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

Richard Sempéré^{a,*}, Bruno Charrière^{a,b}, Javier Castro-Jiménez^a, Kimitaka Kawamura^c, Christos Panagiotopoulos^a

^a Aix-Marseille Univ., Mediterranean Institute of Oceanography (MIO), Marseille, Université de Toulon, CNRS/IRD, France

^b CEFREM, Université de Perpignan, CNRS, 66860 Perpignan Cedex, France

^c Chubu Institute for Advanced Studies, Chubu University, Kasugai, Aichi 487-8501, Japan

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ABSTRACT

The Mediterranean Sea is a semi-enclosed marine environment surrounded by densely populated areas. This ecosystem is under strong anthropogenic pressure at present. Riverine waters are important input pathways of water-soluble organic compounds that potentially contribute to the dissolved organic carbon (DOC) pool. Here, we report the first ever measurements of bi-functional carboxylic acids such as α , ω -dicarboxylic acids (or diacids) and related polar compounds ω -oxoacids (or ketoacids) (BCAs = α , ω -dicarboxylic acids + ω -oxoacids), along with the DOC levels in Rhone River waters. Surface water samples were collected from February 2006 to June 2009 approximately 50 km above the Rhone River mouth, which is the main supplier of freshwater to the Mediterranean Sea. The BCA concentrations averaged $32.4 \pm 15.3 \mu\text{g l}^{-1}$, and exhibited a wide range of values from $13.2 \mu\text{g l}^{-1}$ (Spring 2008) to $71.2 \mu\text{g l}^{-1}$ (winter 2007). The contribution of carbon from BCAs to the DOC pool (BCA-C) accounted for 0.28 to 1.42% of the DOC. Although no seasonal trend was evident in the studied period, our results showed that the highest BCA concentrations did not always follow high water discharges. α , ω -dicarboxylic acids are the most abundant compound class ($20.7 \pm 10.6 \mu\text{g l}^{-1}$), which is followed by ω -oxoacids ($11.7 \pm 6.2 \mu\text{g l}^{-1}$). The Rhone River was estimated to deliver between 1.37 and 16.4 t d^{-1} of BCA to the Gulf of Lions. Assuming a mean water discharge of $\sim 1790 \text{ m}^3 \text{ s}^{-1}$, a broad estimate suggests a loading of 750–4000 t yr^{-1} BCAs to the northwestern Mediterranean Sea. Our results indicated that glyoxylic acid (ωC_2) was the most abundant BCA followed by oxalic acid (C_2di) and fumaric acid (*trans* configuration of unsaturated C_4 diacid). This result indicates that there is a different molecular distribution between the aquatic and atmospheric compartments, including rainwaters and aerosols, for which previous studies highlighted a predominance of oxalic acid, which was followed by malonic and/or succinic acid. Runoff and riverine biological process (rather than photochemical oxidation reactions) are hypothesized to control the BCA occurrence and molecular distribution in the Rhone River and thus their inputs to the coastal NW Mediterranean Sea, although the environmental implications of this stock of BCA are still unknown.

1. Introduction

Low-molecular-weight (LMW: C_2 - C_9) α , ω -dicarboxylic acids (diacids) and related polar compounds such as ω -oxoacids (or ketoacids) hereafter called BCAs (bi-functional carboxylic acids = diacids + ketoacids) are ubiquitous water-soluble organic compounds. These chemicals have been detected in a variety of environmental compartments and regions, including atmospheric aerosols and precipitation (Sempéré and Kawamura, 1996;

Kawamura and Bikkina, 2016), snowpacks and ice cores (Narukawa et al., 2002; Kawamura et al., 2001), marine sediments (Gogou et al., 2000), lakes (Bertilsson and Tranvik, 2000; Brinkmann et al., 2003) and seawaters (Goldstone et al., 2002; Tedetti et al., 2006). BCAs can originate in the atmosphere from several natural processes, such as direct biogenic emission (Kawamura and Gagosian, 1990), ozonolysis, as well as photooxidation of precursor organic compounds (Sempéré and Kawamura, 2003; Kawamura et al., 2005; Rinaldi et al., 2011). These chemicals can also be released to the atmospheric compartment at important levels by several anthropogenic sources, such as incomplete combustion of fossil fuels and biomass burning (Kawamura et al.,

* Corresponding author.

E-mail address: richard.sempere@mio.osupytheas.fr (R. Sempéré).

2013). In streams and seawater, BCAs may be produced by phytoplankton photorespiration (Steinberg and Bada, 1984) photochemical degradation of dissolved organic matter (DOM) (Kirk, 1994; Pullin et al., 2004) and microbial degradation of long-chain lipids (Kester, 1963). BCAs can also reach to seawater by diffusion from surface sediments (especially for oxalic acid) (Peltzer and Bada, 1981), inputs of terrigenous material from rivers (Pullin et al., 2004) and wet and dry depositions processes (Sempéré and Kawamura, 2003).

Aerosol particles enriched with BCAs can play important roles in several biogeochemical and physical processes, contributing to the radiative forcing at the Earth's surface. The BCA hygroscopic properties make these chemicals capable of acting as cloud condensation nuclei (Kerminen et al., 2000). BCAs also participate in many biological processes in aquatic systems, such as by serving as important intermediates in the tricarboxylic acid and glyoxylate cycles as well as in the catabolism and anabolism of amino acids (Steinberg and Bada, 1982). In addition, BCAs could represent a non-negligible fraction of LMW DOM and have a potential role in the organic carbon cycle in the natural environment (Tedetti et al., 2006). However, because of analytical difficulties, studies on the BCA occurrence in seawaters are limited to a few measurements performed in coastal waters from the Pacific Ocean where one dicarboxylic acid, i.e., oxalic acid, and two ketocarboxylic acids (glyoxylic and pyruvic) were detected (Steinberg and Bada, 1982, 1984) and the Sargasso Sea and coastal waters off Florida, where ketocarboxylic acids (glyoxylic and pyruvic) and dicarbonyls (methylglyoxal and glyoxal) were measured (Mopper and Stahovec, 1986; Kieber and Mopper, 1987; Zhou and Mopper, 1997). Even fewer data exist for semi-enclosed marine environments, such as the Mediterranean Sea. Only one study reported the surface water concentrations of a homologous series of BCA from samples collected in 2005 at levels of approximately $50 \mu\text{g l}^{-1}$ in the northwestern (NW) Mediterranean Sea (Tedetti et al., 2006).

