



Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol

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Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol

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Abstract

To investigate the impact of marine aerosols on global climate change it is important to study their chemical composition and size distribution. Amino acids are a component of the organic nitrogen in aerosols, particles containing amino acids have been found to be efficient ice nuclei.

The main aim of this study was to investigate the L- and D-free amino acid composition as possible tracers of primary biological production in Antarctic aerosols from three different areas: two continental bases, Mario Zucchelli Station (MZS) on the coast of the Ross Sea, Concordia Station at Dome C on the Antarctic Plateau, and the Southern Ocean near the Antarctic continent. Studying the size distribution of amino acids in aerosols allowed us to characterize this component of the water-soluble organic carbon (WSOC) in marine aerosols near their source and after long-range transport. The presence of only free L-amino acids in our samples is indicative of the prevalence of phytoplanktonic material. Sampling at these three points allowed us to study the reactivity of these compounds during long-range transport.

The mean total amino acid concentration detected at MZS was 11 pmol m^{-3} , a higher percentage of amino acids were found in the fine fraction. The aerosol samples collected at Dome C had the lowest amino acid values (0.7 and 0.8 pmol m^{-3}) and the coarse particles were found to be enriched with amino acids compared to the coastal site. The amino acid composition had also changed suggesting that physical and chemical transformations had occurred during long range transport.

During the sampling cruise on the R/V *Italica* on the Southern Ocean, high concentrations of amino acids were found in the total suspended particles, this we attribute to the presence of intact biological material in the sample.

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1 Introduction

The organic composition of marine aerosols is particularly interesting as it contributes a substantial portion of the aerosol mass, especially in the submicron size fraction (Bigg, 2007). The study of marine aerosols is of interest as anything that can change their size, composition or concentration in the atmosphere may have an impact on the Earth's climate, since as noted by O'Dowd et al. (2004) "Marine aerosol contributes significantly to the global aerosol load and consequently has an important impact on both the Earth's albedo and climate". This is because, the sheer extension of the ocean means that marine aerosol is one of the most important natural aerosol sources on a global scale (O'Dowd and De Leeuw, 2007; Rinaldi et al., 2010). Several studies (Facchini et al., 2008a, b; Rinaldi et al., 2010) have demonstrated that the organic chemical composition of marine aerosols is due to a combination of different factors, such as primary emission via bubble bursting and the subsequent transformation into secondary aerosol. During the primary emission *via* bubble bursting processes, the presence of phytoplankton can further alter the organic chemical composition and physical properties of marine aerosols (Kuznetsova et al., 2005).

The organic 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 are an active component of the organic nitrogen content of aerosols because they have been shown to enhance the ice nucleating ability of atmospheric particles (Szyrmer and Zawadzki, 1997). These compounds can also serve as a source of nutrients for marine ecosystems thanks to their high bioavailability (Zhang et al., 2002).

A large number of studies have confirmed the presence of amino acids in the condensed phase of aerosols (Gorzelska and Galloway, 1990; Spitzzy, 1990; Milne and Zika, 1993; Saxena and Hildemann, 1996; Zhang et al., 2002; Zhang and Anastasio, 2003; Mandalakis et al., 2010, 2011; Ge et al., 2011 and its references), in rainwater

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(Mopper and Zika, 1987; Mace et al., 2003a, b), fog (Zhang and Anastasio, 2001), and in dew water (Scheller, 2001). They can be present as dissolved combined amino acids (proteins and peptides) (Kuznetsova et al., 2005; Ge et al., 2011), dissolved free amino acids from the hydrolysis of the combined amino acids (Mopper and Zika, 1987; Milne and Zika, 1993), and particulate amino acids (from solid microorganisms and debris particles inside the liquid aerosol phase) (Kuznetsova et al., 2005).

