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Global Biogeochemical Cycles

RESEARCH ARTICLE

10.1029/2018GB006165

Key Points:

- Here we present the first results of a study of the distribution of BCAs (including dicarboxylic and oxoacids) in a surface Arctic Ocean
- Arctic Rivers provide large amount of BCA to the Arctic Ocean, a process that might be increased with global warming
- BCAs have been recognized as major water soluble organic compounds that potentially may act for a part as cloud condensation nuclei (CCN)

Supporting Information:

- Supporting Information S1

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Dicarboxylic and Oxocarboxylic Acids in the Arctic Coastal Ocean (Beaufort Sea-Mackenzie Margin)

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Abstract The distribution of bifunctional carboxylic acids (BCAs) is largely reported as primary or secondary organic aerosols. However, sparse studies describe the distribution of these organic compounds in fluvial and marine environments. In the context of a global warming, we present the first results of a study of the distribution of BCAs in a surface Arctic coastal area near the mouth of the Mackenzie River. These results showed that the Beaufort Sea is an area with elevated BCA content among which glyoxylic acid is predominant, in contrast to low concentrations and predominance of oxalic acid in aerosols reported elsewhere. The carbon fraction of BCAs represents 1.8% to 4.5% of dissolved organic carbon pool in Arctic Ocean. This study reinforces the hypothesis that aquatic biological processes govern the molecular distribution of BCA in marine/river waters, whereas photochemical oxidation reactions regulate their molecular distribution in rain and aerosols. Our results indicate that the Mackenzie River is an important source of BCAs in the Arctic Ocean during July–October period, with a first estimate of 35×10^3 tons of BCAs including 12×10^3 tons of diacids and 23×10^3 tons of oxoacids.

1. Introduction

Low-molecular-weight (C2–C10) bifunctional carboxylic acids (BCAs) including α , ω -dicarboxylic acids (diacids) and ω -oxoacids together with α -dicarbonyls have been detected in snowpacks and ice cores (Kawamura, Yokoyama, et al., 2001; Narukawa et al., 2002), continental and marine aerosols (Bikkina, Kawamura, Imanishi, et al., 2015; Bikkina, Kawamura, & Miyazaki, 2015; Kawamura & Ikushima, 1993; Kawamura et al., 1996; Kawamura & Sakaguchi, 1999; Kawamura, Steinberg, et al., 2001; Kundu et al., 2010; Legrand et al., 2007; Narukawa et al., 2002, 2003), and marine and riverine dissolved organic matter (DOM; Sempéré et al., 2018; Tedetti et al., 2006). BCAs in DOM are very likely associated with phytoplankton photorespiration (Steinberg & Bada, 1984) and photochemical/microbial degradation of DOM (Pullin et al., 2004). In the atmosphere, BCAs have been recognized as major water soluble organic compounds that potentially may act for a part as cloud condensation nuclei (CCN; Kerminen et al., 1999; Marsh et al., 2016; Sempéré & Kawamura, 1994), although inorganic ions such as ammonium and sulfate may have more influence on the CCN activity (Medina et al., 2007). In addition, such compounds are used as a proxy of photochemical oxidation reactions (Kawamura & Gagosian, 1990; Sempéré & Kawamura, 2003). Previous studies showed that BCAs may be produced by incomplete combustion of fossil fuels (Kawamura & Kaplan, 1987), biomass burning (Kawamura & Bikkina, 2016; Kundu et al., 2010; Narukawa et al., 1999), and photooxidation of precursor organic compounds (Bikkina et al., 2014; Claeys et al., 2010; Kawamura & Gagosian, 1990; Kawamura & Yasui, 2005; Kawamura et al., 1996; Miyazaki et al., 2014; Rinaldi et al., 2011).

In atmospheric aerosols, glyoxylic acid is the most abundant oxocarboxylic acid (Eugene et al., 2016 and references therein). Glyoxylic acid can be produced by hydroxyl radical oxidation reaction on glyoxal and glycolic acid as well as complex oxidation reaction of oxygenated aromatic compounds (Pillar et al., 2014, 2015). Note that Huang et al. (2018) highlighted the formation of diacids such as oxalic or malonic acids by hydroxyl radical (HO \cdot) reaction on phenolic woody compounds like acetosyringone or syringaldehyde whereas Tomaz et al. (2018) reported the formation of BCA (oxalic, maleic, and succinic acids) by OH

radical oxidation of phenol, catechol, guaiacol, or vanillin emitted during biomass burning. In addition, oxalic acid, which represents 50% of total diacids in organic aerosol as well as glyoxylic and maleic acids can be produced, by OH radical oxidation and direct photolysis of polyphenols (Pillar et al., 2014). In the aqueous phase of aerosols, OH oxidation of succinic, glutaric, or adipic acids originated from biomass burning can produce malonic, glyoxylic, and oxalic acids (Tomaz et al., 2018).

Therefore, examination of molecular distribution of these compounds may provide information on the intensity of biotic and photochemical oxidation reactions of organic matter in rivers and seawater. Because they are semi volatile species, they may potentially be transferred from marine surface waters to the atmosphere contributing to the secondary water soluble organic aerosol reservoir and have a potential impact on the climate due to their CCN properties (Marsh et al., 2016). However, little is known regarding BCA production in DOM, especially in the Arctic system, which is an interesting place to study those processes. Actually, expected increase in freshwater discharge due to global warming (Frey & McClelland, 2009; Peterson, 2002) coupled with changes in the mobility of organic matter trapped in frozen soils will very likely give rise to an increase of DOM flux at high latitudes (Barber & Hanesiak, 2005; Doxaran et al., 2015; Lawrence & Slater, 2005; Zhang et al., 2017). Indeed, the Arctic and Antarctic Oceans trapped 50% of the global terrestrial organic carbon pool in permafrost regions (Hugelius et al., 2014; Tarnocai et al., 2009), which are now experiencing the global warming (Foley, 2005; Kug et al., 2015).

