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## Aerosol and snow transfer processes: An investigation on the behavior of water-soluble organic compounds and ionic species



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### HIGHLIGHTS

- The air-snow transfer processes were evaluated using water soluble compounds.
- This is the first study about amino acids and sugar concentration in surface snow.
- Water soluble organic fractions of Antarctic aerosol and snow were investigated.

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### ABSTRACT

The concentrations of water-soluble compounds (ions, carboxylic acids, amino acids, sugars, phenolic compounds) in aerosol and snow have been determined at the coastal Italian base "Mario Zucchelli" (Antarctica) during the 2014–2015 austral summer. The main aim of this research was to investigate the air-snow transfer processes of a number of classes of chemical compounds and investigate their potential as tracers for specific sources.

The composition and particle size distribution of Antarctic aerosol was measured, and water-soluble compounds accounted for 66% of the PM<sub>10</sub> total mass concentration. The major ions Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> made up 99% of the total water soluble compound concentration indicating that sea spray input was the main source of aerosol. These ionic species were found mainly in the coarse fraction of the aerosol resulting in enhanced deposition, as reflected by the snow composition.

Biogenic sources were identified using chemical markers such as carboxylic acids, amino acids, sugars and phenolic compounds. This study describes the first characterization of amino acids and sugar concentrations in surface snow. High concentrations of amino acids were found after a snowfall event, their presence is probably due to the degradation of biological material scavenged during the snow event. Alcohol sugars increased in concentration after the snow event, suggesting a deposition of primary biological particles, such as airborne fungal spores.

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### 1. Introduction

Chemical markers provide unique information on the sources of aerosol and the chemical processes that took place during atmospheric transport. Their applicability to paleoclimatic studies of ice cores from polar regions, offers exceptional potential to evaluate the role and influence of aerosol in anthropogenic and natural forcing of climate change.

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Several studies have been conducted to evaluate the relationships between the concentrations of some markers in air and snow. So far, only the relationship between ionic compounds and carboxylic acids has been investigated since they are the most easily detectable in most matrices. Wolff et al. (1998) determined the most abundant ionic compounds in the aerosol, fresh snow and firn cores from three coastal Antarctic stations and highlighted the difficulties in studying processes in an area where environmental conditions change frequently. Investigations on the depositional fluxes of non-sea salt sulfate and methanesulfonic acid allowed an assessment of the spatial variation of marine biogenic sulfur (Minikin et al., 1998) to be made.

At Dome C on the Antarctic plateau, it was demonstrated that nitrate and chloride can be caught by the surface snow through dry deposition and adsorption processes (Udisti et al., 2004). The interactions of carboxylic acid at the air-snow interface has been studied in the Arctic (Narukawa et al., 2002), and underlined the compositional difference between aerosol and snow samples.

Ionic species such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are the most abundant compounds in Antarctic aerosol (Udisti et al., 2012) because the main source of aerosol in polar regions is fine sea spray emitted by bubble bursting because they are distant from any anthropogenic or continental emission sources.

Carboxylic acids (CA) may have different emission sources to the atmosphere (Kawamura et al., 1996a). Some anthropogenic organic pollutants that act as CA precursors, once emitted into the atmosphere they can undergo photochemical reactions or react with strong oxidants, such as ozone (Kawamura et al., 1996b). It is thought that the main natural source for CA is photochemical reactions after the release of alkenes by phytoplankton (Xu et al., 2013).

Several organic compound classes, such as sugars and amino acids, are emitted from biogenic sources into the atmosphere. Bioaerosol (bacteria, fungi, viruses, pollen, cell debris) contains primary saccharides such as glucose and sucrose (Medeiros et al., 2006). Arabinol and mannitol can be used as tracers for airborne fungal spores (Bauer et al., 2008), and are also the main carbohydrates in lichens and bacteria (Medeiros et al., 2006).

Levoglucosan, the most abundant anhydrosugar, is a specific atmospheric tracer of biomass burning (Simoneit and Elias, 2001). Some studies have demonstrated that the composition of phenolic compounds (PC) in atmospheric aerosol is linked to the type of vegetation that was burned (Simoneit, 2002), although Zangrando et al. (2016) have suggested that these compounds may have an additional marine source. A possible correlation between primary marine production and amino acids has also been identified (Barbaro et al., 2015b).

The main aim of this study was to investigate the behavior of water-soluble compounds during aerosol-snow transfer processes. Aerosol and snow samples were collected at Faraglione Camp, about 3 km from the Italian station "Mario Zucchelli", called MZS (Terra Nova Bay, Antarctica) during the 2014–2015 austral summer. Our research focused on several classes of compounds, such as ionic species ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , methanesulfonate (MSA),  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ), CA ( $\text{C}_2$ -oxalic,  $\text{C}_2$ -glycolic,  $\text{C}_3$ -malonic,  $\text{C}_4$ -succinic,  $h\text{C}_4$ -malic,  $cis$ - $us\text{C}_4$ -maleic,  $trans$ - $us\text{C}_4$ -fumaric,  $\text{C}_5$ -glutaric,  $\text{C}_6$ -adipic,  $\text{C}_7$ -pimelic,  $a\text{C}_7$ -benzoic,  $\text{C}_8$ -suberic), sugars (monosaccharides, disaccharides, alcohol sugars and anhydrosugars), amino acids (AA) and PC (vanillin, syringyl and coumaryl compounds). This is the first study of potential relationships between sugars, AA and PC in aerosol and snow samples from the same site.

## 2. Material and methods

### 2.1. Collection and processing of aerosol samples

Aerosol samples ( $n = 7$ ) were collected using a multi-stage Andersen impactor (TE-6070, Tisch Environmental Inc., Cleves, OH, USA) placed at Campo Faraglione ( $74^\circ 41' \text{ S}$ ,  $164^\circ 06' \text{ E}$ ), 3 km south of the Italian MZS (Victoria Land, Antarctica) from the 6th of November 2014 to the 13th of January 2015.