Several emission sources can affect not only the total concentration of dissolved free amino acids in the atmosphere, but also the amino acid composition of the aerosol. Amino acids have been detected in volcanic emissions (Mukhin et al., 1978; Scalabrin et al., 2012), biomass burning has also been suggested as a possible source of amino acids as part of the WSOC content (Mace et al., 2003a; Chan et al., 2005). The different amino acids found in continental particles are thought to have been originally produced by plants, pollens and algae, as well as fungi and bacterial spores (Milne and Zika, 1993; Scheller, 2001; Zhang and Anastasio, 2003; Mace et al., 2003a) and can be found in high concentrations in soil and desert dust. The continental contribution was evaluated by Mace et al. (2003b), who found that biogenic amino acids were present in the fine particles and that coarse particles contained amino acids from mainly anthropogenic sources. The anthropogenic sources currently identified are tobacco smoke (Ge et al., 2011), incinerators, waste collection centers and sewage treatment plants (Leach et al., 1999). Zhang and Anastasio (2002) identified livestock farming as the main source of amino acid ornithine in Californian aerosols. Matsumoto and Uematsu (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. Several studies investigated the free dissolved amino acids in marine aerosols (Gorzelska and Galloway, 1990; McCarthy et al., 1998; Mace et al., 2003; Matsumoto and Uematsu, 2005; Kuznetsova et al., 2005; Weydan and Preston, 2008; Mandalakis et al., 2011) but few studies have been conducted in the polar regions. Schmale et al. (2013) conducted a complete study on the characterization of Sub-Antarctic marine aerosols and they identified hatching pen-

guins as a source of amino acids in the aerosol of Bird Island in the Southern Atlantic Ocean. To our knowledge, this paper is the first to investigate the different compositions and particle-size distributions of amino acids in Antarctic aerosols.

Chirality is an important feature of amino acids and the homochirality of life on Earth occurs because L-amino acids are the only enantiomers used during the biosynthesis of proteins and peptides (Cronin and Pizzarello, 1997). The principal biochemical source of D-amino acids are peptidoglycans, the main structural components of bacterial cell walls (Voet and Voet, 1999). Chiral information can be useful in revealing the primary and secondary origins of aerosol components as demonstrated by several recent studies (Kuznetsova et al., 2005; Wedyan and Preston, 2008; Nozière et al., 2011; González et al., 2011, 2014). Amino acid enantiomeric ratios can be powerful markers for characterizing nitrogenous materials (McCarthy et al., 1998). Kuznetsova et al. (2005) indicated that the relative enrichment in L-amino acids may result from planktonic particles that concentrate at the sea surface while D-enantiomers come predominantly from bacteria (Wedyan and Preston, 2008). Therefore the presence of free D-isomers is indicative of a larger proportion of bacteria in aerosols (Wedyan and Preston, 2008).

The aims of this study are to investigate the occurrence and concentration levels of dissolved free L- and D-amino acids in the Antarctic aerosols, to determine how these compounds produced from the seawater surface are distributed in size-segregated aerosols, and to study their compositional and distribution changes after long-range atmospheric transport.

Due to their long distance from anthropogenic and continental emission sources, polar regions are excellent natural laboratories for conducting studies on the behavior, evolution and fate of marine aerosols. In Antarctica, long-range atmospheric transport of anthropogenic pollutants is minimal because the continent is surrounded by the Southern Ocean. This means that natural sources are the main contributors to atmospheric aerosols (Bargagli, 2008). Aerosol measurements in Antarctica also provide

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dominant wind direction (from the south-west). Aerosol samples from the terrestrial bases (MZS and DC) were collected using a TE-6070, PM₁₀ high-volume air sampler (average flow 1.21 m³ min⁻¹) equipped with a Model TE-235 five-stage high-volume cascade impactor (Tisch Environmental Inc.) fitted with a high-volume back-up filter (Quartz Fiber Filter Media 8" × 10") and a 5.625" × 5.375" Slotted Quartz Fiber filter for collecting particle size fractions in the following ranges: 10.0–7.2, 7.2–3.0, 3.0–1.5, 1.5–0.95, 0.95–0.49, < 0.49 μm. The sampling period for each sample was 10 days, for a total air volume of ~ 15 000 m³ per sample.

During the oceanographic cruise, airborne aerosols were collected onto a circular quartz fiber filter (SKC Inc., Eighty Four, To-13 model) using a TE 5000 High Volume Air Sampler (Tisch Environmental Inc.) to determine the TSP (total suspended particulate) fraction, defined as particles with a diameter > 1 μm. To avoid contamination from the ship's exhaust, air samples were automatically taken under wind sector control. The sampler was located at the bow and sampling only took place when the wind came from between -135° to 135° relative to the bow and ship direction and when the relative wind speed was > 1 m s⁻¹. The sample collection was set to five days, but the actual sampling time varied, subject to wind sector and speed control as well as cruise events. Due to these events the actual aerosol sampling volumes varied from between 511 and 2156 m³. The sea voyage track chart is reported in Fig. 1.