The continental shelf of the Southern Beaufort Sea in the Arctic Ocean receives freshwater from the Mackenzie River (Hilton et al., 2015), which currently contributes the fourth-largest freshwater discharge to the Arctic Ocean (Gordeev, 2006) and is the dominant source of terrestrial DOM to this region (Doxaran et al., 2012). Arctic riverine DOM includes a large amount of DOM originating from soils that include thawing of the permafrost (Carmack et al., 2004; Emmerton et al., 2008; Holmes et al., 2002; Matsuoka et al., 2012) with chromophoric properties originating from watersheds and lakes (Matsuoka et al., 2012; Para et al., 2013). The Mackenzie River discharges water masses of approximately 4,000 m³/s during winter (from December to May) to about approximately 25,000 m³/s during summer (from June to August; O'Brien et al., 2006) and provides a dissolved organic carbon (DOC) flux of approximately 1.04–1.76 TgC/year to the coastal Beaufort Sea (Raymond et al., 2007). Such a DOC flux in this area is expected to increase due to an increased permafrost thawing relative to enhanced air temperatures (Intergovernmental Panel on Climate Change (IPCC), 2014), as well as subsequent increase of mobility and discharge toward the river and the coastal area, in which various organic compounds are not clearly determined (Dittmar & Kattner, 2003; Guo et al., 2007; Walvoord & Striegl, 2007).

This study aims to improve our knowledge of BCA flux and the molecular distribution of BCAs in the DOM pool in the coastal Arctic system considering that they might be potentially transferred (for the most volatile) from surface water to the atmosphere. In addition, such a study may contribute to better understanding of the origin, photochemical and biotic transformation of DOM in the river that is provided to the Arctic coastal waters.

2. Materials and Methods

2.1. Sampling

This study was conducted during the period of open water over the Canadian shelf of the Beaufort Sea on board the R/V ice-breaker Canadian Coast Guard Research ship (CCGS) Amundsen as part of the Mackenzie Light and Carbon (MALINA) cruise held from 30 July to 27 August 2009 (Figure 1 and Table 1). For the study of BCAs, seawater sampling was performed in 20 stations at the surface layer between 0.5 and 4 m in depth and at the deep chlorophyll a maximum. Seven additional surface fresh and brackish waters were collected near the two river mouths in the Eastern Channel and the Reindeer channel (stations 398, 396, 394, and 392 and 696, 695, and 694, respectively).

2.2. BCA quantification

Seawater samples were concentrated using a solid phase extraction method before the analysis of BCAs by gas chromatography–mass spectrometry (Tedetti et al., 2006). The details concerning the used materials and methods are presented in the SI text. To quantify BCAs in the seawater matrix, a method of standard addition was applied. Several standard solutions containing BCAs were spiked into natural seawater in order to

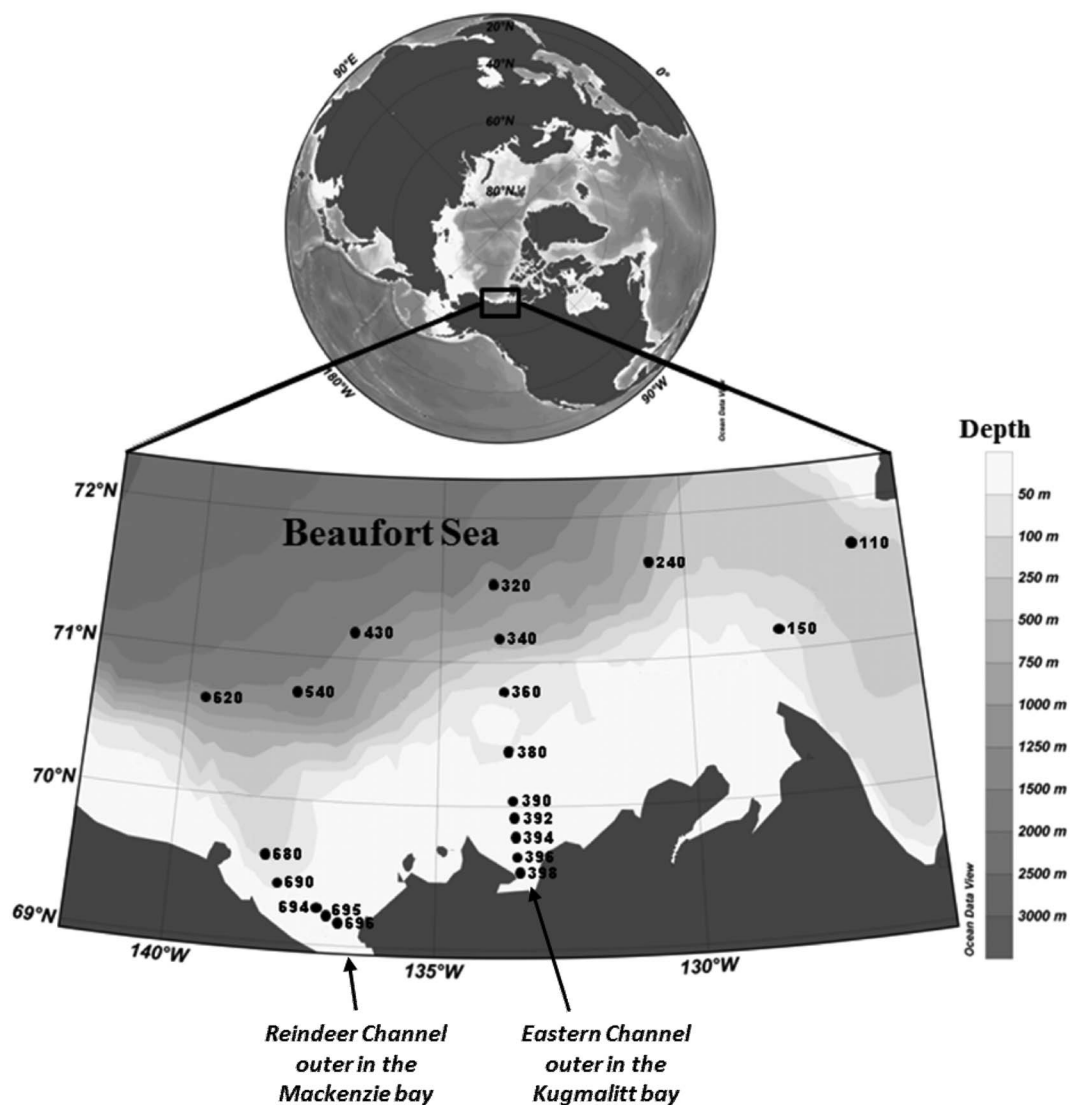


Figure 1. Locations and station numbers investigated during the Mackenzie Light and Carbon cruise over the Canadian shelf of the Beaufort Sea in front of the Mackenzie River.

