCA on the order of 62.1-668

286 and 1.37-16.36 t d⁻¹, respectively (Table 1). Assuming a mean water discharge during our study of
 287 1787 m³ s⁻¹, a broad estimate suggests that Rhone River provides 750-4000 t yr⁻¹ BCAs to the
 288 Mediterranean Sea [load = BCA concentrations (min or max in µg.l⁻¹) * mean flow rate (Q in m³ yr⁻¹)].
 289 The estimates of BCA concentration ranges are based on 23 daily samples, representative of the Rhone
 290 River flow. These fluxes estimates mainly depends of the annual river flow which, on a 10 years study
 291 (Sempéré et al., 2000), vary from 1300 to 2000 m³ s⁻¹ (our calculation is based on a mean river flow of
 292 1787 m³ s⁻¹ during our study period). The mean annual flux, calculated as the BCAs weighted mean
 293 concentration (35.5 µg l⁻¹) multiplied by the mean flow rate (1787 m³ s⁻¹) over the studied period is
 294 estimated to 2003 t yr⁻¹. Compared to other identified compounds within the Rhone in the same period
 295 of sampling, the above BCAs fluxes are approximately one order of magnitude lower than those of
 296 dissolved carbohydrates (10-31 kt yr⁻¹) (Panagiotopoulos et al. 2012).



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299 **Figure 4.** Contribution of the BCA-C (BCA-C are the contribution of carbon from BCAs) to the DOC content
 300 (%) in the Rhone River during the period from February 2006 to June 2009.

301

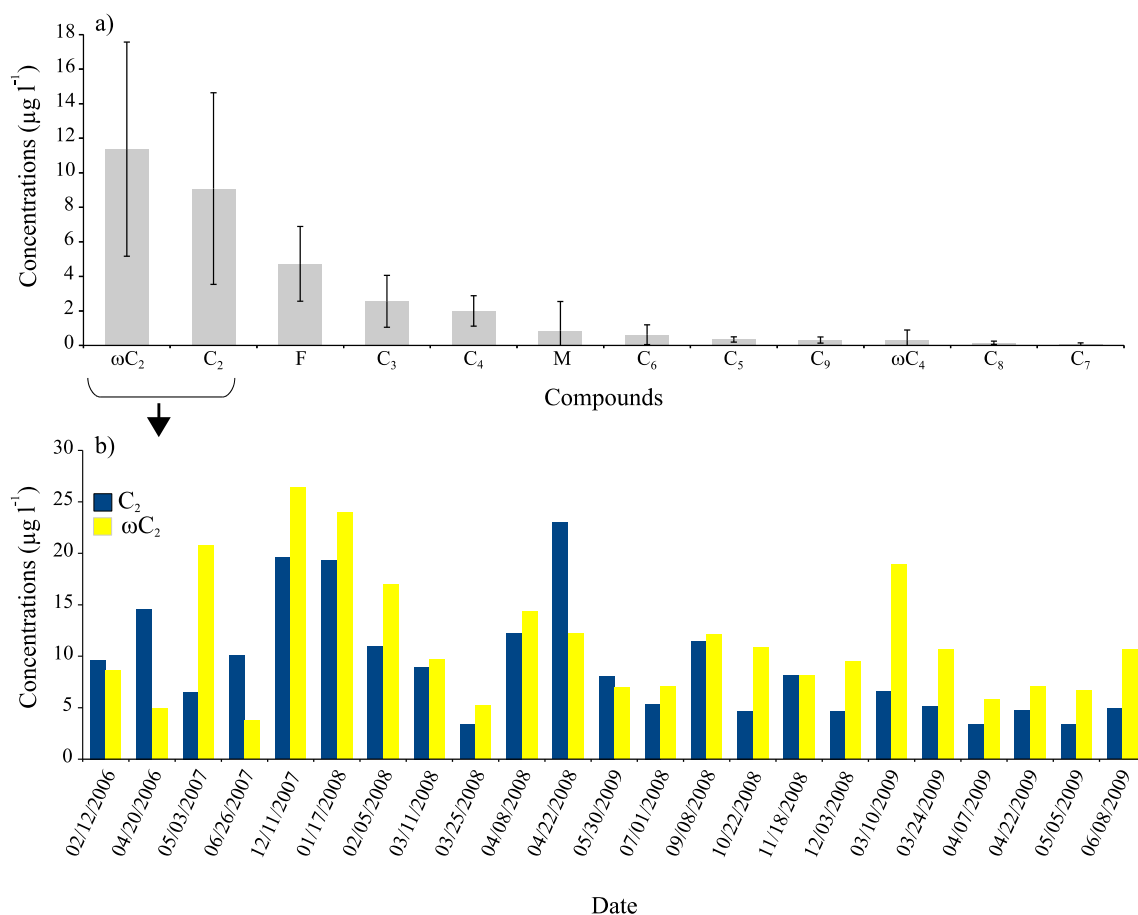
302 3.3. Molecular composition and relative abundance of BCAs