All filters were pre-combusted (4 h at 400 °C in a muffle furnace), to avoid contamination they were wrapped in two aluminum foils, after sampling they were re-wrapped in clean double aluminum foil and were stored at -20 °C prior to analysis. Field blank samples were collected by loading, carrying and installing the filter holder into the instrument with the air pump closed.

2.2 Sample processing

To avoid contamination from laboratory air particles and from the operator, samples were handled under a clean laminar flow bench (class 100). The pre-analytical and sample extraction protocol has been previously described in detail by Zangrando

et al. (2013) for other compounds. The same protocol is summarized below and was applied to the identification of amino acids in Antarctic samples.

Each quartz fiber filter was cut in half using stainless steel scissors that were previously washed with methanol. Filters were broken into small pieces using clean tweezers, and were placed into 50 mL conical flasks. Slotted quartz fiber filters from the cascade impactor and circular quartz fiber filters from the TSP samplers were treated in the same way. They were spiked with 100 μL of ^{13}C isotopically-labelled amino acid standard solutions (with concentrations ranging between 2 and 3 $\mu\text{g mL}^{-1}$), they were then ultrasonically extracted twice for 15 min in an ice bath with 5 mL and then 2 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.

The larger high volume back-up filters were spiked with 400 μL of internal standard solution and were extracted with 25 mL then 5 mL of ultrapure water in an ultrasonic ice bath as described above.

2.3 Instrumental analysis

The enantiomeric determination of free L- and D-amino acids by HPLC-MS/MS has been described in detail by Barbaro et al. (2014). This instrumental method has been applied to the aqueous extracts of the aerosol samples collected during this study.

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 \times 250 mm CHIROBIOTIC TAG column (Advanced Separation Technologies Inc, USA) with a two mobile eluents. Eluent A is ultrapure water with 0.1 % v/v formic acid and eluent B is ultra pure methanol with 0.1 % v/v formic acid.

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

In this work the amino acids were quantified using the isotope dilution method where an isotopically labeled standard was available, where a labeled standard was unavailable internal standard was used to quantify the analytes, a detailed description of which analytes are quantified with which method can be found in Barbaro et al. (2014). In both cases, the results were corrected for daily instrumental sensitivity variations by evaluating the instrumental response factors.

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

2.4 Quality control

The entire analytical procedure was validated by estimation of trueness, repeatability and efficiency (yield%) of the sample treatment process as described by Bliesner (2006). To ensure that it was fit for purpose for the enantiomeric determination of amino acids in Antarctic aerosol. This evaluation was carried out by spiking five cleaned quartz filters (for each type of filter) with $100 \mu\text{L}$ of a solution containing all the native L- and D-amino acids (with concentrations ranging between 2 and $4 \mu\text{g mL}^{-1}$) and $100 \mu\text{L}$ of a solution containing all the isotopically-labeled ^{13}C -amino acids (concentrations ranging between 2 and $3 \mu\text{g mL}^{-1}$). The filters were subsequently extracted as described above in Sect. 2.2 “Sample processing”.

Tables S1, S2 and S3 report a summary of the yields, trueness and relative standard deviations ($n = 5$) for each type of filter used in this study. Average yields of 61, 56 and 56 % were obtained from the circular, slotted and backup filters respectively. In some cases, these values are lower than those reported in the literature (Mandalakis et al., 2010; Barbaro et al., 2011). Trueness is the most important parameter to determine during a method validation; it refers to the degree of closeness of the determined value

to the known “true” value. It is expressed as an error %, calculated as $(Q - T)/T \times 100$, where Q is the determined value and T is the “true value”.

For the circular filters, all D- and L-amino acids considered in this work were validated with an error percentage ranging from -13 % (D-Leu/D-Ile) to +8 % (L-Tyr).

