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Amino acids in Antarctica: evolution and fate of marine aerosols

E. Barbaro[1,2], R. Zangrando[2], M. Vecchiato[2,3], R. Piazza[1,2], G. Capodaglio[1,2], C. Barbante[2], and A. Gambaro[1,2]

[1]Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca' Foscari, Calle Larga Santa Marta 2137, 30123, Venice, Italy
[2]Institute for the Dynamics of Environmental Processes CNR, Dorsoduro 2137, 30123, Venice, Italy
[3]University of Siena, Department of Physical Sciences, Earth and Environment, Strada Laterina, 8 53100 Siena, Italy

Correspondence to: E. Barbaro (barbaro@unive.it)

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Abstract

The chemical composition and size distribution of marine aerosols constitute an important parameter to investigate the latter's impact on global climate change. Amino acids are an important component of organic nitrogen in aerosols and have the ability to activate and act as cloud condensation nuclei, with important effects on the radiation balance.

In order to understand which physical and chemical transformations occur during transport processes, aerosol samples were collected during four different Antarctic austral summer campaigns.

The mean amino acids concentration detected at the Italian coastal base was $11 \, \text{pmol m}^{-3}$. The main components were fine fractions, establishing a local marine source. Once produced on the sea surface, marine aerosols undergo an ageing process, due to various phenomena such as coagulation, or photochemical transformations. This was demonstrated by using the samples collected on the Antarctic plateau, where the background values of amino acids (0.7 and $0.8 \, \text{pmol m}^{-3}$) were determined, and concentration enrichment in the coarse particles was observed.

Another important source of amino acids in marine aerosols is the presence of biological material, demonstrated through a sampling cruise on the R/V *Italica* on the Southern Ocean.

1 Introduction

Marine aerosols are among the most important natural aerosol systems at the global level, due to the oceans' extent (O'Dowd and De Leeuw, 2007). They play an important role in the Earth system, especially in climate and atmospheric chemistry, as they significantly contribute to the global aerosol burden and influence both direct and indirect radiative forcing as well as a variety of chemical processes (IPCC, 2007).

Knowledge of the chemical composition of these particles is crucial to better understand the mechanisms influencing climate change, due to the ability of these particles to act as cloud condensation nuclei.

Recently, the scientific community has shown particular interest in the organic composition of aerosols, as the latter contribute to a substantial portion of the marine aerosol mass, especially to the submicron size fraction (Bigg, 2007).

Several studies (Rinaldi et al., 2010; Facchini et al., 2008a, b) have demonstrated that the chemical composition of marine organic aerosols is a combination of different primary and secondary sources. Primary emissions result from the interaction of wind stress via bubble bursting processes at the ocean's surface, where the presence of phytoplankton can modulate the chemical and physical proprieties of marine organic aerosols (Kuznetsova et al., 2005). As for secondary organic aerosols, their production involves several mechanisms which have not yet been clarified (Vignati et al., 2010; Spracklen et al., 2008; Myriokefalitakis et al., 2010). However, Bates et al. (1992) demonstrated that the production of secondary marine organic aerosols is associated with biologically-driven emissions of organic compounds from phytoplankton. Lim et al. (2010) studied the role of aqueous chemistry in the formation of secondary organic aerosols, describing a number of photochemical reactions that occur in the atmosphere. A detailed understanding of these mechanisms is essential to quantify the role of marine aerosols in the functioning of the Earth system.

The organic marine fraction of marine aerosols contains water-soluble organic compounds (WSOC), which include numerous species of organic acids, amines, carbonyl compounds and amino acids (Saxena and Hildemann, 1996). Amino acids are ubiquitous compounds, and constitute an important component of the organic nitrogen content of aerosols (Ge et al., 2011). Several studies have determined amino acids concentrations in the condensed phase of aerosols (Mandalakis et al., 2010, 2011; Zhang and Anastasio, 2003), but also in rainwater (Mace et al., 2003a, b), in fog (Zhang and Anastasio, 2001), and in dew water (Scheller, 2001). Amino acids, being an important portion of organic aerosols, can influence the cloud formation or act as ice-forming

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nuclei due to their hygroscopicity (Szyrmer and Zawadzki, 1997; Wedyan and Preston, 2008). De Hann et al. (2009) have postulated that amino acids can contribute to the formation of new particles in the atmosphere. These compounds can also serve as a source of nutrients for marine ecosystems thanks to their high bioavailability (Zhang et al., 2002).

Several sources can affect the content of atmospheric amino acids. Matsumoto and Uematu (2005) describe how long-range transport influences the concentration of amino acids in the North Pacific Ocean, while an evident marine source was verified by Weydan and Preston (2008) in the South Atlantic Ocean. Amino acids can be detected in volcanic emissions (Scalabrin et al., 2012), but biomass burning has also been suggested as a possible source of these WSOC (Chan et al., 2005; Mace et al., 2003a).

The different types of amino acids in continental particles are thought to be produced by plants, pollen and algae, but also by fungi and bacteria spores (Zhang and Anastasio, 2003; Milne and Zika, 1993; Mace et al., 2003a; Scheller, 2001). The continental contribution was evaluated by Mace et al. (2003b), who distinguished the biogenic amino acids present in fine particles from the amino acids contained in anthropogenic coarse particles. Zhang and Anastasio (2002) identified livestock farming as the main source of amino acid ornithine in Californian aerosols. Near the inhabited continent, several sources could produce amino acids in the particle phase, although soil and desert dust probably are the most important sources of high concentrations of amino acids.