Aerosol samples were collected on six pre-combusted (4 h at  $400^\circ \text{C}$  in a muffle furnace) quartz fiber filters with different cut-offs: the sampler accumulated particles with the following size fractions:  $10.0$ – $7.2 \mu\text{m}$ ,  $7.2$ – $3.0 \mu\text{m}$ ,  $3.0$ – $1.5 \mu\text{m}$ ,  $1.5$ – $0.95 \mu\text{m}$ ,  $0.95$ – $0.49 \mu\text{m}$  on slotted filters and the  $<0.49 \mu\text{m}$  particle size on a

backup filter at an average sampling airflow of  $1.1 \text{ m}^3 \text{ min}^{-1}$ . Samples were collected for 10 days, as previous tests showed that this exposure time was necessary to quantify species at very low concentrations (Barbaro et al., 2015a, 2015b, 2016, 2017; Zangrando et al., 2016). Further sampling details are available in Table S2. Three field blank samples were collected by loading, carrying and installing the filter on the instrument with the air pump switched off, removing it after 10 min, following the same procedure used for installation and removal of the sample filters. Samples and blanks were wrapped in a double layer of aluminum foil and stored at  $-20^\circ \text{C}$  until analysis.

The pre-analytical protocol to determine the ionic species ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ , MSA,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) and 12 CA ( $\text{C}_2$ -oxalic,  $\text{C}_2$ -glycolic,  $\text{C}_3$ -malonic,  $\text{C}_4$ -succinic,  $h\text{C}_4$ -malic,  $cis$ - $us\text{C}_4$ -maleic,  $trans$ - $us\text{C}_4$ -fumaric,  $\text{C}_5$ -glutaric,  $\text{C}_6$ -adipic,  $\text{C}_7$ -pimelic,  $a\text{C}_7$ -benzoic,  $\text{C}_8$ -suberic acids, Table S1) is described elsewhere (Barbaro et al., 2016). A quarter of each sample filter was broken into small pieces and placed into polyethylene tubes, using steel tweezers. All materials were previously cleaned by sonication with ultrapure water for 30 min at room temperature, and all sample handling was carried out under a class 100 laminar flow hood. Slotted filters were ultrasonicated for 30 min in 7 mL of ultrapure water, while backup filters were extracted with 15 mL of ultrapure water. Extracts were filtered through a  $0.45 \mu\text{m}$  polytetrafluoroethylene (PTFE) filter (ThermoFisher) to remove solid residues before analysis.

Half of each sample filter was used to determine AA, sugars and PC using a previously described method (Barbaro et al., 2015a, 2015b; Zangrando et al., 2016), where filter subsamples were spiked with a  $^{13}\text{C}$ -labelled internal standard mix (AA, PC and levoglucosan), ultrasonicated twice for 15 min in ultrapure water, and filtered through a  $0.45\text{-}\mu\text{m}$  PTFE filter before analysis.

### 2.2. Collection and processing of snow samples

Surface snow samples ( $n = 8$ ) were collected about 30 m from the aerosol sampling site. Snow samples were collected at 10-days intervals, when aerosol filter changing occurred (6 November, 17 November, 27 November, 7 December, 27 December 2014). Three consecutive snow samplings (10, 12 and 13 January 2015) were also performed during a snowfall event that lasted from the 8th to 11th of January 2015. Surface snow samples (ca. 1 cm in depth) were collected in 2-L polyethylene bottles, previously cleaned with ultrapure water and methanol. The samples were melted in an ISO 4 clean room and aliquoted into pre-cleaned vials prior to determination of ionic species and organic compounds. Before analysis for sugars, AA and PC the melted aliquots were spiked with a  $^{13}\text{C}$ -labelled internal standard mix.

### 2.3. Instrumental analysis

The quantification of all anions and CA was performed using an ion chromatograph (Thermo Scientific Dionex TM ICS-5000, Waltham, MA, USA), with an anion exchange column (Dionex Ion Pac AS11  $2 \times 250 \text{ mm}$ ) and guard column (Dionex Ion Pac AG11  $2 \times 50 \text{ mm}$ ), coupled with a single quadrupole mass spectrometer (MSQ PlusTM, ThermoScientific, Bremen, Germany). The ion chromatograph was equipped with a capillary system to simultaneously determine cations using a conductivity detector. Cations were separated using an Ion Pac CS19 – 4 mm capillary cation-exchange column ( $0.4 \times 250 \text{ mm}$ ) equipped with an Ion Pac CG19 – 4 mm guard column ( $0.4 \times 50 \text{ mm}$ ). Further details about the methods for anion and cation determinations are reported by Barbaro et al. (2016).

Quantifications of the AA were obtained using high-performance liquid chromatography with a chiral column

coupled with tandem mass spectrometry for detection (HPLC-MS/MS) (Barbaro et al., 2014). PC were analyzed using reverse-phase chromatography coupled with tandem mass spectrometry (Zangrando et al., 2013), whereas sugars were determined using ion chromatography coupled with mass spectrometry (IC-MS) (Barbaro et al., 2015a).

### 3. Results

#### 3.1. PM<sub>10</sub> composition and particle size distribution

The mean aerosol concentration of all water-soluble compounds (ions, sugars, CA, AA, PC) in PM<sub>10</sub> aerosol samples, obtained from the sum of different size-segregated fractions, was  $0.6 \pm 0.1 \mu\text{g m}^{-3}$ . This total concentration of analyzed compounds represented  $66 \pm 20\%$  of the PM<sub>10</sub> total mass concentrations as determined in other samples taken in parallel (Illuminati et al., 2016).

##### 3.1.1. Ionic compounds in PM<sub>10</sub>

The mean composition of PM<sub>10</sub> aerosol samples showed that inorganic ions were the main species collected on the filters (Fig. S1). The most abundant,  $\text{SO}_4^{2-}$  represented 38% ( $214 \pm 53 \text{ ng m}^{-3}$ ) of the total concentration of the analyzed compounds.  $\text{Mg}^{2+}$  ( $0.10 \pm 0.05 \mu\text{g m}^{-3}$ , 17%) had higher concentrations than  $\text{Cl}^-$  ( $0.07 \pm 0.03 \mu\text{g m}^{-3}$ , 13%) and  $\text{Na}^+$  ( $0.07 \pm 0.03 \mu\text{g m}^{-3}$ , 11%).  $\text{NH}_4^+$  was present at 8% ( $0.05 \pm 0.02 \mu\text{g m}^{-3}$ ), while  $\text{NO}_3^-$  was 6% ( $0.03 \pm 0.02 \mu\text{g m}^{-3}$ ) and MSA 5% ( $0.03 \pm 0.01 \mu\text{g m}^{-3}$ ). Other quantified species represented 1% of the total.