In the backup filters, only D- and L-Hys produced unacceptable errors %, for this reason these compounds were excluded from the quantification. The other amino acids considered in this study were quantified with an accuracy ranging from -9 % (D-Met) to +9 % (D-Ala, L-Thr).

Some amino acids (D-Ala, L-Asn, D-Asn, D-Glu, D-Phe, L-Ser, D-Ser, and D-Val) were excluded from the quantification using the slotted quartz fiber filters as very high error percentages were calculated. We believe that this behavior is probably due to the different mode of use of this sampling support: the slotted quartz fiber filters were used as impact supports while the other supports were used as filters. The other amino acids studied in this work had error % values between -13 % (D-Tyr) and +13 % (D-Leu/D-Ile) and so the method was fit for purpose for their quantification.

The repeatability is determined as the relative standard deviation of the analytical results for the 5 spiked filters. For each type of filter used in this study, the repeatability was always below 10 %.

The method detection limit (MDL) for the analytical procedure is defined as three times the standard deviation of the average values of the field blank ($n = 3$). Tables S1, S2 and S3 report the relative MDLs for each quantified amino acid in the three different sampling supports, the absolute mean blank values ($n = 3$) in these tables are subtracted from the analytical results. All the discussions in the following sections below are based upon blank corrected values.

A comparison between previously published data (Barbaro et al., 2011; Matsumoto and Uematsu, 2005) and the MDLs obtained for each type of filter in this work shows that we obtained lower blank values than those previously reported.

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2.5 Back-trajectory calculation and satellite imagery

Backward air trajectories arriving at MZS, Dome C and R/V *Italica* were computed using a Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) 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 while an isentropic model was employed for the analysis of DC air masses, as suggested by Stohl et al. (2010).

240 h back-trajectories beginning at MZS and DC were calculated for each sampling campaign period. Four runs were computed for every sampling day at six hour intervals and the resulting multiple trajectories were “mean-clustered aggregated” into 6 groups, based on the scree-plot analyses of total spatial variance.

A sensitivity study has been performed to verify the stability of the HYSPLIT back trajectory calculations. We calculated the back-trajectories beginning at 10 m a.g.l. (above ground level), 100, 500 and 1000 m at MZS and DC to evaluate how the trajectories varied with height. The results are shown in Figs. S1–S3, it can be seen that the clusters of simulated air masses have similar trajectories although with different percentages of the total number of calculated back trajectories. For this study we used the 500 m back trajectories because we want to evaluate long range transport. This is because the mean mixed-layer height is 250–400 m a.g.l. at DC (Argentini et al., 2005) while the boundary-layer height is usually below 50 m at the Antarctic coast (Handorf et al., 1999).

We have also estimated the stability of the HYSPLIT model by varying the position of source at MZS as well as DC using a 121 point matrix built by adding or subtracting one degree of latitude or longitude from the real source for each sampling day. These back-trajectories calculated from the 121 simulated sources have the same behavior (Figs. S4–S6), thus confirming the stability of the HYSPLIT calculations.

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Mace et al. (2003b) performed several studies on the coast of Tasmania (Australia), and find mean free total amino acid concentrations that ranged from between 15 and 160 pmol m⁻³.

In this work, we found that the predominant 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 other compounds were present in similar proportions 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). In Fig. 2 it can be seen that the first sample collected between 29 November and 9 December had a higher concentration and a high proportion of Arg (74 %), compared to Gly (11 %). In contrast to this, in the other samples, Gly was the predominant compound, with a proportional percentage between 48 to 56 %, while Arg was present as 18 % of the total.

Scheller (2001) demonstrated that high quantities of Arg were closely linked with plant growth, but the cluster means backward trajectories (Fig. 3) calculated for our samples show that the 1 % of the air masses come from open-ocean areas whilst the major part (99 %) principally come from the interior of the Antarctic continent, areas that are characterized by a lack of vegetation. This suggests that the local marine influence was probably the main source of amino acids in the aerosol collected at MZS and that the concentration of coastal atmospheric amino acids is probably linked to local primary production in the Ross Sea, as suggested by studies in other areas (Meskhidze and Nenes, 2006; Vignati et al., 2010; Yoon et al., 2007; Mueller et al., 2009). We hypothesize that the main source of Arg in the aerosols collected at the coastal Antarctic station MZS was probably a diatom bloom as Arg is involved in their urea cycle (Bromke, 2013). The MODIS data (Fig. 4) show higher chlorophyll concentrations during the period covered by the first sampling period, while a strong decrease in the biomass production index was observed in the other sampling times. This relationship between marine primary production and Arg concentration suggests that this amino

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acid may have a marine biological origin and that its concentration is closely linked to algae growth.