determine the linear range of the calibration and its confidence parameters. The spiked compounds for dicarboxylic acids are as follows: oxalic (C_2), malonic (C_3), maleic (M, C_4), succinic (C_4), fumaric (F, C_4), glutaric (C_5), 2-methylglutaric, 3-methylglutaric, adipic (C_6), 3-methyladipic, pimelic (C_7), suberic (C_8), azelaic (C_9), and sebacic (C_{10}) acids or oxocarboxylic acids, that is, glyoxylic (ωC_2) and 4-oxobutanoic (ωC_4) acids and glyoxal as an α -dicarbonyl compound. The spiked solutions were added to the seawater samples collected at the stations 320 and 696. Station 320 represents the basin area with a salinity of 26.5 and a DOC content of 701 $\mu\text{gC/L}$. Station 696 is at the river mouth. This sample has the lowest salinity ($S = 0.2$) and the maximum DOC content (4,735 $\mu\text{gC/L}$; Para et al., 2013). The linear regression lines obtained in these two different seawaters were similar, indicating no matrix effect due to salinity and no overload of the solid phase extraction (SPE) cartridge for the sample with the higher DOC content. Considering the correlation coefficient, glyoxal ($r^2 = 0.47$) cannot be quantified. The other compounds can be quantitatively estimated because they have a correct correlation coefficient ($r^2 \geq 0.97$), and their slopes and y intercepts are significantly ($p < 0.01$) different from zero (t test).

Table 1
Sampling Location, Sampling Date, Bottom Depth, Temperature, Salinity, DOC, and Chlorophyll Content of Each Sampling Station

Station	Latitude (°N)	Longitude (°E)	Sampling date	Pressure (dbars)	Bottom depth (m)	Temperature (°C)	Salinity (psu)	DOC (µgC/L)	Chlorophyll (µg/L)
110	71.70	126.50	6 Aug 2009	3	395	4.4	29	858	0.1
110 dcm	71.70	126.50	6 Aug 2009	63	392	-1.3	32	860	0.3
150	71.15	128.16	7 Aug 2009	4	60	3.5	29	904	
150 dcm	71.15	128.16	7 Aug 2009	60	60	-1.2	32	827	
240	71.68	130.75	5 Aug 2009	3	465	3.2	29	743	
240 dcm	71.68	130.75	5 Aug 2009	56	465	-1.2	32	804	
320	71.55	133.96	9 Aug 2009	3	1,141	-0.8	27	701	0.0
320 dcm	71.55	133.96	9 Aug 2009	70	1,141	-1.2	32	713	0.1
340	71.17	133.84	9 Aug 2009	3	553	0.1	27	734	
340 dcm	71.17	133.84	9 Aug 2009	60	553	-1.2	31	760	
360	70.80	133.73	8 Aug 2009	3	75	-0.2	26	700	
360 dcm	70.80	133.73	8 Aug 2009	50	74	-1.1	31	770	
380	70.39	133.61	8 Aug 2009	3	60	4.4	28	892	0.1
380 dcm	70.39	133.61	8 Aug 2009	48	60	-0.9	32	833	2.0
390	70.18	133.57	31 Jul 2009	4	40	5.2	27	1,264	0.8
392	70.01	133.52	3 Aug 2009	0.5	27	3.2	28	1,256	
394	69.85	133.50	3 Aug 2009	4	14	5.4	28	1,977	0.6
396	69.68	133.46	16 Aug 2009	0.5	6	8.2	17	2,894	
398	69.53	133.42	16 Aug 2009	0.5	3	8.8	16	3,084	2.5
430	71.18	136.75	18 Aug 2009	3	1,300	-0.8	26	711	0.1
430 dcm	71.18	136.75	18 Aug 2009	65	1,300	-1.1	32	701	0.6
540	70.75	137.84	17 Aug 2009	4	1,514	-0.4	26	762	0.1
540 dcm	70.75	137.84	17 Aug 2009	70	1,514	-1.1	32	737	0.6
620	70.66	139.66	11 Aug 2009	4	1,538	2.1	22	1,126	0.1
680	69.61	138.24	10 Aug 2009	3	105	5.4	22	1,544	0.2
690	69.48	137.93	1 Aug 2009	4	40	4.7	22	1,507	0.1
694	69.25	137.20	13 Aug 2009	0.50	8	9.3	9	3,799	2.7
695	69.20	137.01	13 Aug 2009	0.50	5	9.3	8	4,104	1.4
696	69.16	136.81	13 Aug 2009	0.50	3	10.1	0	4,735	3.2

Note. dcm means deep chlorophyll maximum.

3. Results and Discussion

3.1. Hydrological System of the Mackenzie Estuary and Beaufort Sea

According to physical and biogeochemical specificity, three areas might be considered (Para et al., 2013) including the delta area close to the river mouth with a salinity lower than 10 (stations 694, 695, and 696), an intermediate area with a salinity range of 16 to 22 (stations 396, 398, 620, 680, and 690) and the marine area with a salinity higher than 25 (all other stations). Environmental parameters as sampling location, temperature, salinity, DOC, and chlorophyll content are presented in Table 1.

As shown by the salinity distribution (Figures 1 and 2), the Reindeer Channel (western channel, station series 696 to 620) was more influenced by the river plume than the eastern outer channel at the Kugmallit Bay (station series 398 to 320). DOC concentrations decreased from the delta toward the Northeast sector, and DOC and salinity relationships indicated a near-conservative behavior when salinity was less than 25 (Para et al., 2013). The DOC distribution among the three surface water salinity sectors observed for the Canadian shelf increased from 852 ± 180 µgC/L in the “marine” sector (salinity > 25) to $1,272 \pm 540$ and $3,720 \pm 1,044$ µgC/L in the “intermediate” ($16 \leq$ salinity ≤ 22) and in the “delta” sector (salinity < 10), respectively (Para et al., 2013).