Due to their distance from anthropogenic and continental emission sources, polar regions are excellent natural laboratories to conduct studies on the behavior, evolution and fate of marine aerosols. In Antarctica, a continent surrounded by the Southern Ocean, long-range atmospheric transport of anthropogenic pollutants is minimal, whereas natural sources such as seawater provide the main contributions to marine aerosols. Aerosol measurements in Antarctica provide information on natural

background concentrations and processes, such as particle formation and growth (Bargagli, 2008; Bourcier et al., 2010; Gambaro et al., 2008).

The main aim of this study was to estimate how the amino acids produced from seawater surface were distributed in the size-segregated aerosols in Antarctica. Physical transformations of particles were also investigated after transport phenomena, where many physical and chemical processes occur. Four different Antarctic austral summer campaigns were conducted to pursue our investigation: in two consecutive field campaigns, aerosols were collected on the Antarctic plateau near the Italian–French base of Concordia Station; one sampling period was carried out at the Italian coastal base "Mario Zucchelli Station" (MZS); finally, shipboard aerosols were sampled on the R/V *Italica* on the Southern Ocean, near Antarctica.

The present study permits us to identify the main factors affecting particle amino acids concentrations, as well as the particle size in which the single amino acid is released from bubble bursting phenomena. The aerosols collected on the Antarctic plateau allowed to define the changes in amino acid composition that take place when marine aerosols get transported inland. A cascade impactor was used in the terrestrial base to investigate amino acids distribution on particles with a diameter below 10 μm, while a TSP (total suspended particles) sampler was employed on the ship in order to detect amino acids in particles with a diameter above 1 μm.

To our knowledge, this is the first investigation that considers the different composition of amino acids present and their particle-size distribution in Antarctic aerosols.

2 Experimental section

2.1 Sample collection

Aerosol samplings were carried out during four different Antarctic austral summer campaigns, in the framework of the "Progetto Nazionale di Ricerche in Antartide" (PNRA). Five aerosol samples were collected at the Italian base "Mario Zucchelli Station" (MZS),

from 29 November 2010 to 18 January 2011. At the Italian–French base "Concordia Station" (Dome C), four aerosol samples were collected from 19 December 2011 to 28 January 2012; finally, five airborne samples were obtained from 7 December 2012 to 26 January 2013. Amino acids were also determined in other seven samples retrieved on the Ross Sea (Antarctica) on the R/V *Italica* from 13 January to 19 February 2012 (Supplement Table S1). The sampling sites are shown in Fig. 1.

Aerosol samples in terrestrial bases were collected using a TE-6070, PM_{10} high-volume air sampler (average flow $1.21\,m^3\,min^{-1}$) provided with a Model TE-235 five-stage high-volume cascade impactor (Tisch Environmental Inc., Cleves, OH) equipped with a high-volume back-up filter (Quartz Fiber Filter Media $8'' \times 10''$) and with a $5.625'' \times 5.375''$ Slotted Quartz Fiber for collecting particle size range in the following range: 10.0–$7.2\,\mu m$, 7.2–$3.0\,\mu m$, 3.0–$1.5\,\mu m$, 1.5–$0.95\,\mu m$, 0.95–$0.49\,\mu m$, $< 0.49\,\mu m$. The sampling campaign lasted 10 days, with a total air volume of $\sim 15\,000\,m^3$ per sample.

During the oceanographic cruise, airborne aerosols were collected by means of a circular quartz fiber filter (quartz fiber filter (QFF) (SKC Inc., Eighty Four, To-13 model)) using a TE 5000 High Volume Air Sampler (Tisch Environmental Inc., OH).To avoid contamination from the ship's exhaust, air samples were automatically controlled by a wind sector, in order to start sampling only when the relative wind direction changed from -135 to $135\,°C$ of the bow, and when the relative wind was above $1\,m\,s^{-1}$. Collection was scheduled to last about five days, but this time frame was subject to variations, due to the wind selector and to cruise events. The airborne sampling volumes varied between 511 and $2156\,m^3$. The track chart is reported in Supplement Fig. S1.

All filters were pre-combusted ($4\,h$ in a $400\,°C$ in a muffle furnace), wrapped in two aluminum foils before sampling, and stored in aluminum at $-20\,°C$ after sampling and until analysis. Blank samples were collected by loading, carrying and installing the filter holder in the instrument with the air pump closed.

During the austral summer campaign of 2010–2011, the sampling site was at the Faraglione Camp ($74°42'\,S$–$164°06'\,E$), about $3\,km$ south of the MZS in Victoria Land.

The site is a promontory at 57 m a.s.l. It was chosen because it is located in a valley that is separated from the main station area by a hill, and pollution from the research station is therefore negligible.

During the austral summers of 2011–2012 and 2012–2013, the sampling site was in the East Antarctic plateau (75°06′ S–123°20′ E), about 1 km south-west of the Dome C buildings, upwind of the dominant wind (from south-west).

2.2 Sample processing

In order to avoid contamination from laboratory air particles and from the operator, samples were handled under a laminar flow bench (class 100). The same pre-analytical protocol used for phenolic compounds determination (Zangrando et al., 2013) was applied to identify amino acids in Antarctic samples. This unique procedure permits to determine a number of compounds in a single precious sample. Each quartz fiber support was cut in half using stainless steel scissors that were previously washed with methanol. Filters were broken into small pieces, placed into 50 mL conical flasks, and spiked with internal standard solutions.

Slotted quartz fiber supports and circular quartz fiber filters were spiked with 100 µL of isotopically-labelled ^{13}C amino acid standard solutions (with concentrations ranging between 2 and 3 µg mL^{-1}) and extracted with 5 and then 2 mL of ultrapure water by ultrasonication. This operation was carried out by adding ice into an ultrasonic bath in order to avoid the degradation or evaporation of the compounds. 400 µL of internal standard solution were spiked into small pieces of back-up filter, which was extracted with 25 and then 5 mL of ultrapure water.