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

tutes a major source of reduced carbon to the Mediterranean Sea (Sempéré et al., 2000). The occurrence of BCA in riverine surface waters and relative inputs of BCA to Mediterranean waters are poorly characterized, and to best of our knowledge no data exist for the Rhone River which is the main supplier of organic carbon to the whole Mediterranean Sea.

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

2. Experimental

2.1. Sampling area description

The Rhone River is 816 km long with a drainage basin area of $100 \times 10^3 \text{ km}^2$ and average annual discharge of $53 \times 10^9 \text{ m}^3$ of water and 2–10 Mt of sediments (Ibañez et al., 1997; Sempéré et al., 2000; Pont et al., 2002; Durrieu de Madron et al., 2003; Rabouille et al., 2008; Eyrolle et al., 2012; Sadaoui et al., 2016). The river stage fluctuates by 2–6 m annually, and it has a peak discharge in early spring and late autumn and a minimum in the summer (Pont et al., 2002). The Rhone Delta is divided into two outlets, the Petit Rhone and the Grand Rhone, corresponding to 20% and 80% of the water flow, respectively (Ibañez et al., 1997). The water samples analyzed in this study were collected between June 2006 and June 2009 at the town of Arles (Fig. 1), which is located on the Grand Rhone (47.5 km upstream of the Mediterranean Sea). The collection site was chosen from routinely studied sites over the last two decades by French scientific community (Sempéré et al., 2000; Pont et al., 2002; Sicre et al., 2008; Ollivier et al., 2010; Panagiotopoulos et al., 2012). Water samples were collected at the SORA observatory station near the Compagnie Nationale du Rhone (CNR; <http://www.cnr.tm.fr/fr/>) gauging station in Arles at 7 m from the right bank and 0.5 m under the surface. During the sampling period, the Rhone water discharge varied from 450 to $3821 \text{ m}^3 \text{ s}^{-1}$ (mean = $1787 \pm 835 \text{ m}^3 \text{ s}^{-1}$).

2.2. Sample collection

Rhone River water (1–2 L) samples were collected between February 2006 and June 2009 (Table 1) using pre-cleaned glass bottles (rinsed with a 2% HCl solution and baked for 6 h at $450 \text{ }^\circ\text{C}$). The bottles were rinsed three times with the sample, closed with Teflon-lined screw caps, and kept in the dark at $4 \text{ }^\circ\text{C}$ until filtration. The samples were brought to the laboratory on dry ice ($< 24 \text{ h}$) and filtered through $0.7\text{-}\mu\text{m}$ filters (GF/F-47 mm precombusted for 6 h at $500 \text{ }^\circ\text{C}$; $P < 50 \text{ mm Hg}$) to remove the water particulate phase. Prior to filtration, the $0.7\text{-}\mu\text{m}$ GF/F filters were flushed with (100 ml) Milli-Q water and a small volume of the sample to minimize contamination (Yoro et al., 1999). Triplicate sub-samples were collected for DOC analyses and transferred into 10-ml glass ampoules (Wheaton®), which were previously precombusted for 6 h at $450 \text{ }^\circ\text{C}$ and rinsed 3 times with sample. Then, $20 \mu\text{L}$ of H_3PO_4 acid was added as a preservative (final pH ~ 2), and the ampoules were flame-sealed. The ampoules were stored in darkness at $4 \text{ }^\circ\text{C}$ until further analyses. The remaining sample was used for dissolved BCA analyses and stored in precombusted (6 h , $450 \text{ }^\circ\text{C}$) Pyrex bottles with a bactericide HgCl_2 (10 mg l^{-1}), in dark at $-4 \text{ }^\circ\text{C}$.