Meteorological conditions play an important role in aerosol formation processes. The first sampling period (29 November–9 December) was characterized by temperatures ranging between -10 and -1.5 °C, while in the successive sampling periods, the temperature was always above -2 °C (PNRA-ENEA, 2014). Studies conducted on the sea surface microlayer (Grammatika and Zimmerman, 2001; Knulst et al., 2003) established that air temperatures < -5 °C create surface slurries which may result in the expulsion of salts and particulate organic matter. Under such conditions, near-surface turbulence was increased, leading to an increase of material in the microlayer, where bubble formation and bursting actively contributed to the transport mechanisms. Leck and Bigg (2005) showed that the main occurrences of fine aerosol formation in the arctic atmosphere were observed when the ice pack is cracking forming leads that melt and refreeze. Our first sample was collected when the pack ice was melting and refreezing, and we did in fact observe the highest concentration of total amino acids in the fine aerosols during this period.

The hypothesis of a local marine source for the aerosols collected at the coastal station MZS was also confirmed by the distribution of the amino acids in the different particle size fractions. Figure 2 shows that 98 % of the total free amino acids are generally found in the fine particles (< 1 μm, combined S5 and B filters). While the remaining 2 % is evenly distributed over the other coarser fractions > 1 μm (filter stages S1 to S4). Our experimental data supports the observations of O'Dowd et al. (2004) and Keene et al. (2007) who showed that WSOC in sea spray submicron particles are mostly associated with the smallest size fraction (0.1–0.25 μm). Other authors (Facchini et al., 2008b; Modini et al., 2010) have shown that WSOC were present in all aerosol size fractions and confirm that the greatest enrichment was in the fine fraction. Our observations are in line with this literature data as amino acids are part of the WSOC family of compounds and so should have the same behavior in sea spray submicron particles.

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3.2 The determination of free amino acids at a remote continental area

Concordia Station at Dome C is an ideal site for studying the chemical composition of remote Antarctic aerosol. Several studies (Fattori et al., 2005; Jourdain et al., 2008; Becagli et al., 2012; Udisti et al., 2012) have investigated the distribution of inorganic compounds and of a few organic molecules (e.g., methanesulfonic acid) in aerosol, but the free amino acid concentration and composition has not yet been studied.

Figure 5 shows the concentrations of free amino acids collected during both field campaigns, and shows a similarity between the trends and compositions of the analyzed compounds between the various size fractions. 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 (Tables S2 and S3) in all samples collected in both field campaigns. The concentrations of D-amino acids were always below MDLs, as seen in our coastal results. It was observed that Gly, L-Asp and L-Ala together accounted for about 80 % of the total amino acid content. The total mean free amino acid concentrations, as the sum of the free amino acid concentrations in all the sample stages, were 0.8 pmol m^{-3} for the 2011–2012 campaign and 0.7 pmol m^{-3} for 2012–2013 campaign (Fig. 5). To our knowledge, these mean concentrations areas are lower than those reported in the literature (Gorzelska and Galloway, 1990; Milne and Zika, 1993; 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; Scalabrin et al., 2012), suggesting that this aerosol composition may describe the amino acid global background concentration.

In Fig. 5b, the sample collected from 27 December 2012 to 06 January 2013 shows an altered concentration profile, with the highest concentrations in one of the coarse fractions (S4 stage $1.5\text{--}0.95 \mu\text{m}$). After evaluating the wind roses and activity at the base for each sample in the two summer campaigns, we believe that these samples were contaminated by human activity at Concordia station (Fig. S7).