The extracts were combined and filtered through a 0.45 µm PTFE filter in order to remove particulate and filter traces before instrumental analysis.

2.3 Instrumental analysis

The enantiomeric determination of amino acids in the aerosol samples was conducted using a method previously developed by Barbaro et al. (2014). An Agilent 1100 Series HPLC Systems (Waldbronn, Germany; with a binary pump, vacuum degasser, autosampler) was coupled with an API 4000 Triple Quadrupole Mass Spectrometer (Applied Biosystem/MSD SCIEX, Concord, Ontario, Canada) using a TurboV electrospray source that operated in positive mode by multiple reaction monitoring (MRM).

Chromatographic separation was performed using a $2.1\,mm \times 250\,mm$ CHIROBIOTIC TAG column (Advanced Separation Technologies Inc, USA) with a mobile phase gradient elution consisting of ultrapure water with 0.1 % formic acid (eluent A) and methanol with 0.1 % formic acid (eluent B).

The binary elution gradient program at a flow rate of $0.2\,mL\,min^{-1}$ was used as follows: 0–15 min, isocratic elution with 30 % of eluent B; 15–20 min, gradient from 30 to 100 % B; 20–25 min washing step with 100 % of eluent B; 27–30 min, equilibration at 30 % eluent B. The injection volume was 10 µL.

In this work, the internal standard and isotope dilution methods were used for the quantification of amino acids, and the results were corrected by evaluating instrumental response factors.

Reagents and materials used for this study and the quality control are reported in the Supplement.

2.4 Back-trajectory calculation and satellite imagery

Backward air trajectories arriving at MZS, Dome C and R/V *Italica* were computed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion models (Draxler and Rolph, 2013). The meteorological data used for computing all the backward trajectories were the NCEP/NCAR Global Reanalysis Data. For MZS data, a vertical velocity model was used as vertical motion while isoentropic

model was employed for the analysis of Dome C air masses, as suggested by Stohl et al. (2010).

240 h normal back-trajectories beginning 500 m a.g.l. (agl) at MZS and Dome C were calculated during each sampling campaign period. Four runs were computed for every sampling day starting every six hours and the resulting trajectories were mean-clustered into 6 groups.

For the oceanographic cruise, trajectory matrices were performed in order to simulate the ship's itinerary. In this case, for each 24 h sampling event, 5 day backward trajectories were computed.

The data related to chlorophyll were obtained via an Aqua/MODIS NASA satellite continually orbiting the globe (http://neo.sci.gsfc.nasa.gov/).

3 Results and discussion

3.1 Free amino acid determination in coastal area

Thirty-six amino acids were investigated in the particulate matter collected at Faraglione Camp near the coastal Italian base MZS. Five samples were collected between 29 November 2010 and 18 January 2011 with a cascade impactor in order to evaluate the dimensional distribution of amino acids in the coastal airborne samples (Fig. 2).

Nine L-amino acids (L-Ala, L-Asp, L-Arg, L-Glu, L-Phe, L-Pro, L-Tyr, L-Thr) and glycine (Gly) had concentrations higher than the method detection limits (MDLs) (Supplement Tables S3 and S4), while all D-amino acids were below MDLs, probably due to a negligible presence of bacteria (Wedyan and Preston, 2008; Kuznetsova et al., 2005).

The total concentration of amino acids, calculated from the sum of their six size distributions in all aerosol samples, have a median value of 5 pmol m^{-3} and an average

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value of 11 pmol m^{-3}, due to the higher amino acid concentration in the first sample, as shown in Fig. 2.

The average concentration of amino acids determined in this study was very similar to those found in the literature for marine aerosols in remote areas. Matsumoto and Uematsu (2005) reported an average free amino acid concentration of 10.7 pmol m^{-3} in the Pacific Ocean, while Gorzelska and Galloway (1990) and Wedyan and Preston (2008) observed a mean of 3 and 20 pmol m^{-3} respectively in the Atlantic Ocean. Scalabrin et al. (2012) have determined an average concentration of 2.8 pmol m^{-3} using the same sampling method at the Arctic coastal station.

However, higher average concentrations of amino acids were individuated in the Mediterranean areas. Barbaro et al. (2011) determined a mean value of 334 pmol m^{-3} in the Venice Lagoon (Italy); Mandalakis et al. (2010, 2011) found 166 and 172 pmol m^{-3} respectively in the Eastern Mediterranean and in Greece; in the austral hemisphere, Mace et al. (2003b) have performed several studies in Tasmania (Australia), finding amino acid concentrations that ranged between 15 and 160 pmol m^{-3}.

In the present work, the dominant compounds were Gly and Arg, which together constituted 66–85 % of the total amino acid content. Gly and Arg had different proportions in the five samples, while the others compounds presented similar compositions in all the samples, with average percentages of 9 % for Glu, 7 % for Ala, 5 % for Thr, 4 % for Asp, 2 % for Val while 1 % for other amino acids (Phe, Tyr and Pro).

The first sample collected between 29 November and 9 December had a higher concentration of Arg (74 %), while Gly was 11 %. In contrast, in the other samples, Gly was the dominant compound, with a percentage between 48 to 56 %, while arginine was about 18 %.

Scheller (2001) has demonstrated that high quantities of Arg were closely linked with plant growth, but the cluster means backward trajectories (Supplement Fig. S2) conducted for our samples shows that air masses come from open-sea regions (1 %) and principally from the internal Antarctic continent (99 %), characterized by their lack of vegetation. These considerations suggest that local marine influence was the main

source of amino acids in MZS and that the concentration of atmospheric amino acid was linked to the primary production in the sea, as also confirmed by other studies (Meskhidze and Nenes, 2006; Vignati et al., 2010; Yoon et al., 2007; Mueller et al., 2009).