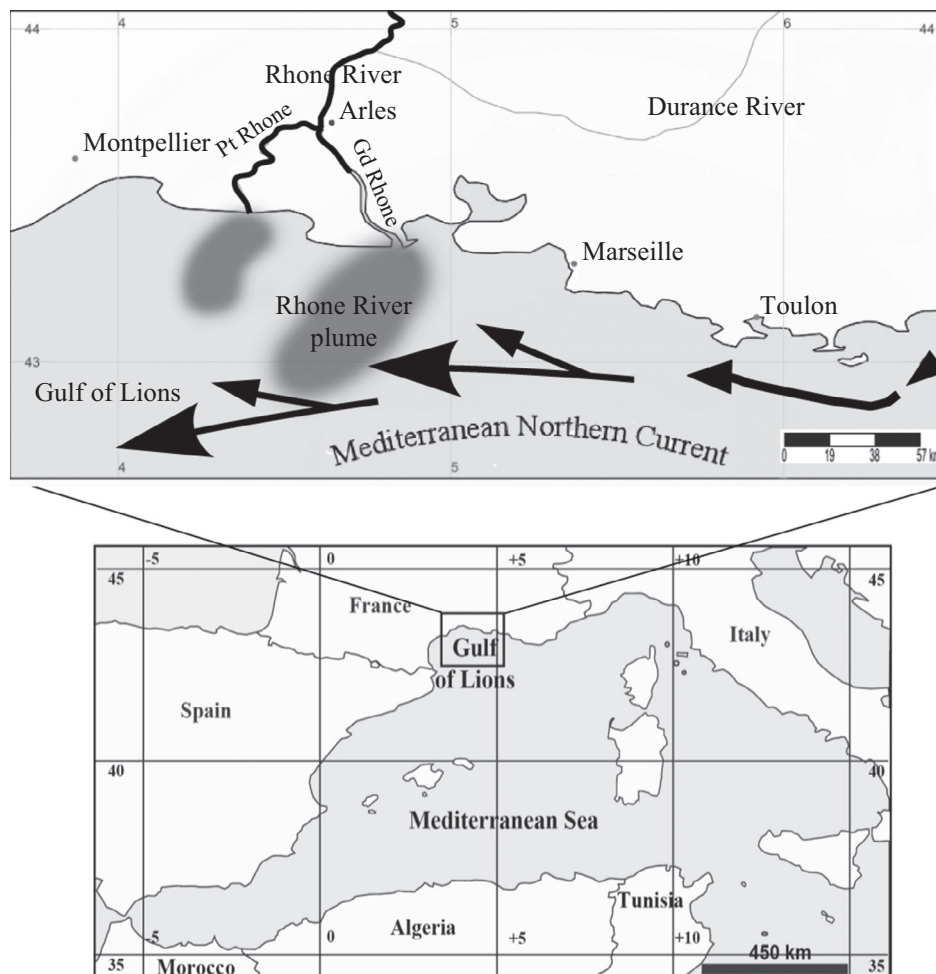


Fig. 1. Rhone River mouth area and sampling location (Arles). Gd Rhone and Pt Rhone indicate “Grand Rhone” and “Petit Rhone”, respectively, which are the two functional arms of the river.

Table 1
The Rhone River water discharge (Q); dissolved organic carbon (DOC); bi-functional carboxylic acids, including the sum of the dicarboxylic acid and ketoacid (BCA) concentrations and fluxes; the fraction of carbon in BCAs (BCA-C) concentrations and the BCA-C/DOC ratios measured in 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

* Flood event.

2.3. Diacids and ketoacids determination

α , ω -dicarboxylic acids (or diacids) and ω -oxoacids (or ketoacids) (Fig. 2) were determined by the method of Tedetti et al. (2006). Briefly, 100 ml of the sample was first concentrated to 3–4 ml using a rotary evaporator under vacuum. The sample was then transferred into a 25-ml pear-shaped flask, further concentrated by the rotary evaporator, and finally concentrated to almost dryness under a nitrogen stream. A total of 0.25 ml of 14% $\text{BF}_3/1$ -butanol was immediately added to the sample, and the flask was sealed with a glass stopper, Teflon tape, and clamp. The organic acids and reagent were mixed under ultrasonication for 1 min and then heated at 100 °C for 30 min to derive dibutyl esters for the carboxyl group and dibutoxy acetal for the aldehyde group. The derivatives were extracted with 5 mL of *n*-hexane after adding 3 ml of Milli-Q water and 0.2 ml of acetonitrile. The hexane layer was further washed with Milli-Q water (3×3 ml). The derivatives were dried using a rotary evaporator, and a nitrogen stream, and were finally dissolved in 100 μl of *n*-hexane.

A volume of 1 μl of the *n*-hexane solution containing the derivatives was injected onto an Agilent 6850 gas chromatograph equipped with a 7683B split/splitless auto-injector that was used in the pulsed splitless mode. The GC was interfaced with an Agilent 5975 C mass spectrometer that was configured in the electron impact (EI) mode. Chromatographic separation of dibutyl esters was accomplished with a fused-silica capillary Agilent J&W GC HP-5MS column (Agilent Technologies, 30 m, phase: (5%-phenylmethylpolysiloxane). Compounds were identified by comparison of the retention times and mass spectra with those of standards and quantified using a spike experiment of diacids in a natural Rhone sample by GC-MS selected ion monitoring mode (SIM) (Tedetti et al., 2006). Samples were analyzed in duplicate, and all

identified compounds showed good reproducibility, with relative standard deviation (RSD) less than 10%. Blanks had Milli-Q water as the sample; the blanks for oxalic acid were <5% of real samples. The blank values were subtracted for all samples. Concentrations of BCAs in water samples were determined using spike experiments.

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

2.4. DOC determination

The DOC was measured using a Shimadzu (Model TOC-V total) carbon analyzer with a quartz combustion column filled with 1.2% Pt on silica pillows (Sempéré et al., 2008). Prior to analysis, samples were sparged for 10 min by CO_2 -free pure air to remove inorganic carbon. A four-point calibration curve was conducted daily using standards prepared by diluting a stock solution of potassium hydrogen phthalate in Milli-Q water. Then, 100 μl of sample was injected 3–4 times for each sample and standard; the analytical precision of the procedure was an average of 2%. The precision of the TOC analysis was determined by the standard deviation of triple or quadruple analysis of the same sample. The accuracy of the