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Cluster means backward trajectories analysis of all the samples collected during both summer campaigns revealed a prominent marine source (Fig. 3). During the Antarctic summer, the surface inversion over the polar ice cap is relatively weak and aerosols produced on the ocean's surface can be transported through the upper troposphere to the Antarctic plateau where they are easily mixed down to the surface (Cunningham and Zoller, 1981). There are also some transfer mechanisms from the lower stratosphere to the upper troposphere that occur near the coast of the Antarctic continent. Aerosol from different sources mixes into the upper troposphere, and this air descends uniformly over the Antarctic plateau due to surface cooling flows off the plateau causing the katabatic wind. This means during the summer, there is a continuous flux of relatively clean air from the upper troposphere with aerosol from high altitude input and long range transport (Cunningham and Zoller, 1981; Stohl and Sodemann, 2010).

The analysis of the size distribution of the free amino acids (Fig. 5) combined with the air mass back trajectories (Fig. 3) allowed us to identify the aerosol sources and the transformation mechanisms that these aerosols undergo during long-range transport. Our results suggest that amino acids were present in the fine particles over the surface of the Southern Ocean from bubble bursting processes. The air masses subsequently passed into the upper troposphere and then over the continent where they remained for several days before descending onto the ice sheet. These fine aerosol particles can grow during long-range transport, due to condensation of molecules from the gas phase, by collision of small and large particles (coagulation) (Petzold and Karcher, 2012; Roiger et al., 2012), this is unlikely in Antarctica where the intense cold probably promotes ice-nucleation phenomena, a process that is helped by the presence of amino acids (Szyrmer and Zawadzi, 1997). The concentration of free amino acids in the coarse particles of aerosols collected at DC had mean values of 407 and 421 fmol m⁻³ (see Fig. 5) for the two field campaigns, while our coastal data had a mean free amino acids concentration of 264 fmol m⁻³ (Fig. 2). The aerosols collected at DC were characterized by a prevalence of free amino acids in the fine fraction, with a notable enrichment of amino acids in the coarse particles (13% of the total in 2011–2012 and 23%

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of the total in 2012–2013) compared to coastal aerosol. In fact, during our 2010–2011 sampling campaign at MZS, which is located near the aerosol source, we observed only 2% of total free amino acids in the coarse particles. The most likely explanation for this enrichment of amino acids in the coarse fraction, is that the fine fraction has been subjected to processes that increased the particle size of the aerosol. The most likely process is ice nucleation during long-range transport promoted by the intense cold over the plateau and presence of amino acids in the aerosol particles (Szyrmer and Zawadzki, 1997).

The chemical composition of aerosols may change during long-range transport due to photochemical, chemical and ionic reactions (Milne and Zika, 1993; Nozière and Còrdova, 2008; De Haan et al., 2009). Milne and Zika (1993) verified that amino acids are destroyed *via* reactions with photochemically formed oxidants such as hydroxyl radicals, to form products such as the ammonium ion, amides and keto-acids. However, in the upper atmosphere, the chemical processes take place at slower rates than in the boundary layer (Roiger et al., 2012). In aqueous-phase aerosols, glyoxal can react with amino acids, leading to scavenging processes (De Haan et al., 2009). Recent studies on organic aerosol growth mechanisms (Maria et al., 2004) underlined that oxidation processes that remove hydrophobic organic compounds, are slower in large carbonaceous aerosols.

From the physicochemical proprieties of amino acids, a “hydropathy” index can be made, as suggested by Pommie et al. (2004). This classifies the amino acids as hydrophilic (Asp, Hyp, Glu, Asn, Lys, Gln, Arg), hydrophobic (Ala, Val, Leu, Ile, Met, Phe) or neutral (Gly, Pro, Ser, Thr, Tyr, Hys). This helps in evaluating the contribution of each kind of amino to each class of aerosols collected over the three different field campaigns. Figure 6 shows that the hydrophilic components were predominant in the locally produced marine aerosols released into the atmosphere near MZS, while hydrophobic compounds were dominant in the aerosols collected at the continental station (DC). The low abundance of hydrophobic amino acids in coastal aerosols was also observed 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 allows us to hypothesize that a higher proportion of hydrophilic amino acids reflects a higher water content in the aerosol. This is a very important indication, because aerosol containing amino acids behave as enhanced ice-nuclei activators (Szyrmer and Zawadzki, 1997).