303

Among diacids, short-chain diacids were found to be the most abundant compound class in the
 304 Rhone River. Oxalic acid (C₂) was most abundant (27.1 ± 7.0%) diacid, followed by fumaric
 305 (unsaturated C₄), malonic (C₃) and succinic (C₄) acids. On the other hand, two oxoacids glyoxylic acid
 306 (ωC₂) and 4-oxobutanoic acid (ωC₄), were detected, and ωC₂ was always predominant (Table 2, Fig. 5
 307 a, b). Other oxoacids (ωC₃-ωC₉) were not detected or found at trace levels, and they were not

308 quantified or presented in this study. Short-chain diacids (C_2 - C_4) are more abundant than longer-chain
309 diacids, which is a common trend with aerosol and rainwater molecular distributions (Kawamura and
310 Bikkina, 2016 and references therein). Surprisingly, ωC_2 is usually the most abundant BCA (18 out of
311 23 followed by oxalic and fumaric acids) (Table 2; Fig. 5 a, b, and 6). Interestingly, such a molecular
312 distribution differs from that usually reported in the atmosphere for which a predominance of oxalic
313 acid is usually more abundant than ωC_2 which is followed either by malonic (C_3) or succinic (C_4) acid
314 according to aging of the aerosols (Sempéré et al., 2003; Kawamura and Bikkina, 2016). Long-chain
315 diacids are generally less abundant, while there are similar proportions of glutaric (C_5), adipic (C_6) and
316 azelaic (C_9) acids. It is of interest that such a predominance of glyoxylic acid over oxalic acid was also
317 reported for a seawater study based on a limited number of coastal seawater samples (Tedetti et al.,
318 2006) (Fig. 7).

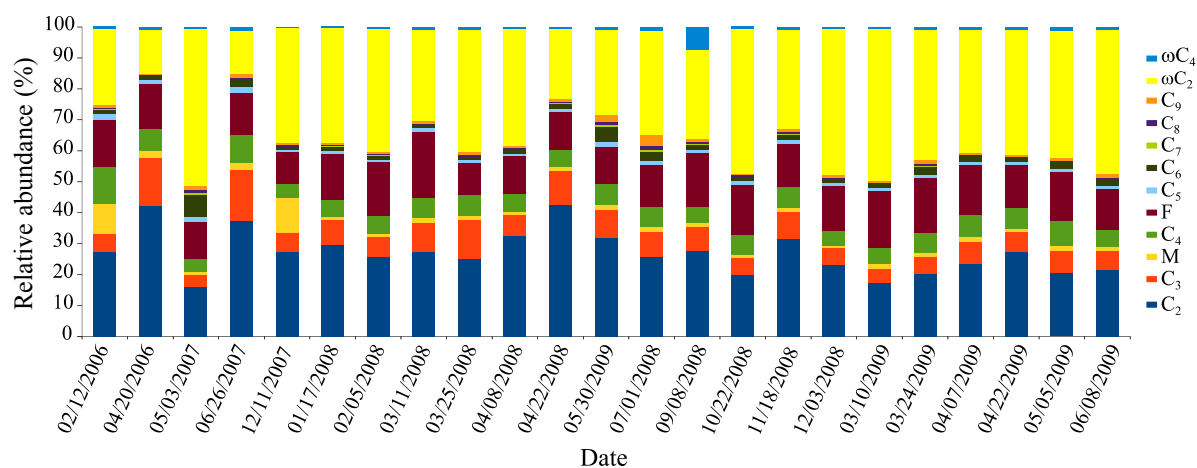
319 This lower relative abundance of oxalic acid might also be due to a lower efficiency of
320 photochemical oxidation reactions producing oxalic acid in surface waters than in the aqueous phase
321 of the atmosphere. Indeed hydroxyl radical ($\bullet OH$) a strong oxidant in natural waters, involved in
322 oxalic acid formation, react preferentially with scavengers such as bromide in sea water (i.e. 93% of
323 $\bullet OH$ react with Br^- in sea water (Mopper and Zhou, 1990)) while $\bullet OH$ scavenger in atmospheric
324 waters are dissolved organic compounds, which are poorly characterized (Araki et al., 2013).
325 Moreover Warneck (2003) and Ervens et al. (2003, 2004) evidenced the photochemical production of
326 oxalic acid in marine atmosphere from acetylene, ethylene and aromatic compounds with glyoxal as an
327 intermediate compound of oxidation reactions. Oxalic acid is the main dicarboxylic acid since it
328 represents the end product of the oxidation of several organic chemical compounds (Ervens et al.,
329 2004).