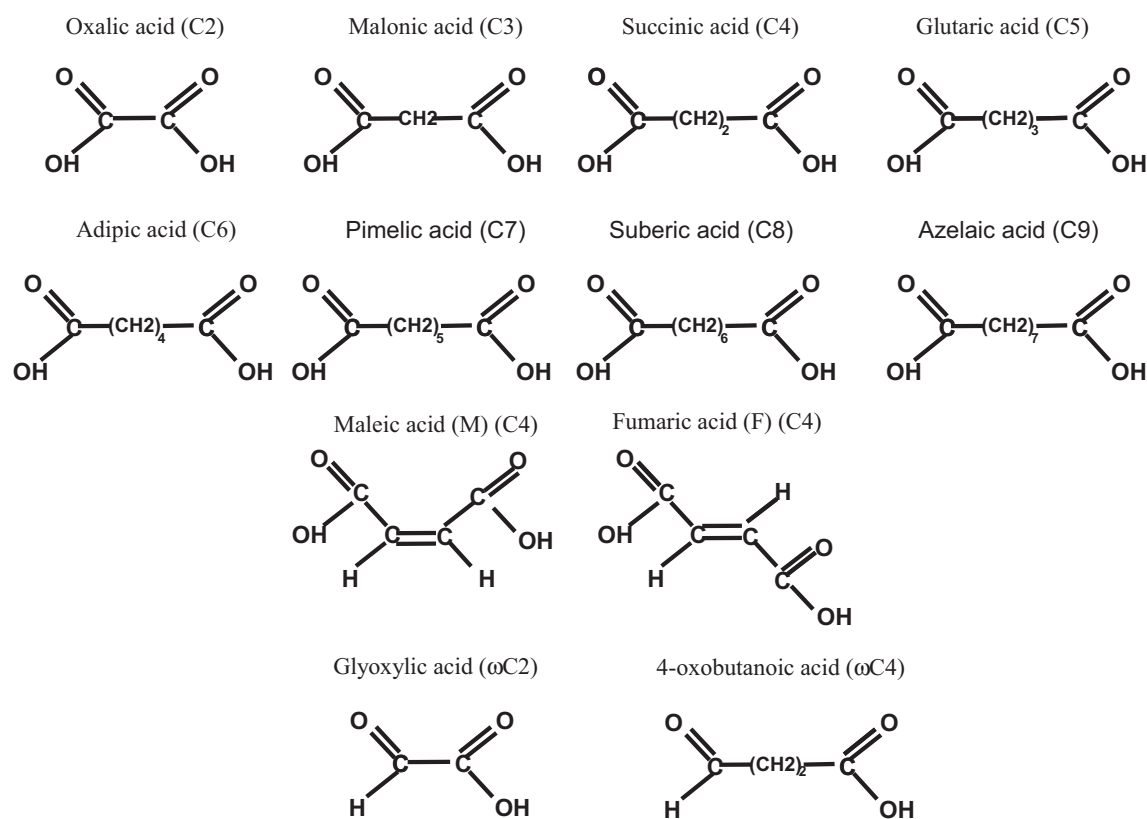


Fig. 2. Chemical structure of dicarboxylic acids and ketoacids detected in the Rhone River water. Cn means dicarboxylic acid with n carbons, and M and F are abbreviations for the unsaturated diacids maleic and fumaric acids, respectively. Cn ω indicates ω -oxocarboxylic acid with n carbons and Gly means glyoxylic acid.

instrument and the system blank were determined by analyzing reference materials (D. Hansell, Rosenstiel School of Marine and Atmospheric Science, Miami, USA), including the Deep Atlantic Water (DAW) and low carbon water (LCW) reference materials. The average DOC concentrations in the DAW and LCW reference standards were $45 \pm 2 \mu\text{M C}$, $n = 24$ and $1 \pm 0.3 \mu\text{M C}$, $n = 24$, respectively. The nominal analytical precision of the procedure was within 1%.

3. Results and discussion

3.1. Water discharge and DOC concentrations in the Rhone River

General information regarding the Rhone River annual discharge as well as the bulk parameter features (water discharge, total suspended matter, organic carbon content of particles, and POM concentrations) during the sampling period (Feb. 2006–June 2009) are described in detail in Panagiotopoulos et al. (2012). Briefly, during the sampling period, water discharges ranged from 450 to $3820 \text{ m}^3 \text{ s}^{-1}$, with peak values occurring during the “flood” events of April 2008 ($3244 \text{ m}^3 \text{ s}^{-1}$), May 2008 ($3821 \text{ m}^3 \text{ s}^{-1}$), September 2008 ($2983 \text{ m}^3 \text{ s}^{-1}$), and October 2008 ($3817 \text{ m}^3 \text{ s}^{-1}$) (Table 1). It is worth noting that the events that occurred in May

and September 2008 were not related to physical phenomena resulting in floods (i.e., artificial water release from dam); therefore, they were not considered in the annual fluxes estimates (Panagiotopoulos et al., 2012). The DOC concentrations were generally $>1000 \mu\text{g l}^{-1}$, averaging $1640 \pm 372 \mu\text{g l}^{-1}$; however, their maximum values did not always coincide with the high water discharge values, as one would expect (Table 1). Such DOC values are slightly lower, but in good agreement with previous studies carried out in the Rhone River (Sempéré et al., 2000).

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

The BCA concentrations (as sum of compounds) exhibited a wide range of values from $13.2 \mu\text{g l}^{-1}$ (March 2008) to $71.2 \mu\text{g l}^{-1}$ (December 2007) (Fig. 3). The arithmetic mean concentration is $32.4 \mu\text{g l}^{-1}$ (sum of concentrations $C_i/n = 23$) while the weighted mean concentration ($\sum Q_i C_i / \sum Q_i$) would be $35.5 \mu\text{g l}^{-1}$. The contribution of carbon from BCAs to the DOC pool (BCA-C) accounted for 0.28–1.42% of DOC (Table 1, Fig. 4). Individual BCA concentrations are presented in Table 2. The α , ω -dicarboxylic acids (C_2 – C_9), and two ω -oxocarboxylic (C_2 and C_4) acids concentrations averaged ($20.7 \pm 10.6 \mu\text{g l}^{-1}$) and ($11.7 \pm 6.2 \mu\text{g l}^{-1}$), respectively and they were detected for the first time in the Rhone River