The aerosol composition and the particle size distribution of ionic species can be used to define sources. Aerosol collected at the coastal base MZS has a characteristic sea salt input, indicated by the high content of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  (Hillamo et al., 1998).  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  were mainly in the coarse fraction ( $>1 \mu\text{m}$ ) (Fig. S2). Two different sources of  $\text{SO}_4^{2-}$  can be recognized by distinguishing between non-sea salt sulfate (nss- $\text{SO}_4^{2-}$ ) and sea salt sulfate (ss- $\text{SO}_4^{2-}$ ). Ss- $\text{SO}_4^{2-}$  was mainly distributed on particles with a diameter above  $1 \mu\text{m}$  (Fig. S3), and is calculated against other markers of sea salt input, such as  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . In the 2014–2015 samples, the contribution of sea salt to sulfate concentrations was determined using the  $\text{SO}_4^{2-}$  to  $\text{Na}^+$  ratio, ratios higher than the seawater value of 0.25 are indicative of seawater plus other sources. The values calculated in all fractions, ranged by 0.5 in the coarse fraction (diameter above  $3 \mu\text{m}$ ) to 37 in the  $<0.49 \mu\text{m}$  fraction. These values suggest inputs of sulfate not just from sea salt particles (Jourdain and Legrand, 2002). The main source of nss- $\text{SO}_4^{2-}$ , as well as MSA, is emission by phytoplankton bloom in the oceans (Fattori et al., 2005). These two species were mainly distributed on the  $<0.49 \mu\text{m}$  fraction (Figs. S2 and S3) and showed high correlation ( $R^2 = 0.87$ ) in the aerosol data. Ammonium was mainly distributed in the  $<0.49 \mu\text{m}$  fraction (Fig. S2), suggesting that its main source was the ocean (Jickells et al., 2003; O'Dowd et al., 2004; Johnson and Bell, 2008). The ionic composition, concentration and particle size distributions were similar to data obtained from the same sampling site during the austral summer of 2010–11 (Barbaro et al., 2017).

##### 3.1.2. Carboxylic acids (CA) in PM<sub>10</sub>

Although the other water soluble organic compounds (WSOC) quantified in the present research were below 1% of the total concentration of all the determined chemical species (Fig. S1), they may provide useful information based on their composition and particle size distributions. CA are major contributors to organic aerosol mass (Sempere and Kawamura, 2003). The total mean concentration of CA in our PM<sub>10</sub> samples was  $0.8 \pm 0.5 \text{ ng m}^{-3}$ , the

mean concentrations reported are associated with a high standard deviations due to the very low concentrations in Antarctic samples.

The CA detected in our samples were C<sub>3</sub>-malonic acid (with an average concentration of  $0.2 \pm 0.1 \text{ ng m}^{-3}$ ), C<sub>4</sub>-succinic acid ( $0.2 \pm 0.1 \text{ ng m}^{-3}$ ), C<sub>5</sub>-glutaric acid ( $0.1 \pm 0.1 \text{ ng m}^{-3}$ ), C<sub>2</sub>-oxalic acid ( $0.09 \pm 0.08 \text{ ng m}^{-3}$ ), hC<sub>4</sub>-malic acid ( $0.09 \pm 0.06 \text{ ng m}^{-3}$ ), C<sub>7</sub>-pimelic acid ( $0.04 \pm 0.01 \text{ ng m}^{-3}$ ), C<sub>6</sub>-adipic acid ( $0.04 \pm 0.02 \text{ ng m}^{-3}$ ), and C<sub>2</sub>-glycolic acid ( $0.013 \pm 0.009 \text{ ng m}^{-3}$ ). These compounds were mainly distributed in the  $<0.49 \mu\text{m}$  fractions (Fig. S4) due to their nature of being secondary aerosol products in the atmosphere. The concentrations of CA determined in the 2014–2015 campaign were 10 times lower than those found during the austral summer of 2010–2011 (Barbaro et al., 2017). The main difference resides in the concentrations of C<sub>2</sub>-oxalic acid: in the aerosol samples from 2010 to 2011, the mean concentration was  $3 \pm 1 \text{ ng m}^{-3}$ , whilst in the 2014–2015 samples the mean concentration was  $0.09 \pm 0.08 \text{ pg m}^{-3}$ . This difference can be explained by differences in the photochemical production of CA after the release of alkenes by phytoplankton (Xu et al., 2013). C<sub>2</sub>-oxalic acid is an end-product of various oxidation/decomposition reactions in the atmosphere (Kawamura and Sakaguchi, 1999), whereas the presence of long chain CA suggests incomplete photochemical degradation of alkenes in the atmosphere. The C<sub>3</sub>-malonic/C<sub>4</sub>-succinic ratio can be used as an indicator of enhanced photochemical production of diacids (Kawamura and Ikushima, 1993), as C<sub>4</sub>-succinic acid can be degraded to C<sub>3</sub>-malonic acid by decarboxylation reactions activated by OH radicals (Fu et al., 2013). The C<sub>3</sub>/C<sub>4</sub> ratios in the marine aerosols collected at low-to mid-latitudes in the Northern Hemisphere vary between 0.9 and 5.8 with an average of 2.3, which were about three times higher than those found in urban aerosol (Fu et al., 2013). These values suggested that C<sub>3</sub>-malonic acid is photochemically produced during long range transport from continents to the marine atmosphere (Fu et al., 2013). The mean C<sub>3</sub>/C<sub>4</sub> ratio calculated in the 2014/2015 Antarctic samples ranged between 0.8 and 2.3 with an average value of 1.45, suggesting that aerosol contained these species underwent long range transport processes, where photochemical degradation occurred. These ratio values were very similar to the ratios obtained in the 2010–11 Antarctic samples (C<sub>3</sub>/C<sub>4</sub> ratio of 1.5) (Barbaro et al., 2017).