3.2. General Concentration Levels and Relative Abundance of BCAs in the Mackenzie River and Beaufort Sea

We found an almost conservative behavior with salinity (Figure 2; $r^2 = 0.78$) and concentrations of BCAs, which were 233 ± 14 µg/L in the delta, 167 ± 31 in the intermediate, and 100 ± 16 µg/L in the marine sectors (Table 2), indicating that the Mackenzie River is an important source of BCAs in the Arctic Ocean. By

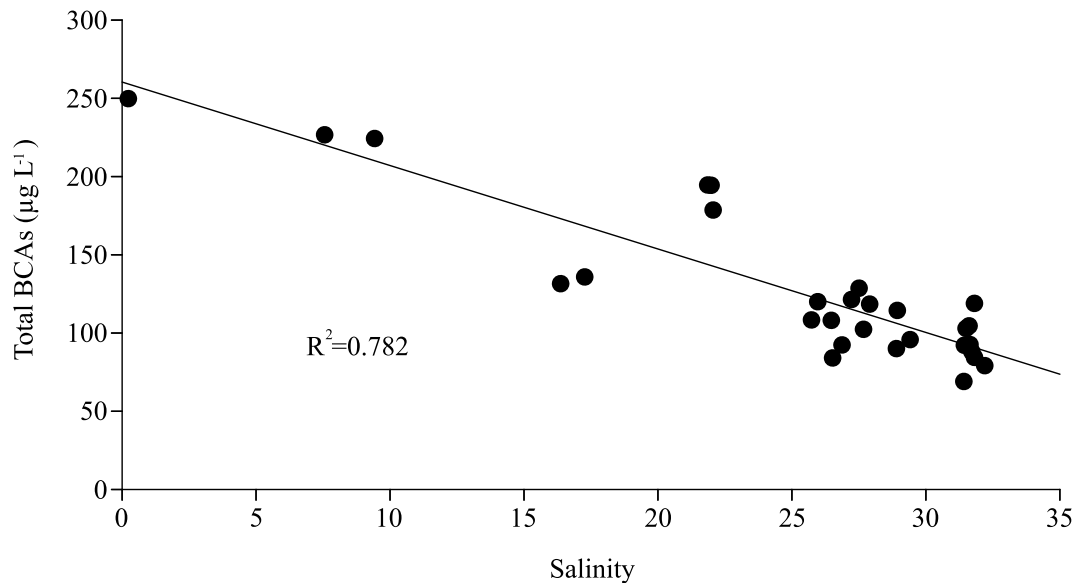


Figure 2. Correlation between the water sample salinity from the McKenzie River to the Beaufort Sea and concentrations of total BCAs. BCA = bifunctional carboxylic acid.

contrast, BCA portions of the DOC budget were maximum ($3.7\% \pm 1.1\%$) in the marine ($S > 25$) and minimum in the delta ($S < 10$) ($1.8\% \pm 0.1\%$) sectors (Table 2). This trend is even more pronounced in the Kugmallit Bay corresponding to stations 398 to 320 (4,735 to 1,126 $\mu\text{gC/L}$) with C-BCA/DOC content increasing from 1.4% at the Mackenzie River mouth (St. 398; $S = 16.4$) to 4.4% at the 230-km offshore (St. 320; $S = 26.5$; Figure 3) indicating that BCAs comprised a larger fraction of DOC in marine waters, although the concentrations were lower. A comparison with other organic species identified in seawater indicated that dicarboxylic acids and oxoacids (marine sector: $100.1 \pm 15.9 \mu\text{g/L}$; Table 2) prevailed over polysaccharides ($56.8 \pm 21 \mu\text{g/L}$) and amino acids ($8.2 \pm 1.6 \mu\text{g/L}$; Panagiotopoulos et al., 2014; Shen

Table 2
Concentrations and Relative Abundances of Each BCA and Their Contributions to the DOC Budget for the Three Sectors

	Concentration (Av. \pm SD in $\mu\text{g/L}$)			Relative abundance (Av. \pm SD in percent)		
	$S < 10$	$16 \leq S \leq 22$	$S > 25$	$S < 10$	$16 \leq S \leq 22$	$S > 25$
	Delta	Intermediate	Marine	Delta	Intermediate	Marine
Dicarboxylic Acids						
Oxalic, C ₂	36.1 ± 3.3	28.1 ± 6.8	14.2 ± 2.1	15.4 ± 1.3	16.8 ± 2.2	11.6 ± 1.7
Malonic, C ₃	35.2 ± 2.7	20.0 ± 3.9	7.4 ± 2.0	15.1 ± 0.9	12.4 ± 3.6	7.8 ± 1.3
Malein, M	2.0 ± 0.7	1.2 ± 0.7	0.5 ± 0.3	0.9 ± 0.4	0.7 ± 0.3	0.6 ± 0.3
Fumaric, F	0.6 ± 0.1	0.5 ± 0.3	0.2 ± 0.2	0.3 ± 0.1	0.3 ± 0.2	0.3 ± 0.2
Succinic, C ₄	2.5 ± 0.2	2.7 ± 2.3	1.1 ± 0.6	1.1 ± 0.2	1.6 ± 1.1	1.4 ± 0.6
Glutaric, C ₅	0.7 ± 0.1	0.4 ± 0.3	0.4 ± 0.4	0.3 ± 0.1	0.3 ± 0.1	0.5 ± 0.5
Adipic, C ₆	1.1 ± 1.1	0.3 ± 0.1	0.3 ± 0.4	0.5 ± 0.5	0.2 ± 0.1	0.4 ± 0.5
Sebacic, C ₁₀	1.1 ± 1.9	1.9 ± 2.7	2.3 ± 4.9	0.4 ± 0.7	1.0 ± 1.4	3.7 ± 8.4
Oxoacids						
Glyoxylic, ωC_2	145.0 ± 12.0	105.2 ± 21.9	69.8 ± 14.4	62.0 ± 2.3	62.9 ± 5.6	68.4 ± 9.4
4-oxobutanoic, ωC_4	9.3 ± 0.8	6.5 ± 2.2	3.9 ± 1.0	4.0 ± 0.5	3.9 ± 1.0	5.4 ± 1.1
Total BCAs ($\mu\text{g/L}$)	234 ± 14	167 ± 31	100 ± 16			
Total C-BCA ($\mu\text{g/L}$)	77 ± 5	55 ± 11	33 ± 5			
DOC ($\mu\text{g/L}$)	$4,212 \pm 477$	$2,175 \pm 851$	883 ± 297			
C-BCA/DOC (%)	1.8 ± 0.1	4.5 ± 0.4	3.7 ± 1.1			

Note. BCA = bifunctional carboxylic acid; DOC = dissolved organic carbon.