The main source of Arg in the aerosols collected in the coastal Antarctic station MZS was probably linked to the urea cycle in diatoms (Bromke, 2013).

The MODIS data (Fig. 3) show higher chlorophyll concentration during the period referred to the first sample, while a strong decrease in the biomass production index was observed during the remaining sampling time. This relationship between marine primary production and Arg concentration suggests that this amino acid may have a marine biological origin and that its concentration is closely linked to algae growth.

Meteorological conditions play an important role in the processes of aerosol formation. Indeed, the first sampling period (29 November–9 December) was characterized by temperatures ranging between -10 and $-1.5\,^\circ$C, while in the next sampling period, the temperature was always above $-2\,^\circ$C (PNRA-ENEA, 2014). Studies conducted on the sea microlayer (Knulst et al., 2003; Grammatika and Zimmerman, 2001) have established that air temperature $< -5\,^\circ$C create surface slurries which may result in the expulsion of salts and particulate organic matter. In such conditions, near-surface turbulence was increased, leading to an increase of material in the microlayer, where bubbles also actively contributed as transport mechanisms. Leck and Bigg (2005) have shown that the main occurrences of fine aerosol formation in the atmosphere were observed during periods of lead melting and refreezing. In fact, the first sample was collected when melting and refreezing of pack ice occurred, and we have observed the highest concentration of total amino acid in the fine aerosols.

The local marine source of the aerosols collected in the coastal station MZS was also confirmed by the distribution of amino acids in the different particle fractions. Figure 2 shows that the highest concentration of amino acids (11 342 fmol m^{-3} as mean value, 98 %) was generally observed in fine particles ($< 1\,\mu$m), while a much lower average value of 265 fmol m^{-3} (2 %) for total amino acid concentration was observed in the

coarse fraction (> 1 µm). Our experimental evidence corresponds to the enrichment of WSOC (e.g. amino acids) in sea spray submicron particles described by O'Dowd et al. (2004) and Keene et al. (2007). WSOC were present in all aerosol size fractions, but the greatest enrichment was associated with the smallest size fraction (0.1–0.25 µm) (Keene et al., 2007; Facchini et al., 2008b; Modini et al., 2010). The correlation between the increased enrichment of aerosol organic fraction and the decrease of particles dimension is in agreement with the thermodynamic prediction of bubble bursting processes under conditions in which the ocean surface layer becomes concentrated with surfactant material, which, in addition to inorganic salts, can be incorporated into sea spray drops (Oppo et al., 1999).

3.2 Free amino acid determination in remote continental area

The study of "background aerosols" is very important to estimate the impact of anthropogenic sources on the atmosphere and to study the natural phenomena that occur in atmospheric aerosols. Dome C Station is situated on the ice sheet in the Eastern Antarctic plateau, where the only possible anthropogenic contamination can come from the station itself, the airplane and the traverse used to supply it. This location is ideal for studying the chemical composition of "background" aerosols.

In this remote area, our samples were collected during two consecutive austral summer field campaigns (19 December 2011–28 January 2012 and 7 December–26 January 2013) in order to evaluate the size-distribution of amino acids concentration and the variability between two different years.

In this sampling site, several studies (Jourdain et al., 2008; Becagli et al., 2012; Udisti et al., 2012; Fattori et al., 2005) were carried out to investigate the distribution of inorganic compounds and of a few organic molecules (e.g. methansulfonic acid). However, the amino acids pattern had not been studied yet.

Figure 4 shows the concentrations of amino acids for both field campaigns, demonstrating the similarity between the trends and compositions of the analyzed compounds.

Ten amino acids (L-Ala, L-Arg, L-Asp, L-Glu, L-Leu, Gly, L-Phe, L-Thr, L-Tyr, L-Val) had concentrations above MDLs (Supplement Tables S3 and S4) in all samples collected in both field campaigns. The concentration of D-amino acids was always below MDLs, as also reported in our coastal results.

5 Gly, L-Asp and L-Ala were the major amino acid compounds, which together accounted for about 80 % of the total amino acid content.

The total average concentrations of these amino acids, obtained from the sum of the amino acids concentrations in all stage sampled, were respectively 0.8 and 0.7 pmol m^{-3} for the 2011–2012 and 2012–2013 austral summer Antarctic fields
10 (Fig. 4). To our knowledge, these mean concentrations were the lowest concentrations detected in all investigated areas (Milne and Zika, 1993; Scalabrin et al., 2012; Mace et al., 2003b; Kuznetsova et al., 2005; Matsumoto and Uematsu, 2005; Wedyan and Preston, 2008; Mandalakis et al., 2010, 2011; Barbaro et al., 2011; Gorzelska and Galloway, 1990), confirming that this type of aerosol characterization describes the amino
15 acids concentration in very aged "background aerosols".

The background profile of amino acids was altered by the higher concentrations in the coarse fraction 1.5–0.95 µm of the sample collected from 27 December 2012 to 6 January 2013 (Fig. 4b). Having evaluated the wind roses for each sample in the two summer field campaigns, we consider that these samples were the only ones to be
20 contaminated by human activities at the Dome C station (Supplement Fig. S3).

A prominent marine source was revealed by the cluster means backward trajectories analyses analysis of all the samples collected during both austral summer campaigns (Supplement Figs. S4 and S5). During the Antarctic austral summer, the surface inversion over the polar ice cap is relatively weak and aerosols produced on the ocean's
25 surface and transported through the upper troposphere can be easily mixed down to the surface (Cunningham and Zoller, 1981). There are also some mechanisms of transport from the lower stratosphere to the upper troposphere near the coast of the Antarctic continent. The materials returning to different sources can be mixed into the upper troposphere, and this air generally descends over the polar plateau, thanks also

to the cooling of the latter's surface. During the summer, there is a continuous flux of air from the upper troposphere (Cunningham and Zoller, 1981; Stohl and Sodemann, 2010).