##### 3.1.3. Sugars in PM<sub>10</sub>

Anhydrosugars, sugar alcohols, monosaccharides and disaccharides are among the major classes of WSOC in atmospheric aerosol (Yttri et al., 2007). The sum of the mean concentrations of all sugars in PM<sub>10</sub> samples collected during the austral summer 2014–2015 was  $0.7 \pm 0.6 \text{ ng m}^{-3}$  and sugars represented 0.1% of the total detected compounds. The most abundant class of sugars were monosaccharides (MS), with a total mean PM<sub>10</sub> concentration of  $0.4 \pm 0.4 \text{ ng m}^{-3}$ , while glucose represented 48% of the total PM<sub>10</sub> sugar concentration. The concentration of glucose in the 2014–2015 samples ( $0.4 \pm 0.3 \text{ ng m}^{-3}$ ) showed considerable temporal variability and was higher than the mean concentrations found during the austral summer 2010–2011 campaign at the same sampling site ( $84 \pm 5 \text{ pg m}^{-3}$ ) (Barbaro et al., 2015a). The difference between these two sampling campaigns can be explained by the particle size distribution of glucose. During 2010–2011, glucose was essentially found in the aerosol fine fraction ( $<1 \mu\text{m}$ ) only (Barbaro et al., 2015a), while during 2014–2015, 21% of glucose was found in the  $>3.0 \mu\text{m}$  fraction (Fig. S5). The additional occurrence of glucose in the coarse particles ( $>1 \mu\text{m}$ ) may be due to degradation of polysaccharides occurred during long range transport processes (Leck et al., 2013). Biological degradation, as a source of sugars, is also indicated by the higher mean concentration of sucrose ( $96 \text{ pg m}^{-3}$ ) in the 2014–2015 samples compared to the mean

concentration ( $3 \text{ pg m}^{-3}$ ) in the 2010–2011 samples (Barbaro et al., 2015a). Sugar alcohols, such as mannitol and arabitol, had a mean concentration of  $170 \text{ pg m}^{-3}$  in the 2014–2015 samples and were mainly found in the coarse fraction ( $>3 \text{ }\mu\text{m}$ ) (Fig. S5). This particle size distribution confirms the association with primary biological particles such as airborne fungal spores (Yttri et al., 2007; Bauer et al., 2008).

The main anhydrosugar present in 2014–2015 was levoglucosan ( $14 \text{ pg m}^{-3}$ ), mannosan was also detected in a few samples. Levoglucosan was mainly found in the  $<0.49 \text{ }\mu\text{m}$  fraction (Fig. S5), suggesting long-range atmospheric transport from sites where biomass burning occurred. Indeed, levoglucosan is now recognized as a specific biomarker of cellulose combustion (Kuo et al., 2011).

### 3.1.4. Free amino acids (AA) in $\text{PM}_{10}$

The composition and particle size distribution of AA were evaluated to investigate their use as possible tracers of primary biological matter as suggested in previous studies (Barbaro et al., 2015b). Since further investigations about their aerosol behavior and aerosol-snow transfer processes are necessary before applying these compounds as tracers in climate studies.

Ten L-AA (L-Ala, L-Asp, L-Arg, L-Glu, L-Leu, L-Phe, L-Pro, L-Tyr, L-Thr) and Gly were detected in the aerosol samples collected at MZS in 2014–2015. The mean total concentration of free AA ( $0.04 \pm 0.03 \text{ ng m}^{-3}$ ) was lower than those found in 2010–2011 ( $0.2 \pm 0.1 \text{ ng m}^{-3}$ ) (Barbaro et al., 2015b). Gly was the most abundant compound (60% of the total free AA), while other percentages of AA were homogeneously distributed (9% for L-Glu; 6% for L-Arg and L-Ala; 5% for L-Leu; 4% for L-Pro; 3% for L-Asp and L-Thr; and 2% for Tyr; 1% for L-Val and L-Phe).

A marine source of free AA was suggested by particle size distribution mostly in the fine fraction ( $<1 \text{ }\mu\text{m}$ ) of our samples (Fig. S6), confirming suggestions from previous studies (O'Dowd et al., 2004; Keene et al., 2007; Facchini et al., 2008; Modini et al., 2010).

### 3.1.5. Phenolic compounds (PC) in $\text{PM}_{10}$

PC can derive from lignin combustion and the presence of these compounds in atmospheric aerosol may indicate which types of plants were burned (Simoneit, 2002). Previous studies of these compounds in Antarctic aerosol (Zangrando et al., 2016) demonstrated that PC had a bad correlation with levoglucosan, specific tracers of biomass burning, suggesting the existence of sources of PC. Further studies of PC were suggested to fully understand their applicability as environmental markers.

The  $<0.49 \text{ }\mu\text{m}$  fraction of aerosol samples from 2014 to 2015 contained 92% of the total PC concentrations with a total mean concentration of  $29 \pm 12 \text{ pg m}^{-3}$  (Fig. S7). Vanillin (VAH) was the most abundant compound (89%,  $0.02 \pm 0.01 \text{ ng m}^{-3}$ ), while the mean concentration of acetovanillone (VAC) was  $2 \pm 1 \text{ pg m}^{-3}$  (7%), and that of vanillic acid (VA)  $0.8 \pm 0.7 \text{ pg m}^{-3}$  (3%). Traces of syringic acid (SyA), homovanillic acid (HA) and syringaldehyde (SyAH) represented 1% of the total concentration of PC in the aerosol samples collected in 2014–2015. The concentrations were similar in 2010–2011 (Zangrando et al., 2016), where the ocean was suggested as a possible local source of PC by ejecting fine particles ( $<1 \text{ }\mu\text{m}$ ) containing organic compounds into the atmosphere (O'Dowd and De Leeuw, 2007). For the 2014–2015 samples evaluated in the present research, the same source can also be suggested and biomass burning can be excluded as the main source of PC. This affirmation can be confirmed by comparing PC concentrations with those of levoglucosan, specific tracers of pyrolysis of cellulose. The correlation coefficient between the sum of PCs and levoglucosan was 0.5, while the ratios of levoglucosan/VAH and levoglucosan/VA were 0.8 and 6.4 respectively. These ratios were

100 times lower than those obtained for aerosol samples affected by biomass burning (Graham et al., 2002; Ward et al., 2006, 2011; Fu et al., 2010), suggesting another natural source for PC (Zangrando et al., 2016).

### 3.2. Composition of surface snow

Superficial snow samples were collected during aerosol sampling to investigate exchanges between the atmosphere and the snow layer. The first sampling period had no precipitation events, while the three samples collected on the 10, 12 and 13 of January 2015 were fresh snow from snowfall that lasted from the 8 to 11 January 2015.