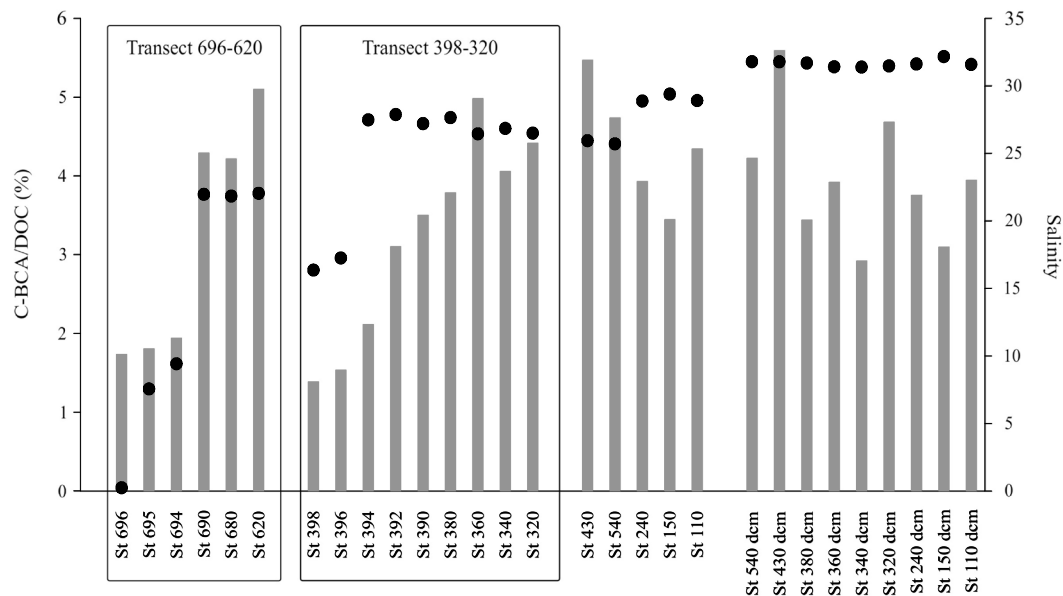


Figure 3. Relative contribution of bifunctional carboxylic acid-carbon (C-bifunctional carboxylic acid/dissolved organic carbon in percent) and salinity (dots) for each station.

et al., 2012). Assuming freshwater concentrations of diacids and oxoacids to be 83 and 167 $\mu\text{g/L}$, respectively (station 696, 0.2 psu), and a flow rate of the MacKenzie River of 25,000 m^3/s during July–October period (Holmes et al., 2012), we can roughly estimate that the Mackenzie River provides 35×10^3 tons of BCAs with 12×10^3 tons of diacids and 23×10^3 tons of oxoacids. Details about the concentration of each individual BCAs are displayed Table S1 in the SI.

Whatever the sector considered, the sum of dicarboxylic acids is predominant over the sum of oxoacids whereas short chain molecules ($<C_4$) are more abundant than longer chain BCAs (C_5 – C_{10}). Albeit relative abundances of BCAs evolve continuously along the river dilution (Figure 4), the following order was observed with $\omega C_2 > C_2\text{di} > C_3\text{di} > \omega C_4$, whatever the sector considered. However, glyoxylic (ωC_2) and oxalic ($C_2\text{di}$) acids were relatively slightly more abundant ($62.0\% \pm 2.3\%$ and $68.4\% \pm 9.4\%$) and less abundant ($15.4\% \pm 1.3\%$ and $11.6\% \pm 1.7\%$), in the marine than in the delta sector, respectively (Table 2). Similarly, relative abundances of malonic acid ($C_3\text{di}$) in total BCAs was 15% in the delta area and decreased to 8% in the marine sector whereas those of sebacic acid ($C_{10}\text{di}$) increased from 0.4% in the delta to 3.7% in the offshore sector. Interestingly, sebacic acid was the only compound that exhibits a higher concentration in the marine sector (Table 2) compared to its initial values in the delta. Sebacic acid is a byproduct from biogenic degradation of organic matter (Wehr et al., 1999), and its increasing abundance in the Beaufort Sea may be related to a direct production from phytoplankton or microorganisms.

3.3. Comparison With Midlatitude

Despite limited observations of BCAs in marine waters, we can compare these results with midlatitudinal (Mediterranean Sea) observations (Sempéré et al., 2018), which are the only available data in river/coastal area systems. This comparison indicates that (1) rivers are the source of BCAs to the ocean and (2) the Arctic Mackenzie River provides much more BCAs than the Rhône River which enters the Mediterranean Sea. For comparison, the DOC content ($4,212 \pm 477 \mu\text{gC/L}$) in the Arctic delta sector is 2.5 times higher than in the Rhône River ($1,644 \pm 835 \mu\text{gC/L}$), whereas BCAs concentration in the MacKenzie outer in brackish waters (delta sector; mean: $234 \pm 14 \mu\text{g/L}$) is 8 times higher than the BCAs concentration in the Rhône River (salinity = 2; mean: $37 \pm 19 \mu\text{g/L}$) (Sempéré et al., 2018). These results clearly show that this river delivers high flux of BCAs to the Arctic Ocean. Interestingly, the DOC

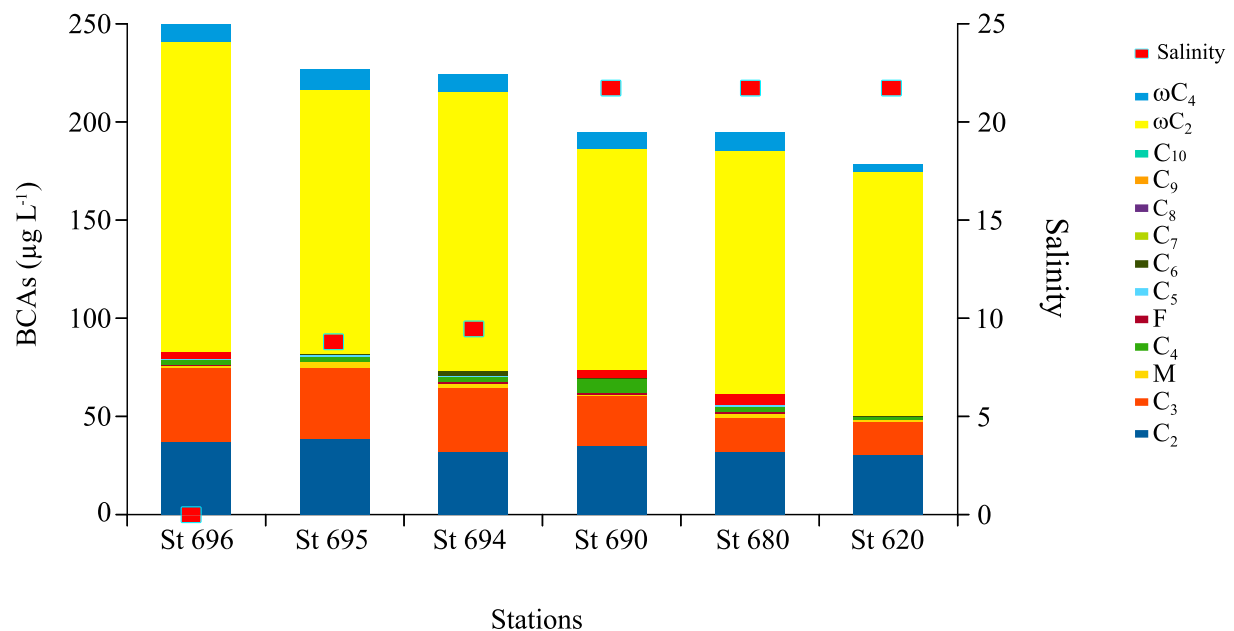


Figure 4. Relative abundances of the BCAs and salinities in the water samples collected along the horizontal subsurface transect of 211 km from the outer of the Reindeer channel (St. 696) to the Mackenzie Canyon (St. 620). BCA = bifunctional carboxylic acid.