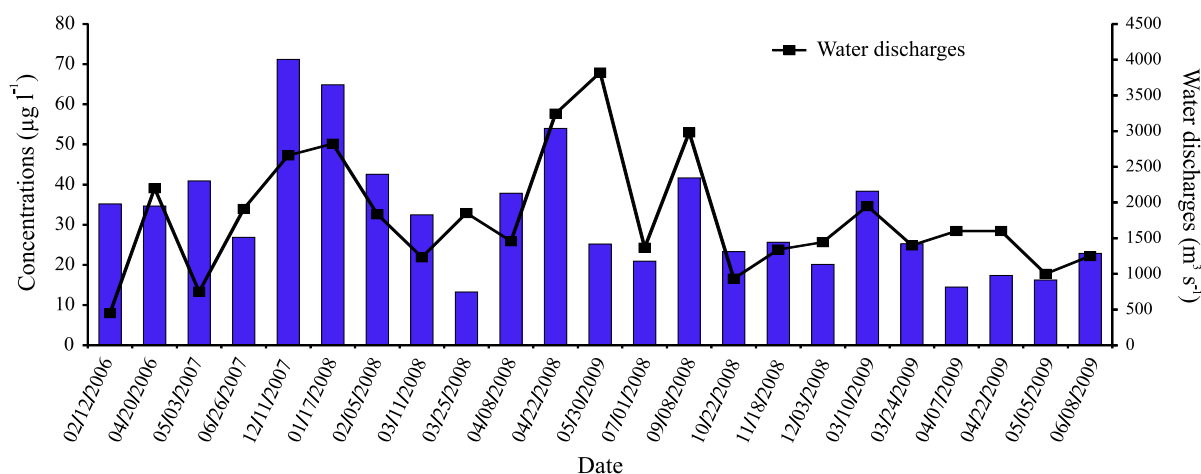


Fig. 3. The total BCA concentrations ($\mu\text{g l}^{-1}$) and water discharge ($\text{m}^3 \text{ s}^{-1}$) in the Rhone River during the period from February 2006 to June 2009.

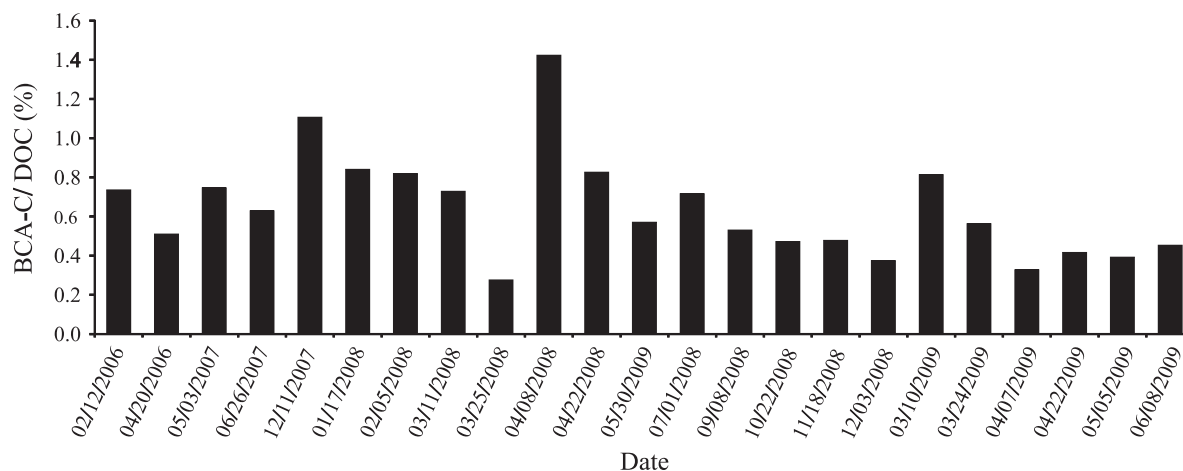


Fig. 4. Contribution of the BCA-C (BCA-C are the contribution of carbon from BCAs) to the DOC content (%) in the Rhone River during the period from February 2006 to June 2009.

Table 2

Concentration ranges and average concentrations of individual dicarboxylic acids and ketoacids 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 \pm 5.54	15.9–42.6	27.1 \pm 7.0
Malonic (C_3)	1.05–5.98	2.56 \pm 1.50	4.0–16.2	8.0–3.2
Maleic acid (C_3)	0.16–8.04	0.86 \pm 1.70	0.82–11.29	2.12 \pm 2.65
Succinic Acid (C_4)	0.88–4.18	2.00 \pm 0.88	4.3–11.9	6.4 \pm 1.6
Fumaric acid (C_4)	1.41–9.68	4.73 \pm 2.16	10.3–21.4	14.7 \pm 2.7
Glyoxylic acid (ωC_2)	3.77–26.43	11.37–6.20	14.1–50.7	35.8 \pm 10.3
Glutaric acid (C_5)	0.11–0.70	0.35 \pm 0.15	0.65–2.11	1.13 \pm 0.38
Adipic acid (C_6)	0.15–3.00	0.62 \pm 0.57	0.89–7.33	1.98 \pm 1.44
4-oxobutanoic acid (ωC_4)	0.10–2.98	0.31 \pm 0.58	0.29–7.16	0.95 \pm 1.37
Pimelic acid (C_7)	0.00–0.23	0.07 \pm 0.08	0–0.81	0.19 \pm 0.25
Suberic acid (C_8)	0.05–0.44	0.16 \pm 0.10	0.22–1.08	0.49 \pm 0.24
Azealic acid (C_9)	0.08–0.79	0.32 \pm 0.18	0.46–3.77	1.06 \pm 0.71

(Table 2). Although no seasonal trend was evident during the study period, the results showed, as for the DOC, that the highest BCA concentrations did not always follow high water discharges (flood events). The highest values were found in winter 2007 and, to a lower extent by the end of winter 2008 (Fig. 3). This is the first study to report a complete series of homologous dicarboxylic and ketoacids in River waters. The Rhone River BCA levels are close to those reported for Mediterranean 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 $\mu\text{g l}^{-1}$; 1–5% of DOC; Sempéré and Kawamura, 1994; Sempéré and Kawamura, 1996). It is worth noting that our BCA-C/DOC values are comparable to those recorded for the water-soluble fraction of marine aerosol particles (2–15% WSOC; Sempéré and Kawamura, 2003). A comparison with other identified organic compounds within the DOC pool for the Rhone River indicated that our BCA concentrations are two to three orders of magnitude higher than the reported values of dissolved water phase PAHs (0.003–0.12 $\mu\text{g l}^{-1}$), one of the most abundant classes of organic contaminant in the marine environment (Bouloubassi and Saliot, 1993; Sicre et al. 2008), and/or the sum of dissolved water phase phthalates (0.61 $\mu\text{g l}^{-1}$; Paluselli et al., 2018). Our BCA values are on the same order of magnitude as natural compounds, such as polysaccharides (180–558 $\mu\text{g l}^{-1}$; Panagiotopoulos et al., 2012) measured in the Rhone River or glycolic acid in the western Mediterranean Sea (24–89 $\mu\text{g l}^{-1}$; Leboulanger et al., 1997). These BCA levels are close to the concentration of the sum of some mono- (acetic, formic) and dicarboxylic/ketoacids acids (pyruvic, oxalic, malonic and succinic acids: equal to 34 $\mu\text{g l}^{-1}$) recorded in Bog Lake drain in Germany (Brinkmann et al., 2003), and they fall within the lower range of values reported for pyruvic (75–6680 $\mu\text{g l}^{-1}$) and oxalic (50–1510 $\mu\text{g l}^{-1}$) acids in sediment pore waters (Xiao et al., 2010). These compounds accounted for 6.4% and 0.7–18% of the DOC, respectively in Bog Lake drain, Germany (Xiao et al., 2010), and in sediment pore waters in Bosten Lac, China (Xiao et al., 2010), and they agree with the present study.