The analysis of the size distribution of amino acids and of air masses (Figs. 4, S4 and S5 of the Supplement) permits us to identify the source of aerosols and several mechanisms undergone by these aerosols during long-range transport. Our results suggest that amino acids were produced in the fine particles on the surface of the Southern Ocean from bubble bursting processes. The air masses subsequently persisted into the upper troposphere over the continent for some days before descending onto the ice sheet. These fine aerosol particles can grow even further during the ageing process, by condensation of molecules from the gas phase, by collision of small and large particles (coagulation) (Petzold and Karcher, 2012; Roiger et al., 2012) or because of the ice-nucleting abitility of amino acids (Szyrmer and Zawadzi, 1997). The concentration of amino acids in the coarse particles of aerosols collected at Dome C had average values of 420 fmol m^{-3} (Fig. 4) for both field campaigns, while our coastal data had a mean concentration of 264 fmol m^{-3} (Fig. 2). This enrichment in the coarse fraction can be explained by the ageing of the aerosols.

The composition of aerosols may change during long-range transport, due to the production and destruction of species via photochemical reactions. McGregor and Anastasio (2001) describe amino acids as highly reactive species in the atmosphere. However, in the upper atmosphere, the chemical processes take place at slower rates than in the boundary layer (Roiger et al., 2012). Milne and Zika (1993) have verified that amino acids are destroyed via reactions with photochemically formed oxidants such as hydroxyl radical, to form products such as ammonium, amides and keto-acids. In aqueous-phase aerosols, glyoxal can react with amino acids, leading to scavenging processes (De Haan et al., 2009). Recent studies related to organic aerosol growth mechanisms (Maria et al., 2004) have underlined that the oxidation process, which is a removal mechanism for hydrophobic organic compounds, is slower in larger carbonaceous aerosols.

The aerosols collected at Dome C station were characterized by the prevalence of amino acids in the back-up filters ($< 0.45\,\mu$m). However, the amino acids fraction in the coarse particles represented a higher percentage (13–23 %) than that of the aerosols generated near the source. In the present work, we have observed only 2 % of amino acids in the coarse particles at the MZS station near the aerosols source.

This evidence suggests that hydrophobic amino acids present in the coarse particles are less reactive. Our hypothesis is confirmed by the behavior of Ala. Ala is classified as hydrophobic (Pommie et al., 2004) and its average concentration for the coarse fraction at Dome C was 70 fmol m^{-3}, the same value quantified in the coarse fraction in the MZS samples. This indicates that the coagulation processes with the relative increase of Ala concentration in larger particles are probably together with slow oxidation processes. Thanks to this phenomenon, Ala significantly contributes to the amino acid content in these "background aerosols".

Depending on the physicochemical proprieties of amino acids, an "hydropathy" index can be estimated, as suggested by Pommie et al. (2004). Amino acids can be divided into hydrophilic (Asp, Hyp, Glu, Asn, Lys, Gln, Arg), hydrophobic (Ala, Val, Leu, Ile, Met, Phe) and neutral (Gly, Pro, Ser, Thr, Tyr, Hys), in order to evaluate the contribution of each class for the aerosols collected in the three different field campaigns.

Figure 5 shows that hydrophilic components were predominant in marine aerosols released into the atmosphere, while hydrophobic compounds considerably increased in the aerosols collected at the continental station. The low abundance of hydrophobic amino acids in coastal aerosols was observed also by Mandalakis et al. (2011), and is probably caused by their lower tendency to dissolve in the aqueous particles contained in coastal aerosols. This classification permits to hypothesize that a higher content in hydrophilic amino acids can reflect a higher water content in the aerosols. This is a very important indication, because amino acids can be involved in cloud formation, behaving as ice-nuclei activators and affecting the balance of atmospheric radiation (Mandalakis et al., 2011; Szyrmer and Zawadzki, 1997).

With regard to the acid-base proprieties of amino acids, some differences can be observed between two different types of aerosols. As described above, the dominant amino acid in the MZS aerosols was Arg, which considerably contributed to the percentage of base compounds (53 %). Neutral components, which represented an important percentage (40 and 68 % for coastal and internal aerosols respectively), were heavily influenced by the presence of Gly. This amino acid is commonly present in large quantities in the aerosols because of a very low atmospheric reactivity (half time of 19 days) (McGregor and Anastasio, 2001) and is usually considered an indicator of long-distance aerosol transport (Barbaro et al., 2011; McGregor and Anastasio, 2001).

Figure 4 shows that the concentration of amino acids for the 2011–2012 austral summer Antarctic campaign was higher than the values reported for the 2012–2013 Antarctic campaign and the Fig. 5 underlines that the main difference between two campaign is the percentages of hydrophilic and neutral amino acids. We suggests that the transport processes of air masses was the main cause of these variations because the time spent from these air masses inland in the 2011–2012 summer was about 36 h (Supplement Fig. S4) while in 2012–2013 between 4 and 7 days (Supplement Fig. S5). A longer time inland can be improved chemical and photochemical reactions, decreasing the concentration of amino acids and modifying the composition where the more stable Gly (neutral component) became the main compound (Fig. 5).

The acid compounds (Asp and Glu) content showed a mismatch between aerosols in the two different stations: the negligible percentage in the coastal MZS (7 %) was in contrast with the important content in the aerosols of Dome C (33 and 26 % respectively for the two consecutive field campaigns).