concentrations are higher in the Mediterranean and Arctic river areas than in the sea although the relative contribution of carbon from BCAs to the DOC pool (C-BCA/DOC in percent) fractions of BCAs in the DOC pool are 3 times lower in the river outers than offshore. For example, the C-BCA/DOC ratio increased from 0.6% in the Rhône River delta to 1.9% in the Mediterranean Sea (Sempéré et al., 2018; Tedetti et al., 2006) and from 1.4% in the Mackenzie River to 4.4% in the Arctic Ocean. This result suggests that BCAs are relatively more recalcitrant to bacterial degradation than the major part of DOC and/or that BCAs are produced in situ in seawaters. Since these molecules have been reported as reactive intermediate products in aquatic media (Xiao & Wu, 2014), the in situ marine production from both biological and photochemical processes very likely regulates their concentrations in marine waters instead of a lack of degradation.

Some differences in the BCAs molecular distributions were observed between the Rhône (Sempéré et al., 2018) and Mackenzie Rivers (Figure 4), with 4-oxobutanoic being 31 times more concentrated in the Mackenzie River outer. The difference is even 5 times more important for malonic (C₃) and adipic (C₆) acids and at least 4 times for maleic (M) and fumaric (F) acids. The different enrichment of each BCA between these two rivers reveals a significant difference between the compound sources in the river drainage basins. Concerning the marine coastal areas, Tedetti et al. (2006) reported similar trends for the Mediterranean Sea with glyoxylic acid being the most abundant with a concentration of 32.3 ± 5.9 µg/L and a contribution of 64.5% to the BCA pool. Glyoxylic acid was approximately 5 times more abundant than oxalic acid in the Arctic Sea and only 2.5 in the Mediterranean Sea samples (Tedetti et al., 2006). Similarly, relative abundances of malonic and 4-oxobutanoic (ω C₄) acids in the Beaufort Sea are 3 and 4 times higher, respectively, than those reported in the Mediterranean Sea (Tedetti et al., 2006). Maleic (M; 0.5 ± 0.3 µg/L), glutaric (C₅; 0.4 ± 0.4 µg/L), adipic (0.3 ± 0.4 µg/L), and fumaric (F; 0.2 ± 0.2 µg/L) acids were also detected but with lower concentrations. As a comparison, the glutaric acid concentration in the Beaufort Sea is 3 times higher than in the Mediterranean Sea. Concentrations of maleic, fumaric, and adipic acids were 30% to 56% higher than concentrations reported in the Mediterranean Sea (Tedetti et al., 2006). Glyoxylic acid (ω C₂) was usually the most abundant BCA followed by oxalic acid (C₂di; Table 2 and Figure 4), whereas the opposite trend was usually reported for atmospheric samples (Kawamura & Bikkina, 2016; Sempéré & Kawamura, 2003), a point that will be discussed later.

3.4. Potential Origin of BCAs in the Arctic Aquatic System

The source inputs of BCAs into the Mackenzie River and the Beaufort Sea are diverse; they might be carried out by the river after leaching in the runoff of soil organic matter (Hedges et al., 1997; Raymond & Saiers, 2010; Spencer et al., 2012) or in situ produced from biological activity (Steinberg & Bada, 1984) or from photochemical oxidation of marine and terrestrial DOM (Kieber & Mopper, 1987; Tedetti et al., 2009). These assumptions would be consistent with isotopic measurement of global organic matter present in the Beaufort Sea (Forest et al., 2010; Magen et al., 2010) revealing at least two distinct sources including planktonic activity and terrigenous input. Source and processes leading to the BCAs content in the Mackenzie River and the Beaufort Sea can be partially understood from the evolution of the relative abundance among the delta, intermediate, and marine sectors.

3.4.1. In Situ Biological Production

In this study, a weak direct link was found between the organic acid content and chlorophyll *a* concentration measured in marine samples (the maximum Pearson correlation coefficient is $r^2 = 0.47$). However, as byproducts of both primary and secondary production, direct relationship between BCA and chlorophyll might be difficult to report. In addition, biological production and degradation generate organic compounds that might be further photooxidized to BCAs (Tedetti et al., 2007). Indeed, when considering marine organism's metabolism linked to BCA production, tricarboxylic and dicarboxylic acids are involved in the citric acid cycle during carbohydrate degradation (Sempéré et al., 2018; Xiao & Wu, 2014, and reference therein). Microbial degradation of long chain lipids (Kester & Foster, 1963) that have been reported for marine waters is also a probable source of BCAs in freshwaters. Then, prokaryotic and eukaryotic activities are one of the possible sources of BCAs. These observations strongly support an autochthonous production of BCAs in the Mackenzie River waters.