330
 331 **Figure 5.** The Mean BCA's concentration ($\mu\text{g l}^{-1}$) distributions (a) and Oxalic (C_2) and Glyoxylic acids (ωC_2)
 332 concentrations ($\mu\text{g l}^{-1}$) (b) in the Rhone River during the period from February 2006 to June 2009.
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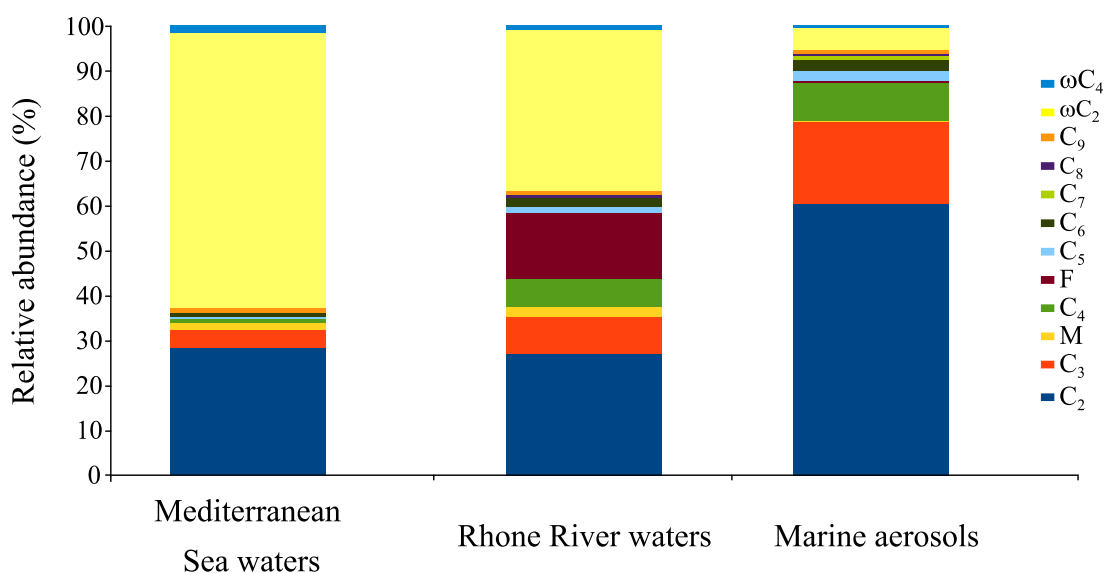
334 Two aliphatic unsaturated diacids were also detected in Rhone River samples, maleic (*cis*
 335 configuration and) and fumaric acid (*trans* configuration). The *cis/trans* ratios are, for most samples,
 336 lower than 1 (0.16 ± 0.2). The highest values were found in December 2006 (0.6) and December 2007
 337 (1.1), indicating a large predominance of fumaric over maleic acid. Notably, the *trans* configuration is
 338 usually more abundant than the *cis* configuration in the marine atmosphere, whereas the opposite trend
 339 was reported for continental samples (Kawamura and Ikushima, 1993; Sempéré and Kawamura,
 340 2003). In the atmosphere, the predominance of the precursor *cis* configuration has been explained by
 341 the photochemical oxidation of benzene or toluene, whose *cis* configuration is preserved in the
 342 structure of the oxidation product. The maleic acid may further be photochemically isomerized to the
 343 *trans* configuration (fumaric acid) in the atmosphere under solar radiation (Kawamura and Ikushima,
 344 1993). These results suggest that the predominance of fumaric acid over maleic acid cannot only be
 345 explained by photochemical isomerization of maleic acid. Because the highest relative abundance of

346 fumaric acid was found in December, photochemical oxidation reactions alone cannot explain the
 347 variations in the M/F ratios. Fumaric acid is also observed in fungi and lichen, and it can also carried
 348 from the land through the Rhone River runoff. Moreover, as an intermediate in the citric acid cycle
 349 that is used by prokaryotes and eukaryotes, fumaric acid is formed by the oxidation of succinate with
 350 succinate dehydrogenase (Krebs and Weitzman, 1987). Although a strict origin of fumarate is difficult
 351 to determine, the biological origin of fumarate cannot be precluded. These data suggest that biological
 352 processes largely contribute to the molecular distribution of BCAs in aquatic systems.