5 A comparison between the concentrations of hydrophobic Ala at the two sampling sites (MZS and DC) shows a very similar average concentration (70 fmol m^{-3}) in the coarse particles. This is an interesting behavior that confirms the hypothesis of limited atmospheric reactivity as proposed by Maria et al. (2004), who suggested a longer hydrophobic aerosol lifetime as a result of the slower oxidation rates. Thanks to this
10 phenomenon, Ala significantly contributes to the amino acid content in these “remote aerosols” as it does not degrade during long range transport.

Figure 5 shows that the concentration of amino acids for the 2011–2012 summer Antarctic campaign was higher than the values reported for the 2012–2013 Antarctic campaign, and underlines that the main difference between the two campaigns is
15 mainly in the percentages of hydrophilic and neutral amino acids present. We suggest that the transport processes of the air masses were the main cause of these variations as the time spent inland by the air masses in the 2011–2012 summer was about 36 h (Fig. 3) whilst in 2012–2013 the time range was between 4 and 7 days (Fig. 3). A longer transportation time from the source to the sampling site allows chemical transformation through photochemical reactions to take place, decreasing the concentration of
20 hydrophilic amino acids thus modifying the composition so that the more stable Gly (a neutral component) becomes the main compound (Fig. 6).

Looking at the acid-base properties of the amino acids, some differences can be observed between two different types of aerosol. As described above, the predominant
25 amino acid in the MZS aerosols was Arg, which contributed considerably to the percentage of basic compounds (53 %). The pH neutral components represented an important percentage (40 and 68 % for coastal and internal aerosols respectively). Gly is mainly present in large quantities in these aerosols because of its very low atmospheric reactivity (half life of 19 days) (McGregor and Anastasio, 2001) and its presence is usually

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considered an indicator of long-range aerosol transport (Milne and Zika, 1993; Barbaro et al., 2011). The acidic compounds (Asp and Glu) composition was quite different in the aerosols from the two different stations: with a low percentage in the coastal samples at MZS (7%) that was in contrast with the higher content in the aerosols from DC (33 and 26% respectively for the two consecutive field campaigns). This result can be explained by a study conducted by Fattori et al. (2005) on the DC aerosol, where high acid content was found. High concentrations of hydrochloric, nitric and sulfuric acids were found in the aerosol fine fraction, promoting a numerous series of acid-base atmospheric reactions that neutralize the basic compounds. In the atmosphere, amino acids are present in very low quantities so it is thought that they do not influence the pH of aerosols. However, the pH of aerosols, can influence the chemical form of the amino acids present.

3.3 Free amino acids during an oceanographic cruise

Measurements of free amino acids were carried out on aerosol samples collected on the Southern Ocean onboard the R/V *Italica* from the 13 January to 19 February 2012. Aerosols were sampled using a TSP sampler that collects particles with a diameter above 1 μm . The first and second samples covered the track between New Zealand (from Lyttelton harbor) and MZS (Antarctica), and the sixth and last samples were collected during the return journey between Antarctica and New Zealand. Samples 3, 4 and 5 were collected on the Ross Sea near the Antarctic continent (Fig. 1). Five L-amino acids (L-Asp, L-Arg, L-Glu, L-Phe, L-Pro) and Gly were present in the samples, while other L- and D-amino acids had concentrations below MDLs (Table S1). The total concentrations of free amino acids varied between 2 and 12 pmol m^{-3} .

The first and last samples had the highest concentrations of free amino acids (Fig. 7), and their relative sampling periods were characterized by temperatures ranging between -1 and 18°C (sample 1), in contrast, temperatures during the remaining sampling periods were always below -1°C , with a lowest value of -8°C (sample 4). Higher temperatures can facilitate metabolic processes and accelerate atmospheric chemical