The higher relative abundances obtained for glyoxylic and sebacic acids increased from 63% to 68% and from 0.4% to 3.7%, respectively, from the delta to the offshore sectors, suggesting a higher in situ production of glyoxylic acid and sebacic acid in the Beaufort Sea that might be consistent with previous observations for the Pacific Ocean waters (Steinberg & Bada, 1984). In aquatic systems, glyoxylic or pyruvic acids have been reported as produced by phytoplankton photorespiration (Steinberg & Bada, 1984), degradation of DOM (Kirk, 1994; Pullin et al., 2004), and microbial degradation of long-chain lipids (Kester & Foster, 1963). Kieber and Mopper (1987) highlighted, in coastal areas under terrestrial input influence, the photochemical production of glyoxylic acid from dissolved humic-rich seawater. The photochemical processes observed in the aqueous phase of aerosols from OH radical oxidation of aromatic compounds (Pillar et al., 2014, 2015; Tomaz et al., 2018) probably occurred in river and estuarine waters. Higher abundances of sebacic acid in the Beaufort Sea suggest that it is a byproduct of biological degradation of organic matter (Wehr et al., 1999) and may be related to a direct production from phytoplankton and microorganisms. These sources and processes that do not exist in the atmosphere can probably explain the higher relative abundance of glyoxylic acid over oxalic acid in an aquatic system (Tedetti et al., 2006; Sempéré et al., 2018; this study) compared to aerosol and rainwater samples (Fu et al., 2013; Kawamura & Bikkina, 2016; Pillar-Little & Guzman, 2018; Sempéré & Kawamura, 1994; Tomaz et al., 2018). Higher concentrations of BCAs observed in the Beaufort Sea compared to the Mediterranean Sea might be connected to a higher input of terrigenous matter from the Mackenzie River and the higher biological activity in the Beaufort Sea (Forest et al., 2013; Tremblay et al., 2014).

3.4.2. Terrigenous Sediment Drainage

Concerning the terrigenous input, the Mackenzie River flows across swampy soil characterized by high microbial activity and the presence of thawing permafrost, carrying a high level of soil material (Doxaran et al., 2012, 2015; O'Brien et al., 2006). The Mackenzie River carries DOM of autochthonous and allochthonous origins, including the degrading remains of vascular plant materials in aged soils (Hedges et al., 1997; Raymond & Saiers, 2010) and the organics derived from recent vascular plant production (Spencer et al., 2012). These substances can easily be leached by runoff, transported toward river water and decomposed by prokaryotes during river transport producing low molecular weight organic acids including BCAs. The DOC content in the Mackenzie River is 2.5 times more elevated than in the Rhône River, and the particulate organic carbon carried by the Mackenzie River (40×10^{10} gC/year; Doxaran et al., 2012) is twice higher than the particulate organic carbon carried by the Rhône River (19×10^{10} gC/year, Panagiotopoulos et al., 2012). Additionally, the bottom sediments in the river system are regularly resuspended and transported into the

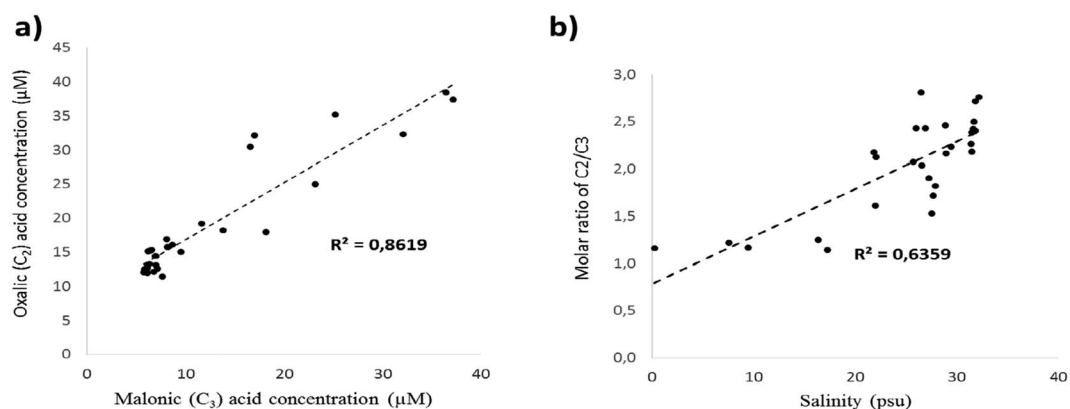


Figure 5. Correlations between oxalic and malonic acids (a) and between C₂/C₃ molar ratio and the salinity of water samples (b).

Beaufort Sea, driving a vertical flux of organic matter (Forest et al., 2010, 2013). The soil compositions include a high diversity of organic compounds including BCAs (Chen et al., 2001; Strobel, 2001) and can be an important source of labile or refractory diacids and oxoacids for the river media and consequently for the oceans.

3.4.3. Possible Photochemical Activity Impacting the BCA Content

In contrast to glyoxylic acid, contents of malonic acid decreased to 36% along this transect. On average, the relative abundance of malonic acid was approximately twofold lower in the delta sector (16%) than offshore (7%). Oxalic acid content also decreased along the Beaufort Sea, with relative abundances ranging from 15.4% to 16.8% in the delta and intermediate sectors, respectively, to 11.6% in the marine sector. These decreasing relative abundances along the salinity gradient could be explained by selective biodegradation processes happening in the Beaufort area (Forest et al., 2013; Ortega-Retuerta et al., 2012) although preferential photochemical degradation could also be considered. Indeed, malonic acid can be photochemically degraded leading to the production of glyoxylic acid in the marine environment as observed in an aqueous medium such as cloudwater (Charbouillot et al., 2012) although the impact of light was limited during the sampling cruise due to the presence of persistent cloud (Para et al., 2013). In addition, the correlations observed between C₂ and C₃ and C₂/C₃ molar ratios and salinity (Figures 5a–5b) suggest that the processes controlling their content are connected or similar along the salinity gradient. Considering the higher content of chromophoric DOM in the upper river compared to the Beaufort Sea, higher available UV-visible light for photochemical oxidations (Doxaran et al., 2012; Song et al., 2013) is more likely in the Beaufort Sea than in the river. Therefore, higher C₂/C₃ ratios for higher salinity areas as we observed might be due to an enhanced photochemical degradation of malonic acid in the seawater. Such a link between these two species has already been observed in atmospheric waters (Väitilingom et al., 2011) and airborne aerosols (Kawamura & Yasui, 2005).

Globally, BCAs can also be produced within the river waters or in Arctic surface waters from photodegradation of potential precursors. It is likely that surface water BCAs are also produced partly by the photochemical oxidation of some polar organic compounds including isoprene and α -/ β -pinene- oxidation products that have been reported as important sources of diacids in the marine atmosphere (Bikkina, Kawamura, Imanishi, et al., 2015; Bikkina, Kawamura, & Miyazaki, 2015).