These evidence can be explained using a study conducted by Fattori et al. (2005) in the Dome C aerosol, where high acidity content was verified. High concentrations of hydrochloric, nitric and sulfuric acids composed the aerosol fine fraction, promoting many acid-base atmospheric reactions with neutralization process but also with an increasing of acid component as demonstrated in our studies.

3.3 Free amino acids during an oceanographic cruise

Measurements of free amino acids in aerosols were conducted on the Southern Ocean on the R/V *Italica* from 13 January to 19 February 2012 (Fig. 6). The sampling was performed using a TSP sampler that collected particles with a diameter above 1 μm.

The first and second samples represented the track between New Zealand (from Littleton harbor) and the MZS (Antarctica), while the sixth and last samples characterized the journey between Antarctica and New Zealand. Samples 3, 4 and 5 were collected on the Ross Sea near the Antarctic continent (Fig. S1 of the Supplement).

Five L-amino acids (L-Asp, L-Arg, L-Glu, L-Phe, L-Pro) and Gly were present in the samples, while other L-amino acids and D-amino acids had concentrations below MDLs (Supplement Table S2).

The total concentrations in free amino acids varied between 2 and 12 $\mathrm{pmol\,m^{-3}}$.

The first and last samples had the highest concentrations in amino acids (Fig. 6), and their relative sampling periods were characterized by temperatures ranging between -1 and $18\,^{\circ}\mathrm{C}$ (sample 1), in contrast with the remaining sampling periods that were always below $-1\,^{\circ}\mathrm{C}$, with the lowest value at $-8\,^{\circ}\mathrm{C}$ (sample 4). While higher temperatures can facilitate metabolic processes and accelerate atmospheric chemical reactions, they can also promote bubble bursting from the sea surface. This could be the main source of amino acids in our on-ship samples, as also demonstrated by the back-trajectory analysis (Supplement Fig. S6a–g), where we have demonstrated only a marine influence (Kuznetsova et al., 2004).

The concentration of amino acids was closely influenced by sea conditions during the sampling. As reported in the field report (Rapporto sulla campagna Antartica, 2012), the navigation from New Zealand to the ice-pack region was characterized by winds always above 30 knots, with maximum values at 60 knots and 12 m of wave height, determining the higher concentration of amino acids in the first samples (12 $\mathrm{pmol\,m^{-3}}$). Along the same track, but under better sea conditions (sample 7), we observed a slight reduction in the concentration of amino acids (8 $\mathrm{pmol\,m^{-3}}$).

These values were very similar to those reported by Matsumoto and Uematsu (2005) in the Pacific Ocean and to those by Wedyan and Preston (2008) and Gorzelska and Galloway (1990) in the Atlantic Ocean.

The lowest concentrations were observed in samples 2 and 6, probably due to the fact that they were collected far from Oceania and from the Antarctic coast, in an area characterized by a strong presence of pack ice and by temperatures below $-1\,^{\circ}$C, and where the bubble bursting process was reduced.

The samples collected near the Antarctic coast (samples 3, 4 and 5) were the most interesting ones because the results could be compared with the amino acids values detected in the coastal station MZS.

The average concentration in the samples collected on the Ross Sea was 3.5 pmol m^{-3}, about half of the values detected in our Southern Ocean samples. Such values seem similar to the concentrations observed in the aerosols collected at the MZS station (median 5 pmol m^{-3}). However, this comparison is irrelevant: for the sampling campaign at the MZS, a cascade impactor was used to collect aerosol samples with particle-size below 10 μm, whereas the data collected during the cruise regarded aerosols with a particle diameter above 1 μm. However, a comparison is possible if the back-up and the fifth slotted filters are excluded.

In the MZS aerosols, the median value of the amino acids concentration into the aerosols with particle size between 0.95 and 10 μm was 1 pmol m^{-3} and this concentration was lower than the ones measured in the cruise's aerosols (3.5 pmol m^{-3}). Aerosols with a diameter above 10 μm, collected with a TSP sampler, can be the main source of amino acids in the samples collected on the R/V *Italica*.

Biological material present in the atmosphere can have a variety of sizes: the diameter of pollens typically varies between 17–58 μm (Stanley and Linskins, 1974); that of fungal spores between 1–30 μm (Gregory, 1973); that of algal spores between 15–120 μm (Coon et al., 1972); that of bacteria between 0.25–8 μm (Thompson, 1981); finally, viruses have diameters that are typically less than 0.3 μm (Taylor, 1988).

The back-trajectory analysis (Supplement Fig. S6c–e) demonstrated that air masses come from inland Antarctica, where no vegetation is present. For this reason, the biological materials that influenced the concentration of amino acids in shipboard aerosols can probably be attributed to algal spores or bacteria. D-amino acids are good biomarkers of bacteria, because some of them are contained in the peptidoglycan membrane (Kuznetsova et al., 2005; Wedyan and Preston, 2008), but in our shipboard samples no relevant concentration of D-amino acids were observed, indicating that the presence of bacteria was negligible.

In these samples, the presence of algal spores was also confirmed by the detection of Pro at 4 % (mean value) of the total concentration of amino acids. Fisher et al. (2004) measured the relevant concentration of Pro in ascospores, demonstrating that this amino acid can be used to identify the presence of spores presence in aerosols. In the MZS aerosols, the presence of spores (typical diameter 15–120 μm) could not be evaluated because the sampler used eliminated the particles above 10 μm. This is probably the reason why Pro concentration was always below MDLs.