During the sampling period (Feb. 2006–June 2009), the Rhone River discharge varied from 450 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 and 1.37–16.36 t d^{-1} , respectively (Table 1). Assuming a mean water discharge during our study of 1787 $\text{m}^3 \text{s}^{-1}$, a broad estimate suggests that Rhone River provides 750–4000 t yr^{-1} BCAs to the Mediterranean Sea [load = BCA concentrations (min or max in $\mu\text{g l}^{-1}$) * mean flow rate (Q in $\text{m}^3 \text{yr}^{-1}$)]. The estimates of BCA concentration ranges are based on 23 daily samples, representative of the Rhone River flow. These fluxes estimates mainly depends of the annual river flow which, on a 10 years study (Sempéré et al., 2000), vary from 1300 to 2000 $\text{m}^3 \text{s}^{-1}$ (our calculation is based on a mean river flow of 1787 $\text{m}^3 \text{s}^{-1}$ during our study period).

The mean annual flux, calculated as the BCAs weighted mean concentration (35.5 $\mu\text{g l}^{-1}$) multiplied by the mean flow rate (1787 $\text{m}^3 \text{s}^{-1}$) over the studied period is estimated to 2003 t yr^{-1} . Compared to other identified compounds within the Rhone in the same period of sampling, the above BCAs fluxes are approximately one order of magnitude lower than those of dissolved carbohydrates (10–31 kt yr^{-1}) (Panagiotopoulos et al., 2012).

3.3. Molecular composition and relative abundance of BCAs

Among diacids, short-chain diacids were found to be the most abundant compound class in the Rhone River. Oxalic acid (C_2) was most abundant (27.1 \pm 7.0%) diacid, followed by fumaric (unsaturated C_4), malonic (C_3) and succinic (C_4) acids. On the other hand, two oxoacids glyoxylic acid (ωC_2) and 4-oxobutanoic acid (ωC_4), were detected, and ωC_2 was always predominant (Table 2, Fig. 5 a, b; Fig. 6). Other oxoacids (ωC_3 – ωC_9) were not detected or found at trace levels, and they were not quantified or presented in this study. Short-chain diacids (C_2 – C_4) are more abundant than longer-chain diacids, which is a common trend with aerosol and rainwater molecular distributions (Kawamura and Bikkina, 2016 and references therein). Surprisingly, ωC_2 is usually the most abundant BCA (18 out of 23 followed by oxalic and fumaric acids) (Table 2; Fig. 5 a, b, and 6). Interestingly, such a molecular distribution differs from that usually reported in the atmosphere (Fig. 7) for which a predominance of oxalic acid is usually more abundant than ωC_2 which is followed either by malonic (C_3) or succinic (C_4) acid according to aging of the aerosols (Sempéré and Kawamura, 2003; Fu et al., 2013; Kawamura and Bikkina, 2016). Long-chain diacids are generally less abundant, while there are similar proportions of glutaric (C_5), adipic (C_6) and azelaic (C_9) acids. It is of interest that such a predominance of glyoxylic acid over oxalic acid was also reported for a seawater study based on a limited number of coastal seawater samples (Tedetti et al., 2006).