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Figure 6. The Relative BCA distribution (%) in the Rhone River during the period from February 2006 to June 2009.



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Figure 7. Mean relative distribution of BCA's in three contrasted environments: Mediterranean Sea waters (Tedetti et al., 2006), Rhone River waters (this study) and Marine aerosols (data from Fu *et al.*, 2013) that are representative of the global Ocean marine aerosols including Mediterranean.

363

364 **3.4. Origin of BCAs in the Rhone River**

365 To the best of our knowledge these are the first data on the baseline concentrations and
366 distributions of BCAs in surface river water, yet little is known about the origin and degradation of
367 such compounds in freshwater ecosystems. The present data set does not allow for a comprehensive
368 study of the origin of BCA in the study area, but some hypothesis about their potential sources can be
369 drawn as follows:

370 (1) *Atmospheric emissions, formation and deposition.* The incomplete combustion of fossil fuels
371 (Kawamura and Kaplan, 1987) and biomass burning (Andreae et al., 1994; Stephanou and Stratigakis,
372 1993; Novakov and Corrigan 1996) could represent important emissions of BCAs to the atmosphere in
373 an area that is largely urbanized and under a strong anthropogenic pressure such as the Gulf of Lions.
374 This airborne release of BCAs, together with their direct formation (as water-soluble fraction of the
375 aerosols), may generate BCA atmospheric stock subject to dry and wet deposition processes which
376 likely contributed to the BCA stock of riverine DOM (Sempéré and Kawamura, 2003). This is
377 consistent with riverine ¹⁴C-DOC studies demonstrating that some part of riverine DOM may be
378 delivered from anthropogenic aerosols in European rivers (Stubbins et al., 2012). In addition, the high
379 levels of hydrocarbons present in the air-water interphase in the study area (Berrojalbiz et al., 2011;
380 Guigue et al., 2011, 2014; Castro-Jiménez et al., 2012) could support the indirect in situ formation of
381 BCAs and enhance their atmospheric deposition. The oxidation of precursor aromatic hydrocarbons
382 and/or unsaturated molecules (e.g., long chain unsaturated fatty acids) has been reported as a potential
383 source of BCAs in the atmosphere (Kawamura and Bikkina, 2016). Available estimates show that
384 approximately 15 tons of PAHs (dissolved + particle water phase) can be delivered annually by the
385 Rhone River to the NW Mediterranean Sea (Sicre et al., 2008). This PAH riverine input is small when
386 compared with our estimates of BCA fluxes from the Rhone (750-4000 t y⁻¹), suggesting that the
387 indirect BCA formation from PAHs offers a minor contribution to the amounts measured in surface
388 waters. However, we compare fluxes that were estimated with different methodologies and based on
389 measurements performed in different years, resulting in large variability. In addition, there is no
390 information on the potential formation of BCA from PAHs on the photic zone, where

391 photodegradation of potential precursors of BCAs, such as PAHs or aliphatic hydrocarbons, could also
392 occurs.

393 (2) *Riverine DOM from terrestrial origin.* The Rhone River, like other rivers, carries the DOM
394 of autochthonous origin, as well as the DOM of terrestrial origin, including the degrading remains of
395 vascular plant materials in aged-soils (Hedges et al., 1997; Raymond and Saiers, 2010) and the DOC
396 derived from recent vascular plant production (Spencer et al., 2012). Such a material can undergo a
397 variety of biogeochemical processes during transport to a coastal area and exhibits an acidic/aldehyde
398 ratio that increases with the diagenetic state (Opsahl and Benner, 1998) although this trend could also
399 be due to abiotic processes, such as adsorption and dissolution of DOM (Hernes et al., 2007). Soil
400 organic matter includes a variety of exudates released from macro- and microorganisms such as simple
401 monocarboxylic and oxalic acids (Schnitzer, 1978) and other organic acids, which are commonly
402 present at a relatively high concentration around plant roots (Drever and Vance, 1994). These
403 substances can easily be leached by runoff and then transported towards river water. Other organic
404 compounds can be decomposed by prokaryotes during river transport producing LMW organic acids,
405 including BCAs. Note that these molecules are known to be readily metabolized by bacteria and their
406 residence time in the soil is likely to be short (a matter of days or less). The concentrations of the
407 molecules are maintained by continuous production from the biota.