Asp was detected in only one sample (sample 5), with a concentration of 502 fmol m^{-3}. This value is very similar to those measured in the two field campaigns above the Antarctic plateau, considering only the slotted filter above 1 μm (446 e 382 fmol m^{-3} respectively for the austral summer field campaigns 2011–2012 and 2012–2013). The back-trajectory analysis (Supplement Fig. S6e) demonstrated that, in the air mass coming from the plateau, aspartic acid was a dominant component of amino acid content.

In the aerosols collected during the cruise, the Arg concentration was very low because the sampling conducted in the R/V *Italica* during the austral summer 2012 excluded fine particles, whereas Arg was one of the most abundant compounds observed in the coastal station.

The neutral components (77 %) gained influence in the shipboard data, for which the particles with diameter > 1 μm were considered. Gly was the dominant component, with concentrations ranging between 1.5 and 4.1 pmol m^{-3}. A very low percentage of

hydrophobic amino acids (2 %) characterized the aerosols collected on the ship, probable due to the major incidence of the local source in the amino acids content.

4 Conclusions

This first study on the distribution of Antarctic amino acids permitted to identify the marine source of aerosols and to study the ageing of aerosols.

Marine emissions of fine particles occurred via bubble bursting processes on the surface of the Southern Ocean. Instead, an enrichment of amino acids in coarse particle was occurred during the "ageing" process as verified in Dome C station. Numerous photochemical events may contribute to decreasing the concentration in amino acids in the fine mode, but the chemical reactions were faster for hydrophilic compounds than for hydrophobic ones, as suggested by Ala enrichment in the aged aerosols.

The study of aerosols with diameter $> 10\,\mu m$ indicated that bubble bursting processes can also emit microorganisms composed by a higher number of neutral amino acids.

The Supplement related to this article is available online at doi:10.5194/acpd-14-17067-2014-supplement.

Author Contribution

E. Barbaro, M. Vecchiato and R. Zangrando designed the experiments, performed the HPLC-MS analyses, and elaborated the data. A. Gambaro and C. Barbante were the principal investigators of the project that supported this work. All the authors have helped in the results discussion and collaborated in writing of the article.

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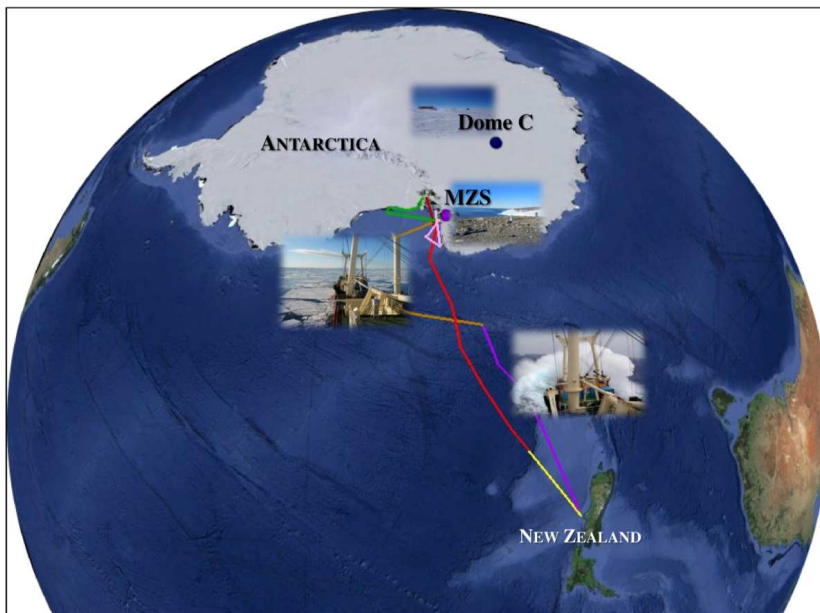
Figure 1. The sampling sites: the Italian base "Mario Zucchelli Station" (MZS) (74°42′ S–164°06′ E), the Italian–French base "Concordia Station" (Dome C) (75°06′ S–123°20′ E) and the track chart of the R/V *Italica*.

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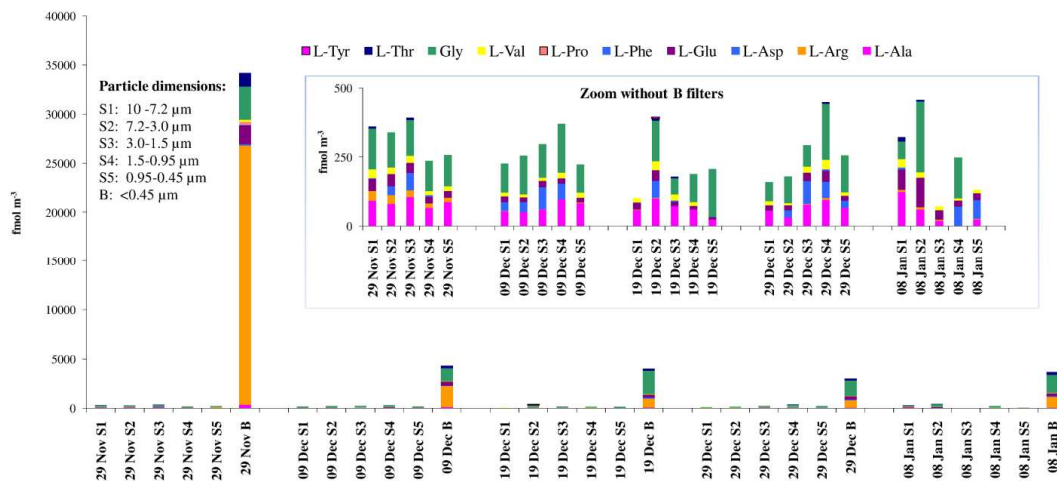
Figure 2. Amino acid size distribution in the samples collected during the austral summer 2010–2011 at the Mario Zucchelli Station (Antarctica).