Aged snow collected before the snow event at MZS had a total mean concentration of water-soluble compounds of  $66 \text{ }\mu\text{g g}^{-1}$ , with  $\text{Na}^+$  ( $22 \text{ }\mu\text{g g}^{-1}$ ),  $\text{Mg}^{2+}$  ( $22 \text{ }\mu\text{g g}^{-1}$ ),  $\text{Cl}^-$  ( $14 \text{ }\mu\text{g g}^{-1}$ ) and  $\text{SO}_4^{2-}$  ( $5 \text{ }\mu\text{g g}^{-1}$ ) as the most abundant species. Dry deposition of marine aerosol was the most plausible source of these compounds on the superficial snow layer. After the snow event (8–11 January), the total concentration of water-soluble species decreased from  $66 \text{ }\mu\text{g g}^{-1}$  to  $9 \text{ }\mu\text{g g}^{-1}$ , probably due to dilution effects (Fig. S8).  $\text{Mg}^{2+}$  ( $3 \text{ }\mu\text{g g}^{-1}$ ),  $\text{SO}_4^{2-}$  ( $1 \text{ }\mu\text{g g}^{-1}$ ),  $\text{Na}^+$  ( $0.6 \text{ }\mu\text{g g}^{-1}$ ) and  $\text{Cl}^-$  ( $0.4 \text{ }\mu\text{g g}^{-1}$ ) were still the most abundant compounds. In contrast, an increase in AA concentration occurred, with concentrations varying from  $0.6 \text{ }\mu\text{g g}^{-1}$  before the snow event to  $3 \text{ }\mu\text{g g}^{-1}$  after snowfall. Degradation of proteinaceous material that fell with the snow could be a possible source of free AA in fresh snow, as this increase was observed in the 12 January samples, when the snowfall had ceased (Fig. 1). An unclear decrease in AA was found on the following sampling day (13 January) and further investigations are needed to understand the behavior of these species in the snowpack.

The deposition of biological material with snowfall was also confirmed by an increase in the concentration of AS such as mannitol and arabitol. Mannitol had a concentration of  $3 \text{ ng g}^{-1}$  on 27 December, while its concentration was  $241 \text{ ng g}^{-1}$  on 10 January, suggesting a deposition of primary biological particles, such as airborne fungal spores (Bauer et al., 2008).

## 4. Discussion

### 4.1. Exchange between atmosphere and snow of water-soluble compounds

Fig. 1 shows the concentrations of analyte in aerosol and snow samples. Aged snow was collected until 27 December 2014, while the samples of 10, 12 and 13 January 2015 were fresh snow after snowfall between the 8 to 11 of January 2015.

The  $\text{PM}_{10}$  concentration of major ions increased and peaked in the second half of December (17–27 December sample, Fig. 1), probably due to seasonal reduction of the pack ice extent. At the end of the field campaign a decrease in concentration was observed, caused by abundant snowfall. The same behavior was observed for the  $\text{PM}_{10}$  mass concentration (Illuminati et al., 2016), suggesting the same cause.

The main ions found in aged snow samples were  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , and sea salt ions were also found in the coarse fraction of particulate matter (Fig. S2). Dry deposition of coarse particles was probably the main process that removed these compounds from the atmosphere. These ions were diluted by snowfall (Kreutz and Mayewski, 1999) as demonstrated by a decrease in ion concentration in fresh snow samples from 10 to 13 January (Fig. 1). In particular,  $\text{Mg}^{2+}$  seems to be the ion most affected by this dilution process (zoom on Fig. 1).

High concentrations of sea salt ions were observed in the 17 November snow sample, when the wind direction was mainly from