408 (3) *Autochthonous production.* Although no report has evaluated the local biological production
409 in freshwaters, the autochthonous origin of BCAs in the Rhone cannot be precluded. When
410 considering marine organism metabolism linked to BCA production, it is also well known that tri- and
411 dicarboxylic acids are involved in the citric acid cycle during carbohydrate degradation. Then,
412 prokaryotic and eukaryotic activities are probably one of the sources of BCAs. Microbial degradation
413 of long chain lipids (Kester and Foster, 1963) that have been reported for marine waters, is also
414 probably a source of BCAs in freshwaters. These observations strongly support an autochthonous
415 production of BCAs in the Rhone River samples.

416 (4) *Photochemical degradation processes of riverine DOM.* DOM degradation processes could
417 play an important role in the BCA formation in the water column and may support the production of
418 BCAs in surface waters from the Rhone River. Previous studies indicated that photochemical

419 oxidation of marine DOM by solar irradiation may provide LMW compounds, such as formaldehyde,
420 pyruvate, oxalate and other LMW organic acids (Kirk, 1994; Kieber et al., 1997; Bertilsson and
421 Tranvick, 1998; 2000; Pullin et al., 2004), and these processes are probably the source of BCAs in
422 freshwater. Similarly, Tedetti et al. (2007) reported high production of C₂-C₉ diacids (particularly
423 C₉di) and C₂-C₉ oxoacids from (·OH)-induced photochemical oxidation of oleic acid (cis-9-
424 octadecenoic) diluted in Milli-Q water in laboratory-controlled conditions. Photochemical oxidative
425 reactions may also occur on terrestrial DOM, which is rich in carboxyl-rich aliphatic molecules
426 (Hetkorn et al., 2006). For instance lignin is susceptible to produce BCAs, as previously shown in the
427 atmosphere (Kawamura and Bikkina, 2016). Direct photochemical reactions can be enhanced through
428 sensitizer production of hydroxyl (·OH) radicals, which are the most reactive oxidants in aquatic
429 systems (E=1.83 V) (Zafiriou et al., 1984) and are essentially produced by nitrate and nitrite photolysis
430 with initiation by UV-B and UV-A (315-400 nm) (Vaughan and Blough, 1998; Mack and Bolton,
431 1999; Zhou and Mopper, 1990). Both the high solar radiation encountered in this area (Sempéré et al.,
432 2015) and the high level of nitrates/nitrites carried by the Rhone River (Moutin et al., 1998) suggest
433 that photochemical oxidation reactions of DOM may induce BCA production in the Rhone River. It is
434 important to note that *in situ* phytoplanktonic activity and photo-oxidation of biogenic emissions from
435 the ocean producing azelaic acid (C₉di) has already been suggested (Kawamura and Gagosian, 1990).

436 The occurrence of BCAs in the surface waters of the Rhone River is likely driven by a
437 combination of the afore-mentioned sources, and there is a predominant role of DOM in their
438 formation. Further research is needed to ascertain the major BCA sources in the area.

439

440 **4. Summary and conclusion**

441 Most diacids and two oxoacids were detected for the first time in riverine surface waters. The
442 concentrations of BCAs are lower than those carbohydrates, but they are two to three orders of
443 magnitude higher than those of representative waterborne anthropogenic compounds such as PAHs or
444 phthalates. The relative abundance of BCAs in surface waters were found to be different from
445 previous results reported for atmospheric samples, and glyoxylic acid was more abundant than oxalic
446 acid in most samples. Different processes might generate these organic acids. The results indicated

447 that the Rhone River delivers significant levels of diacids and oxoacids to the northwestern
448 Mediterranean Sea. A similar situation could be expected for other rivers that drain the Mediterranean
449 Sea, but experimental confirmation is needed. The concentrations of BCAs are lower than those
450 carbohydrates, but they are two to three orders of magnitude higher than those of representative
451 waterborne anthropogenic compounds such as PAHs or phthalates.

452 The presented findings contribute to a better understanding of the sources and production/degradation
453 mechanisms of these molecules and more generally, of organic matter in aquatic systems, although
454 predominance of glyoxylic acid over oxalic acid merits further investigations. The environmental
455 implications and potential impacts of this stock of BCA in Mediterranean waters remain unknown. In
456 addition, the links between BCA and other important anthropogenic compounds (e.g., PAHs) present
457 in the DOC pool in marine and freshwater ecosystems as well as possible transfer of BCAs from
458 surface waters toward lower atmosphere should be further investigated.

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475

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