3.5. Exchange of BCAs Between the Atmosphere and Ocean: Global Implications

Atmospheric wet and dry deposition over the Beaufort Sea can be one important source of BCAs to seawater. BCAs can be produced in the atmosphere due to the incomplete combustion of fossil fuels and biomass burning as well as secondary photochemical oxidations of anthropogenic and natural organic compounds such as isoprene and α -/ β -pinene (Fu et al., 2013; Kawamura & Bikkina, 2016; Wang et al., 2006). A portion of atmospheric BCAs can likely be transferred toward the Mackenzie River and Arctic Ocean waters through wet or dry deposition. In contrast, oceans can be considered as a possible source of glyoxylic acid toward the atmospheric compartment as well (Sempéré & Kawamura, 2003 and references therein). However, companion

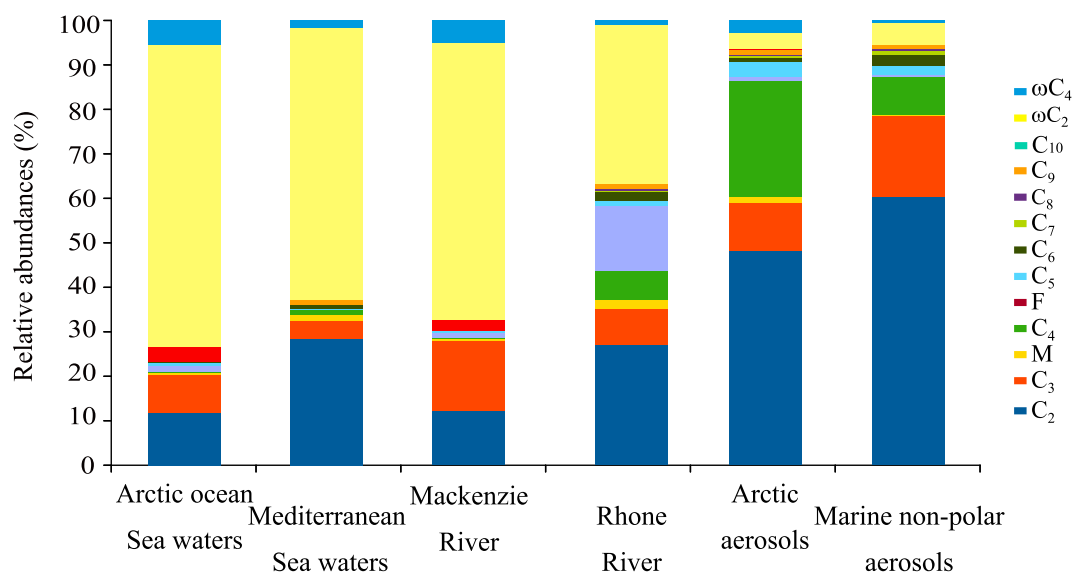


Figure 6. Mean relative abundances of bifunctional carboxylic acids in six contrasted environments: Arctic Ocean waters and Mackenzie River (this study), Mediterranean Sea waters (Tedetti et al., 2006), Rhone River waters (Sempéré et al., 2018), Arctic (Kawamura et al., 2012), and marine nonpolar aerosols (Fu et al., 2013).

study during the cruise (Kawamura et al., 2012) reported lower concentrations of diacids and related compounds in marine aerosols over the Arctic Ocean sector compared to other summer marine aerosols collected in different regions of the globe. Arctic aerosol diacids are also certainly less abundant than in the coastal northwest Mediterranean Sea due to high concentrations resulting from a strong industrial activity observed near the Rhône River in or near the Rhône River in the Mediterranean Sea (Rontani et al., 2012) and intense solar radiation (Sempéré et al., 2018). In contrast, BCA concentrations we report here in the Arctic marine waters are much higher than the BCA concentrations that found in the Rhône River and Mediterranean waters (Sempéré et al., 2015). These results suggested that the Arctic Beaufort Sea is an area with particularly low BCA atmospheric content and elevated BCA in the Arctic surface waters (Figure 6). A link between the chemical composition of surface seawater, rain, and airborne particle seems evident, but our knowledge are limited to evaluate the fluxes at the air/water interface. In this context, it is hard to estimate if the BCAs sources from wet and dry atmospheric deposition into seawater are more important than its sinks by aerosolization from the sea toward atmosphere.

4. Conclusion

Molecular distributions of BCAs and more specifically the predominance of glyoxylic acid over oxalic acid in the Arctic waters differ from the distributions reported in the atmosphere where oxalic acid is usually more abundant than glyoxylic acid, followed either by malonic (C_3) or succinic (C_4) acid according to the aging of the aerosols (Fu et al., 2013; Kawamura & Bikkina, 2016; Sempéré & Kawamura, 2003). Within the chain reactions in the photochemical production of BCAs, oxalic can be considered an oxidation product of glyoxylic acid, whereas the latter is a biological byproduct of marine organisms in aquatic systems (Sempéré et al., 2018; Steinberg & Bada, 1984 and references therein). Therefore, this observation, first reported in the Mediterranean aquatic samples (Sempéré et al., 2018; Tedetti et al., 2006), strongly suggests that aquatic biological processes govern molecular distribution of BCAs in marine/river waters whereas photochemical oxidation reactions regulate their molecular distribution in rain and aerosols. Such comparisons suggest little direct sea-air or air-sea transfer of BCAs in the Arctic sector during the period studied. However, atmospheric diacids may partly originate from photochemical/aqueous phase oxidation of other organic compounds such as biogenic unsaturated fatty acids (e.g., oleic acid) and isoprene (Bikkina et al., 2014; Kawamura & Bikkina, 2016) emitted from the productive arctic waters.

These results might be reconsidered because of the rapid changes already reported in the Arctic climate (IPCC, 2014). Indeed, our results showed a high flux of BCAs from the Mackenzie concentrations into the

Beaufort Sea waters. Moreover, the 50% increase in terrigenous particles carried by the Mackenzie River into the Beaufort Sea reported for the last 10 years (Doxaran et al., 2015), and the huge amount of carbon available from the permafrost thawing in relation to the global warming scenario (Anderson & Amon, 2015; Tarnocai et al., 2009) suggest that the BCA flux to the Arctic Ocean will be significantly increased within the next decades. Considering that the MacKenzie River is only the fourth-largest freshwater provider to the Arctic Ocean, the present results can be extended to the global warming scenario predicting that a huge amount of permafrost soil will be released in the Arctic area like other rivers in the Arctic, that is, the Yukon, Ob, Yenisey, and Lena Rivers, which are also affected by the thawing of the permafrost (Tarnocai et al., 2009; Zhang et al., 2017), supporting the DOM enrichment of BCAs in the Arctic Ocean waters with global warming. Although, aerosol BCA content was low during the sampling period (Kawamura et al., 2012), higher contents of BCAs at the air-sea interface may certainly be expected in the future to enhance the injection of more BCAs into the atmosphere.

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