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

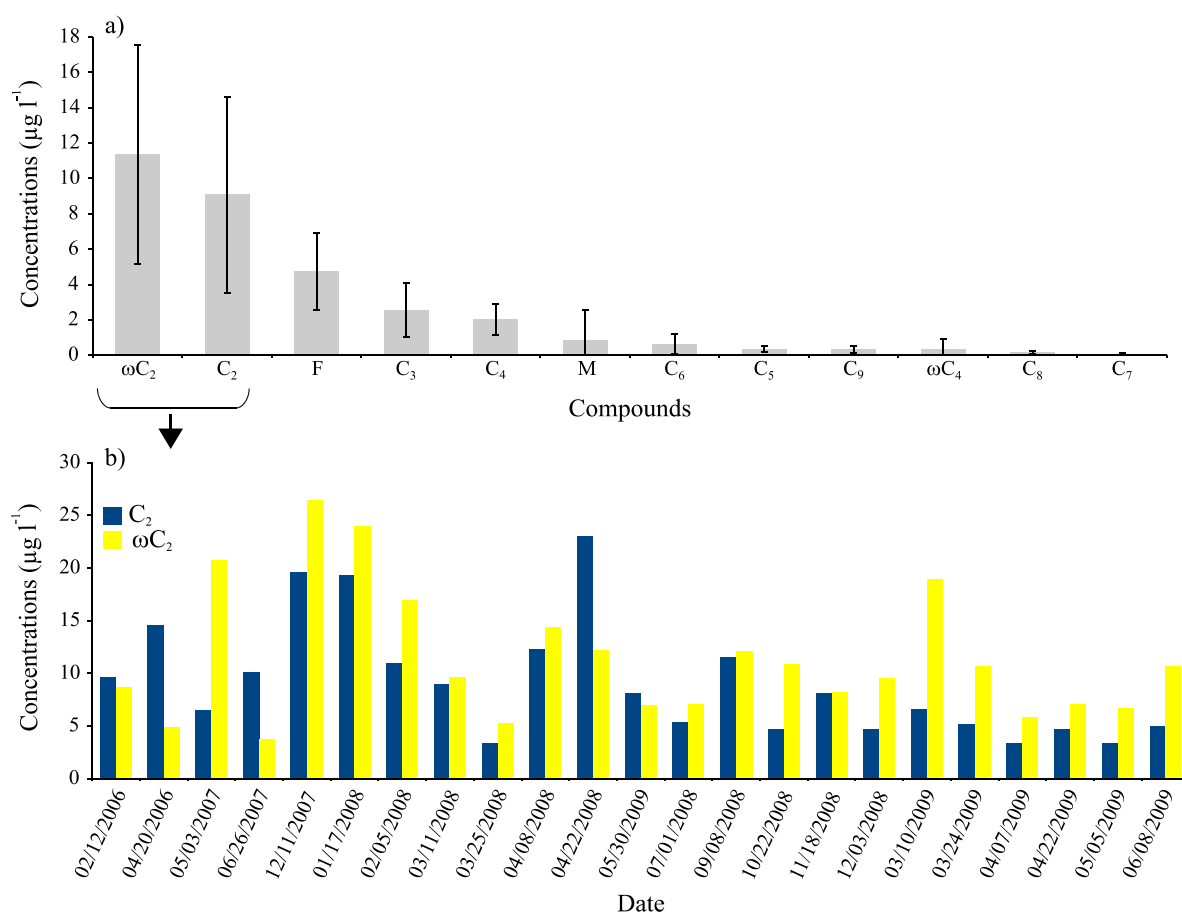


Fig. 5. The Mean BCA's concentration ($\mu\text{g l}^{-1}$) distributions (a) and Oxalic (C_2) and Glyoxylic acids (ωC_2) concentrations ($\mu\text{g l}^{-1}$) (b) in the Rhone River during the period from February 2006 to June 2009.

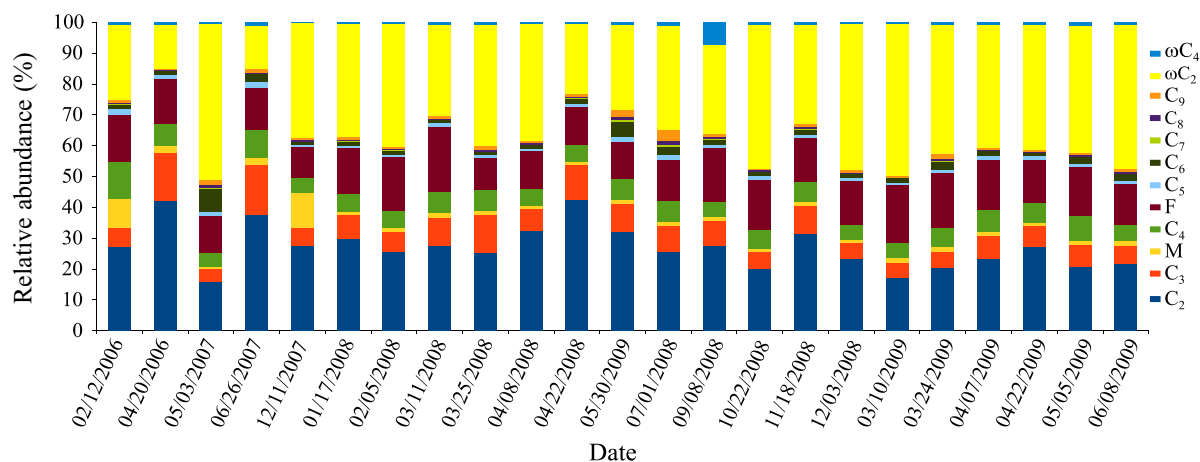


Fig. 6. The Relative BCA distribution (%) in the Rhone River during the period from February 2006 to June 2009.

product of the oxidation of several organic chemical compounds (Ervens et al., 2004).

Two aliphatic unsaturated diacids were also detected in Rhone River samples, maleic (*cis* configuration) and fumaric acid (*trans* configuration). The *cis/trans* ratios are, for most samples, lower than 1 (0.16 ± 0.2). The highest values were found in December 2006 (0.6) and December 2007 (1.1), indicating a large predominance of fumaric over maleic acid. Notably, the *trans* configuration is usually more abundant than the *cis* configuration

in the marine atmosphere, whereas the opposite trend was reported for continental samples (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 2003). In the atmosphere, the predominance of the precursor *cis* configuration has been explained by the photochemical oxidation of benzene or toluene, whose *cis* configuration is preserved in the structure of the oxidation product. The maleic acid may further be photochemically isomerized to the *trans* configuration (fumaric acid) in the atmosphere under solar radiation (Kawamura and Ikushima, 1993). These results sug-

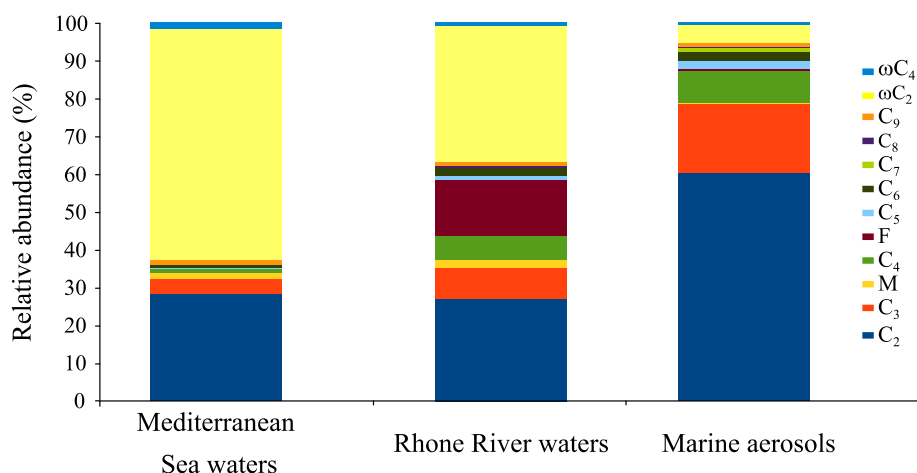


Fig. 7. Mean relative distribution of BCA's in three contrasted environments: Mediterranean Sea waters (Tedetti et al., 2006), Rhone River waters (this study) and Marine aerosols (data from Fu et al., 2013) that are representative of the global Ocean marine aerosols including Mediterranean.