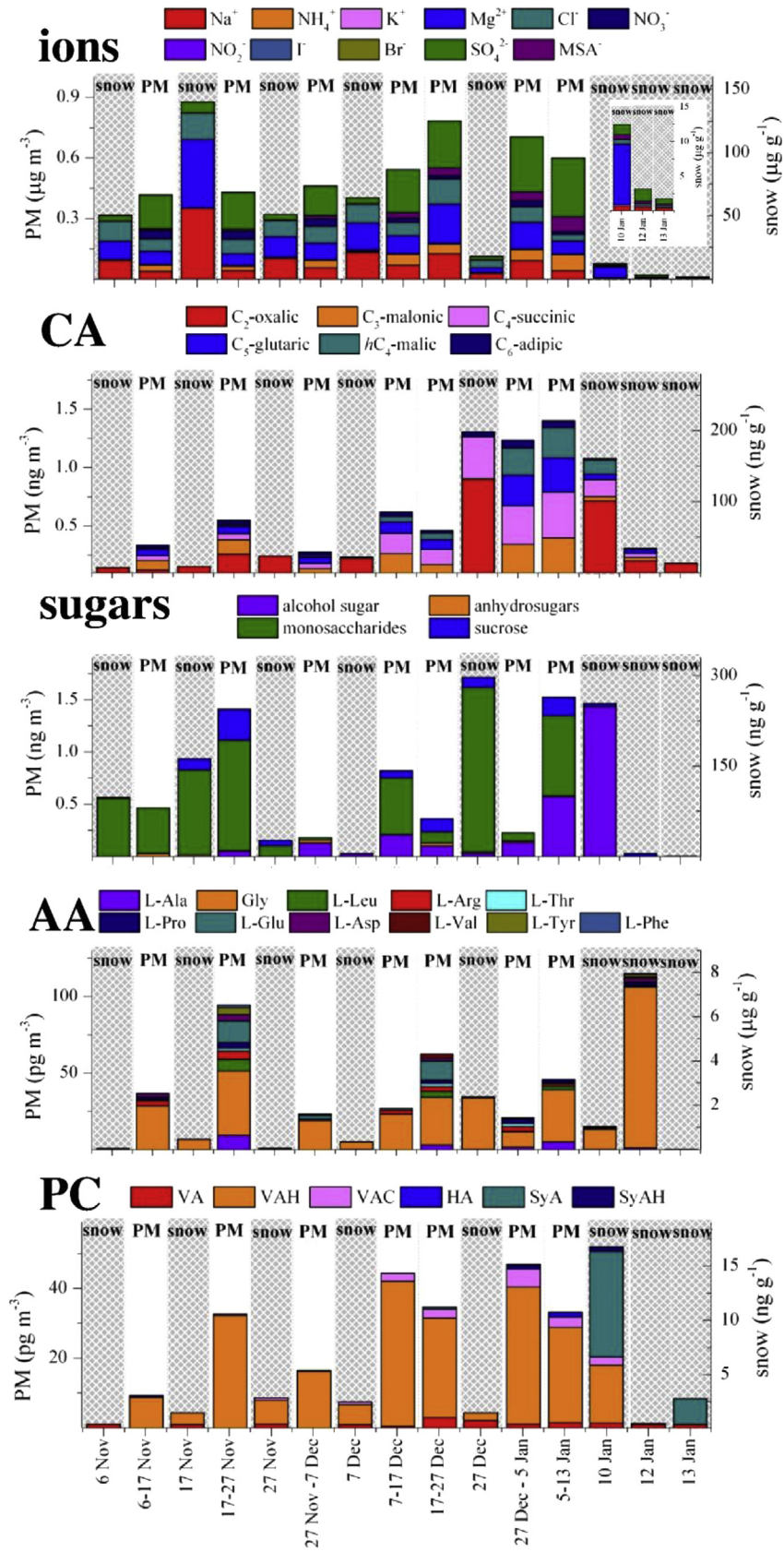


Fig. 1. Concentration trends of each class of compounds investigated in aerosol samples (PM) and snow samples. CA: carboxylic acids; AA: amino acids; PC: phenolic compounds.

the East-South-East direction (Fig. S9). The main source of these sea salt compounds presumed to be dry deposition of material coming from areas with frost flowers as a negative  $\text{nss-SO}_4^{2-}$  value (Fig. S10) was calculated for the 17 November snow samples (Wolff et al., 2003; Kaspari et al., 2005).

$\text{nss-SO}_4^{2-}$  concentrations increased at the beginning of the Antarctic summer (Fig. S10) because its biogenic source is phytoplankton blooms on the ocean surface (Minikin et al., 1998). The concentration of  $\text{nss-SO}_4^{2-}$  before (sample of 27 December), during (snow sample of 10 January) and after the snow fall event of the 10th of January (snow samples of 12 and 13 January) are comparable and show only a small decrease in the 13 January sample (Fig. S11). This observation suggests that wet deposition processes are negligible for this species, and seem to be independent of the accumulation rate due to inefficient scavenging of  $\text{nss-SO}_4^{2-}$  aerosols by Antarctic snow (Kreutz and Mayewski, 1999).

$\text{C}_2$ -oxalic acid was the main CA found in snow samples, while  $\text{C}_3$ -malonic,  $\text{C}_4$ -succinic and  $\text{C}_5$ -glutaric were the main CA in aerosol samples (Fig. 1). There are several possible reasons for this difference between aerosol and snow samples, such as: different evaporation rates, different particle size distributions, or different sources and snow chemistry. CA evaporation from the snow surface is unlikely due to their low volatility and high polarity. Low chain CA, such as  $\text{C}_2$  and  $\text{C}_3$  diacids can exist in the gas phase (Baboukas et al., 2000) but they should be adsorbed onto the snowpack surface more than  $\text{C}_4$  and  $\text{C}_5$  acids due to their polarity. The results in Fig. 1 support absorption on the snow surface because  $\text{C}_2$ -oxalic and  $\text{C}_3$ -malonic were the most abundant species in the snow samples. Deposition velocities of each CA should be similar because they are mainly distributed in the fine fraction (Fig. S4). Differences in their sources and/or snow chemistry are other factors that could influence the concentrations of CAs on the snow surface. Since CAs are water soluble, they are strongly influenced by precipitation events. We can observe higher concentrations of these compounds during snowfall (10 January snow sample) and low dilution effects after that event (12–13 January samples) (Fig. 1). Because  $\text{C}_2$ -oxalic acid is the end-product of several photochemical reactions (Kawamura et al., 1996a), it can be scavenged by both dry and wet deposition, as well as be generated by photochemical processes at the snow surface. In fact, higher concentrations of  $\text{C}_2$ -oxalic acid were found before snowfall in aged snow.

MS such as glucose were the main sugars present in the atmosphere in the first period of sampling campaign, while the concentration of sugar alcohols, such as mannitol and arabitol, increased as the Antarctic summer progressed with increased biological production. This atmospheric trend is also reflected in the snow composition; MS were the most abundant species in the snow samples during the first period, while sugar alcohols were scavenged from the air from 27 December onwards. During snowfall, mannitol was the main compound scavenged to the surface snow, but it underwent considerable dilution after the snow event (Fig. 1).

The main AA detected in aerosol and snow samples was glycine, the most stable of this compound class in the atmosphere (McGregor and Anastasio, 2001). An unclear correlation between the snow and aerosol concentration of glycine is shown in Fig. 1. The observation of an increase in glycine concentration in aged snow was comparable with a decrease in aerosol concentration: for example the decrease in aerosol samples between 27 November–7 December seems to be associated with an increase in the Gly concentration in 7 December snow sample (Fig. 1, Fig. S12). Dry deposition seems to be a negligible factor for the glycine in the snow because higher aerosol concentrations of Gly are not matched to an increase in snow concentrations for this amino acid. The glycine concentration increased after snowfall (8–11 January),

probably due to consecutive degradation of biological material at the snow surface, as seen in the 12 January snow sample (Fig. 1).

For PC, VAH was the dominant species in the aerosol samples while its oxidation product, VA, was significantly present in aged snow (Fig. 1). During snowfall, high concentrations of VAH were observed along with other PCs. However, a large decrease in these compounds was found over the subsequent sampling days. This behavior could be due both to a dilution effect and their semi-volatility, which influences the re-partition of these compounds between snow and the atmosphere. After snowfall VA and SyA, the oxidized forms of VAH and SyAH, were the main PCs present.

## 5. Conclusion

Ionic species, CA, sugars, AA and PC were detected in aerosol and surface snow samples collected at the coastal Italian base in Antarctica from November 2014 to January 2015. Characterization of water-soluble compounds in the aerosol showed that they accounted for about 66% of the  $\text{PM}_{10}$  mass concentration. From this two predominant sources were identified: 1) sea salt input, characterized by high concentrations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ; 2) biogenic input, suggested by the presence of organic compounds, such as AA, sugars and PC. This study on the WSOC aerosol composition was aimed at improving our understanding of the AA, sugars and PC in Antarctic aerosol, a topic that remains poorly studied.