Figure 3. Distribution of chlorophyll concentrations in the Ross Sea for each sampling period obtained through Aqua/MODIS NASA satellite.
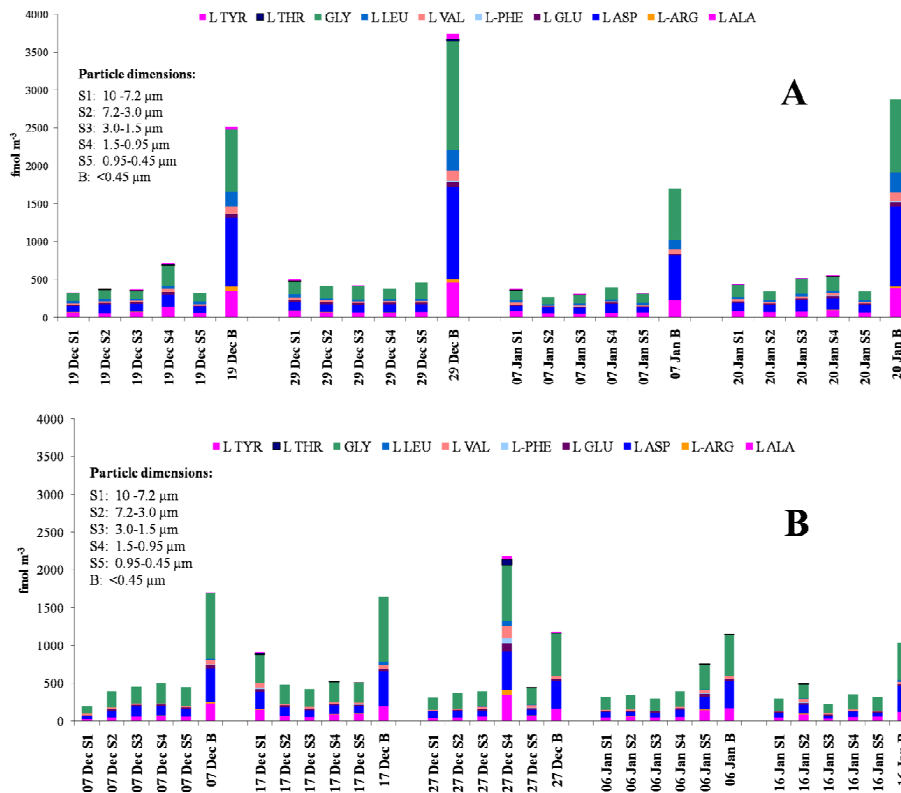
Figure 4. Size distributions of amino acids concentration in the samples collected during the austral summer 2011–2012 **(A)** and during the austral summer 2012–2013 **(B)** at the Italian French base "Concordia Station" (Dome C).
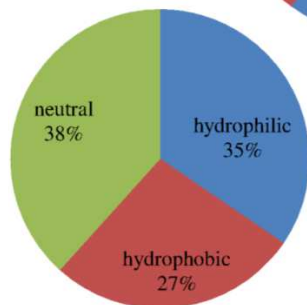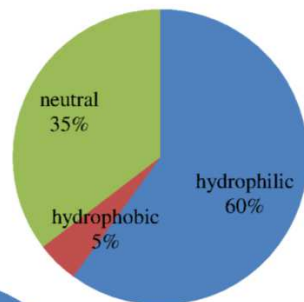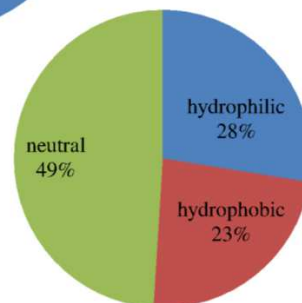
Figure 5. Comparison between theme an percentages of hydrophilic, neutral and hydrophobic contributions of the aerosols sampled at the Mario Zucchelli Station and at Dome C.

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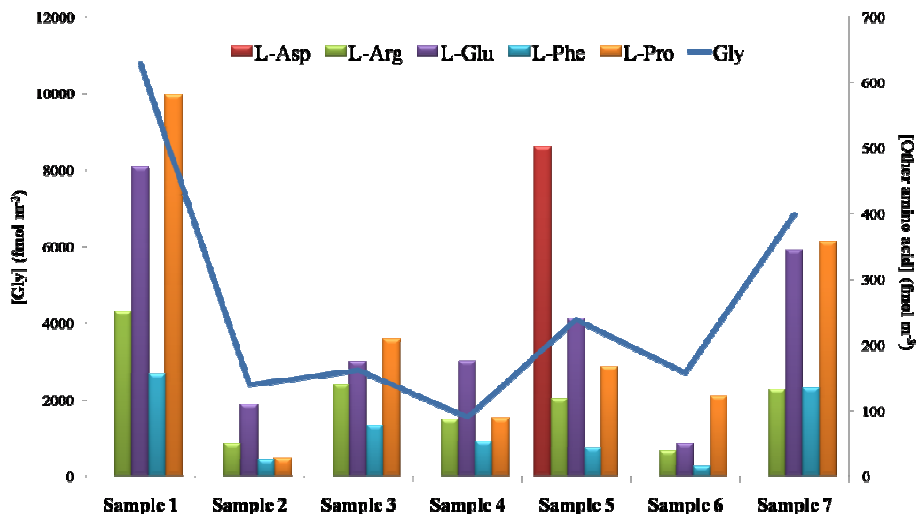Printer-friendly Version

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Figure 6. Amino acid distribution in the aerosols sampled on the R/V *Italica* during the oceanographic cruise on the Southern Ocean during the austral summer 2012.