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

3.4. Origin of BCAs in the Rhone River

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

- (1) *Atmospheric emissions, formation and deposition.* The incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987) and biomass burning (Andreae et al., 1994; Stephanou and Stratigakis, 1993; Novakov and Corrigan, 1996) could represent important emissions of BCAs to the atmosphere in an area that is largely urbanized and under a strong anthropogenic pressure such as the Gulf of Lions. This airborne release of BCAs, together with their direct formation (as water-soluble fraction of the aerosols), may generate BCA atmospheric stock subject to dry and wet deposition processes which likely contributed to the BCA stock of riverine DOM (Sempéré and Kawamura, 2003). This is consistent with riverine ¹⁴C-DOC studies demonstrating that some part of riverine DOM may be delivered from anthropogenic aerosols in European rivers (Stubbins et al., 2012). In addition, the high levels of hydrocarbons present in the air-water interphase in the study area (Berrojalbiz et al., 2011; Guigue et al., 2011, 2014; Castro-Jiménez et al., 2012) could support the indirect *in situ* formation of

BCAs and enhance their atmospheric deposition. The oxidation of precursor aromatic hydrocarbons and/or unsaturated molecules (e.g., long chain unsaturated fatty acids) has been reported as a potential source of BCAs in the atmosphere (Kawamura and Bikina, 2016). Available estimates show that approximately 15 tons of PAHs (dissolved + particle water phase) can be delivered annually by the Rhone River to the NW Mediterranean Sea (Sicre et al., 2008). This PAH riverine input is small when compared with our estimates of BCA fluxes from the Rhone (750–4000 t y⁻¹), suggesting that the indirect BCA formation from PAHs offers a minor contribution to the amounts measured in surface waters. However, we compare fluxes that were estimated with different methodologies and based on measurements performed in different years, resulting in large variability. In addition, there is no information on the potential formation of BCA from PAHs on the photic zone, where photodegradation of potential precursors of BCAs, such as PAHs or aliphatic hydrocarbons, could also occur.

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

- (3) *Autochthonous production.* Although no report has evaluated the local biological production in freshwaters, the autochthonous origin of BCAs in the Rhone cannot be precluded. When considering marine organism metabolism linked to BCA production, it is also well known that tri- and dicarboxylic acids are involved in the citric acid cycle during carbohydrate degradation. Then, prokaryotic and eukaryotic activities are probably one of the sources of BCAs. Microbial degradation of long chain lipids (Kester and Foster, 1963) that have been reported for marine waters, is also probably a source of BCAs in freshwaters. These observations strongly support an autochthonous production of BCAs in the Rhone River samples.
- (4) *Photochemical degradation processes of riverine DOM.* DOM degradation processes could play an important role in the BCA formation in the water column and may support the production of BCAs in surface waters from the Rhone River. Previous studies indicated that photochemical oxidation of marine DOM by solar irradiation may provide LMW compounds, such as formaldehyde, pyruvate, oxalate and other LMW organic acids (Kirk, 1994; Kieber et al., 1997; Bertilsson et al., 1998; Bertilsson and Tranvik, 2000; Pullin et al., 2004), and these processes are probably the source of BCAs in freshwater. Similarly, Tedetti et al. (2007) reported high production of C₂-C₉ diacids (particularly C₉di) and C₂-C₉ oxoacids from (·OH)-induced photochemical oxidation of oleic acid (*cis*-9-octadecenoic) diluted in Milli-Q water in laboratory-controlled conditions. Photochemical oxidative reactions may also occur on terrestrial DOM, which is rich in carboxyl-rich aliphatic molecules (Hertkorn et al., 2006). For instance lignin is susceptible to produce BCAs, as previously shown in the atmosphere (Kawamura and Bikkina, 2016). Direct photochemical reactions can be enhanced through sensitizer production of hydroxyl (·OH) radicals, which are the most reactive oxidants in aquatic systems (E = 1.83 V) (Zafriou et al., 1984) and are essentially produced by nitrate and nitrite photolysis with initiation by UV-B and UV-A (315–400 nm) (Vaughan and Blough, 1998; Mack and Bolton, 1999; Zhou and Mopper, 1990). Both the high solar radiation encountered in this area (Sempéré et al., 2015) and the high level of nitrates/nitrites carried by the Rhone River (Moutin et al., 1998) suggest that photochemical oxidation reactions of DOM may induce BCA production in the Rhone River. It is important to note that *in situ* phytoplanktonic activity and photo-oxidation of biogenic emissions from the ocean producing azelaic acid (C₉di) has already been suggested (Kawamura and Gagosian, 1990).

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

4. Summary and conclusion

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

indicated that the Rhone River delivers significant levels of diacids and oxoacids to the northwestern Mediterranean Sea. A similar situation could be expected for other rivers that drain the Mediterranean Sea, but experimental confirmation is needed. The presented findings contribute to a better understanding of the sources and production/degradation mechanisms of these molecules and more generally, of organic matter in aquatic systems, although predominance of glyoxylic acid over oxalic acid merits further investigations. The environmental implications and potential impacts of this stock of BCA in Mediterranean waters remain unknown. In addition, the links between BCA and other important anthropogenic compounds (e.g., PAHs) present in the DOC pool in marine and freshwater ecosystems as well as possible transfer of BCAs from surface waters toward lower atmosphere should be further investigated.

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