This information was combined with the study of WSOC in surface snow, and is the first to quantify AA and sugars in this matrix. Ions that were mainly distributed in the coarse fraction of atmospheric aerosol, were also the most abundant compounds in snow samples, suggesting that the main air-snow transfer process was dry deposition. The composition of sugars in the snow reflected their aerosol composition. An increase in concentration of alcohol sugars, that are tracers of fungal spores in the atmosphere, was also found in surface snow, suggesting that they could also be markers for this source in climatic studies. AA were an important component of surface snow, but in addition to aerosol input, another possible source could be the decomposition of biological material on the surface, as demonstrated by high concentrations of AA after snowfall.

Investigation of the concentrations of water-soluble compounds in aerosol samples in Antarctica is hampered by their low concentrations, meaning aerosol has to be sampled for 10 days to obtain concentrations above the detection limits. This dramatically reduces the temporal resolution of any study. For this reason, further studies over subsequent Antarctic expeditions will be essential to improve the sample numbers so we can fully understand the applicability of these compounds in the study of ice cores for paleoclimatic investigations.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.05.098>.

## References

- Baboukas, E.D., Kanakidou, M., Mihalopoulos, N., 2000. Carboxylic acids in gas and particulate phase above the Atlantic Ocean. *J. Geophys. Res. Atmos.* 105, 14459–14471.
- Barbaro, E., Padoan, S., Kirchgeorg, T., Zangrando, R., Toscano, G., Barbante, C., Gambaro, A., 2017. Particle size distribution of inorganic and organic ions in coastal and inland Antarctic aerosol. *Environ. Sci. Pollut. Res. Int.* 24, 2724–2733.
- Barbaro, E., Zangrando, R., Kirchgeorg, T., Bazzano, A., Illuminati, S., Annibaldi, A., Rella, S., Truzzi, C., Grotti, M., Ceccarini, A., Malatesta, C., Scarponi, G., Gambaro, A., 2016. An integrated study of the chemical composition of Antarctic aerosol to investigate natural and anthropogenic sources. *Environ. Chem.*
- Barbaro, E., Kirchgeorg, T., Zangrando, R., Vecchiato, M., Piazza, R., Barbante, C., Garnbaro, A., 2015a. Sugars in Antarctic aerosol. *Atmos. Environ.* 118, 135–144.
- Barbaro, E., Zangrando, R., Vecchiato, M., Piazza, R., Cairns, W.R.L., Capodaglio, G., Barbante, C., Gambaro, A., 2015b. Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol. *Atmos. Chem. Phys.* 15, 5457–5469.
- Barbaro, E., Zangrando, R., Vecchiato, M., Turetta, C., Barbante, C., Gambaro, A., 2014. D- and L-amino acids in Antarctic lakes: assessment of a very sensitive HPLC-MS method. *Anal. Bioanal. Chem.* 406, 5259–5270.
- Bauer, H., Claeys, M., Vermeylen, R., Schueller, E., Weinke, G., Berger, A., Puxbaum, H., 2008. Arabitol and mannitol as tracers for the quantification of airborne fungal spores. *Atmos. Environ.* 42, 588–593.
- Facchini, M.C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E.D., de Leeuw, G., Martino, M., Woeltjen, J., O'Dowd, C.D., 2008. Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. *Geophys. Res. Lett.* 35.
- Fattori, I., Becagli, S., Bellandi, S., Castellano, E., Innocenti, M., Mannini, A., Severi, M., Vitale, V., Udisti, R., 2005. Chemical composition and physical features of summer aerosol at Terra Nova Bay and Dome C, Antarctica. *J. Environ. Monit.* 7, 1265–1274.
- Fu, P., Kawamura, K., Usukura, K., Miura, K., 2013. Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise. *Mar. Chem.* 148, 22–32.
- Fu, P.Q., Kawamura, K., Pavuluri, C.M., Swaminathan, T., Chen, J., 2010. Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation. *Atmos. Chem. Phys.* 10, 2663–2689.
- Graham, B., Mayol-Bracero, O.L., Guyon, P., Roberts, G.C., Decesari, S., Facchini, M.C., Artaxo, P., Maenhaut, W., Koll, P., Andreae, M.O., 2002. Water-soluble organic compounds in biomass burning aerosols over Amazonia - 1. Characterization by NMR and GC-MS. *J. Geophys. Res. Atmos.* 107.
- Hillamo, R., Allegrini, I., Sparapani, R., Kerminen, V.M., 1998. Mass size distributions and precursor gas concentrations of major inorganic ions in Antarctic aerosol. *Int. J. Environ. Anal. Chem.* 71, 353–372.
- Illuminati, S., Bau, S., Annibaldi, A., Mantini, C., Libani, G., Truzzi, C., Scarponi, G., 2016. Evolution of size-segregated aerosol mass concentration during the Antarctic summer at Northern Foothills, Victoria Land. *Atmos. Environ.* 125 (Part A), 212–221.
- Jickells, T.D., Kelly, S.D., Baker, A.R., Biswas, K., Dennis, P.F., Spokes, L.J., Witt, M., Yeatman, S.G., 2003. Isotopic evidence for a marine ammonia source. *Geophys. Res. Lett.* 30.
- Johnson, M.T., Bell, T.G., 2008. Coupling between dimethylsulfide emissions and the ocean-atmosphere exchange of ammonia. *Environ. Chem.* 5, 259–267.
- Jourdain, B., Legrand, M., 2002. Year-round records of bulk and size-segregated aerosol composition and HCl and HNO<sub>3</sub> levels in the Dumont d'Urville (coastal Antarctica) atmosphere: implications for sea-salt aerosol fractionation in the winter and summer. *J. Geophys. Res. Atmos.* 107.
- Kaspari, S., Dixon, D.A., Sneed, S.B., Handley, M.J., 2005. Sources and transport pathways of marine aerosol species into West Antarctica. *Ann. Glaciol.* 41, 1–9.
- Kawamura, K., Ikushima, K., 1993. Seasonal-changes in the distribution of dicarboxylic-acids in the urban atmosphere. *Environ. Sci. Technol.* 27, 2227–2235.
- Kawamura, K., Kasukabe, H., Barrie, L.A., 1996a. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations. *Atmos. Environ.* 30, 1709–1722.
- Kawamura, K., Sakaguchi, F., 1999. Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics. *J. Geophys. Res. Atmos.* 104, 3501–3509.
- Kawamura, K., Semere, R., Imai, Y., Fujii, Y., Hayashi, M., 1996b. Water soluble dicarboxylic acids and related compounds in Antarctic aerosols. *J. Geophys. Res. Atmos.* 101, 18721–18728.
- Keene, W.C., Maring, H., Maben, J.R., Kieber, D.J., Pszenny, A.A.P., Dahl, E.E., Izaguirre, M.A., Davis, A.J., Long, M.S., Zhou, X., Smoydzin, L., Sander, R., 2007. Chemical and physical characteristics of nascent aerosols produced by bursting bubbles at a model air-sea interface. *J. Geophys. Res. Atmos.* 112.
- Kreutz, K.J., Mayewski, P.A., 1999. Spatial variability of Antarctic surface snow glaciochemistry: implications for palaeoatmospheric circulation reconstructions. *Antarct. Sci.* 11, 105–118.
- Kuo, L.J., Louchouart, P., Herbert, B.E., 2011. Influence of combustion conditions on yields of solvent-extractable anhydrosugars and lignin phenols in chars: implications for characterizations of biomass combustion residues. *Chemosphere* 85, 797–805.
- Leck, C., Gao, Q., Rad, F.M., Nilsson, U., 2013. Size-resolved atmospheric particulate polysaccharides in the high summer Arctic. *Atmos. Chem. Phys.* 13, 12573–12588.
- McGregor, K.G., Anastasio, C., 2001. Chemistry of fog waters in California's Central Valley: 2. Photochemical transformations of amino acids and alkyl amines. *Atmos. Environ.* 35, 1091–1104.
- Medeiros, P.M., Conte, M.H., Weber, J.C., Simoneit, B.R.T., 2006. Sugars as source indicators of biogenic organic carbon in aerosols collected above the Howland Experimental Forest, Maine. *Atmos. Environ.* 40, 1694–1705.
- Minikin, A., Legrand, M., Hall, J., Wagenbach, D., Kleefeld, C., Wolff, E., Pasteur, E.C., Ducroz, F., 1998. Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation. *J. Geophys. Res. Atmos.* 103, 10975–10990.
- Modini, R.L., Harris, B., Ristovski, Z.D., 2010. The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA). *Atmos. Chem. Phys.* 10, 2867–2877.
- Narukawa, M., Kawamura, K., Li, S.M., Bottenheim, J.W., 2002. Dicarboxylic acids in the Arctic aerosols and snowpacks collected during ALERT 2000. *Atmos. Environ.* 36, 2491–2499.
- O'Dowd, C.D., De Leeuw, G., 2007. Marine aerosol production: a review of the current knowledge. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 365, 1753–1774.
- O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J., Putaud, J.P., 2004. Biogenically driven organic contribution to marine aerosol. *Nature* 431, 676–680.
- Sempere, R., Kawamura, K., 2003. Trans-hemispheric contribution of C-2-C-10 alpha, omega-dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions. *Glob. Biogeochem. Cycles* 17.
- Simoneit, B.R.T., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17, 129–162.
- Simoneit, B.R.T., Elias, V.O., 2001. Detecting organic tracers from biomass burning in the atmosphere. *Mar. Pollut. Bull.* 42, 805–810.
- Udisti, R., Becagli, S., Benassai, S., Castellano, E., Fattori, I., Innocenti, M., Migliori, A., Traversi, R., 2004. Atmosphere-snow interaction by a comparison between aerosol and uppermost snow-layers composition at Dome C, East Antarctica. *Ann. Glaciol.* 39, 53–61.
- Udisti, R., Dayan, U., Becagli, S., Busetto, M., Frosini, D., Legrand, M., Lucarelli, F., Preunkert, S., Severi, M., Traversi, R., Vitale, V., 2012. Sea spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions. *Atmos. Environ.* 52, 109–120.
- Ward, T.J., Hamilton, R.F., Dixon, R.W., Paulsen, M., Simpson, C.D., 2006. Characterization and evaluation of smoke tracers in PM: results from the 2003 Montana wildfire season. *Atmos. Environ.* 40, 7005–7017.
- Ward, T.J., Palmer, C.P., Bergauff, M., Jayanty, R.K.M., Noonan, C.W., 2011. Organic/elemental carbon and woodsmoke tracer concentrations following a community wide woodstove changeout program. *Atmos. Environ.* 45, 5554–5560.
- Wolff, E.W., Hall, J.S., Mulvaney, R., Pasteur, E.C., Wagenbach, D., Legrand, M., 1998. Relationship between chemistry of air, fresh snow and firn cores for aerosol species in coastal Antarctica. *J. Geophys. Res. Atmos.* 103, 11057–11070.
- Wolff, E.W., Rankin, A.M., Rothlisberger, R., 2003. An ice core indicator of Antarctic sea ice production? *Geophys. Res. Lett.* 30.
- Xu, G., Gao, Y., Lin, Q., Li, W., Chen, L., 2013. Characteristics of water-soluble inorganic and organic ions in aerosols over the Southern Ocean and coastal East Antarctica during austral summer. *J. Geophys. Res. Atmos.* 118, 13303–13318.
- Yttri, K.E., Dye, C., Kiss, G., 2007. Ambient aerosol concentrations of sugars and sugar-alcohols at four different sites in Norway. *Atmos. Chem. Phys.* 7, 4267–4279.
- Zangrando, R., Barbaro, E., Vecchiato, M., Kehrwald, N.M., Barbante, C., Gambaro, A., 2016. Levoglucosan and phenols in marine, coastal and inland Antarctic aerosols. *Sci. Total Environ.* 544, 606–616.
- Zangrando, R., Barbaro, E., Zennaro, P., Rossi, S., Kehrwald, N.M., Gabrieli, J., Barbante, C., Gambaro, A., 2013. Molecular markers of biomass burning in Arctic Aerosols. *Environ. Sci. Technol.* 47, 8565–8574.