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reactions, as well as promote bubble bursting from the sea surface. This is probably the main source of amino acids in our on-ship samples, this is also supported by the back-trajectory analysis (Fig. S8a–g), where demonstrate only a marine influence for that period. The concentration of amino acids was strongly influenced by sea conditions during sampling. The field report (Rapporto sulla campagna Antartica, 2012), noted that during navigation from New Zealand to the ice-pack region, the winds were always above 30 knots, with maximum values of 60 knots with wave heights of 12 m. This probably explains the higher total concentration of free amino acids in the first two samples (12 pmol m⁻³). Along the same track, but under calmer sea conditions (sample 7), we observed a slight reduction in the total concentration of free amino acids (8 pmol m⁻³). These values were very similar to those reported by Matsumoto and Uematsu (2005) in the Pacific Ocean and to those reported by Gorzelska and Galloway (1990) and Wedyan and Preston (2008) 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 expansive pack ice and by temperatures below -1 °C, 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 acid values detected in the coastal station MZS. The mean total 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 are similar to the concentrations observed in the aerosols collected at MZS station (median 5 pmol m⁻³). However, this is not a true comparison: for the sampling campaign at MZS, a cascade impactor was used to collect aerosol samples with a particle-size below 10 µm, whereas the data collected during the cruise was for aerosols with a particle diameter above 1 µm. However, if we exclude data from the back-up and the fifth slotted filters, the cascade sampler covers a particle size between 0.95 and 10 µm (stages 1 to 4), making a comparison between the two data sets more feasible. In the MZS aerosols, the median value of the amino acids concentration in the aerosols collected on stages 1 to 4 was 1 pmol m⁻³ and this

cluded fine particles, whereas Arg was one of the most abundant compounds observed in the coastal station (found in the fine fraction).

4 Conclusions

This first study on the size distribution of amino acids in Antarctica has identified possible sources of marine aerosols in this region and has characterized some chemical and physical transformations that take place during transport to the interior of the Antarctic continent.

Marine emissions of fine particles occurred *via* bubble bursting processes on the surface of the Southern Ocean. The mean total amino acid concentration detected at MZS was 11 pmol m^{-3} , with a higher percentage of amino acids were found in the fine fraction. The aerosol samples collected at Dome C had the lowest amino acid values (0.7 and 0.8 pmol m^{-3}) and the coarse particles were found to be enriched with amino acids compared to the coastal site. Numerous chemical and photochemical events may have contributed to a decrease in the concentration in amino acids in the fine fraction, and the chemical reactions were faster for hydrophilic compounds than for hydrophobic ones, as suggested by an observed Ala enrichment.

The presence of only the L-enantiomers of free amino acids in Antarctic aerosols suggests that planktonic particles were the main sources of free amino acids in this area and that these compounds can be modified when transported to the interior of the continent. Gly and Ala, are the most stable compounds, and may be used as biogenic markers of long-range marine aerosols. The back-trajectory analysis demonstrated that the differences in the transport time of air masses inside Antarctica can result in modifications to the percentage of amino acids in the coarse particles.

The study of aerosols with diameters $> 10 \mu\text{m}$ indicated that bubble bursting processes can also emit microorganisms that are composed of a higher number of neutral amino acids.

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Author contributions. 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 discussion of the results and collaborated in writing the article.

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of marine aerosol**

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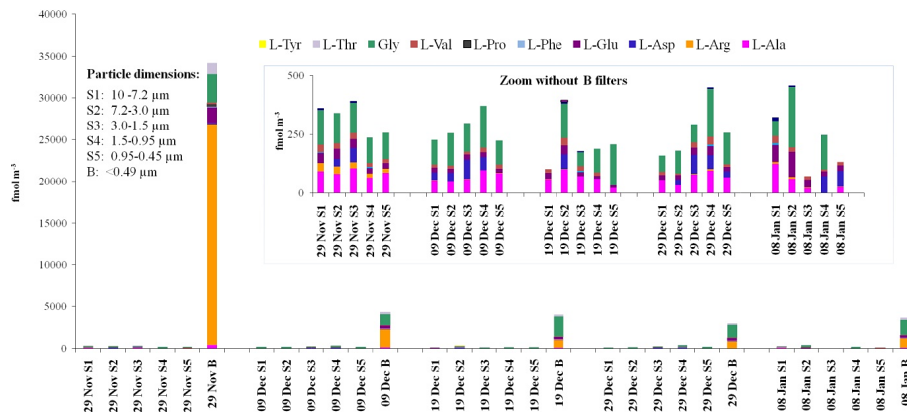


Figure 2. Amino acid size distribution in the samples collected during the summer of 2010–2011 at “Mario Zucchelli Station” (Antarctica).

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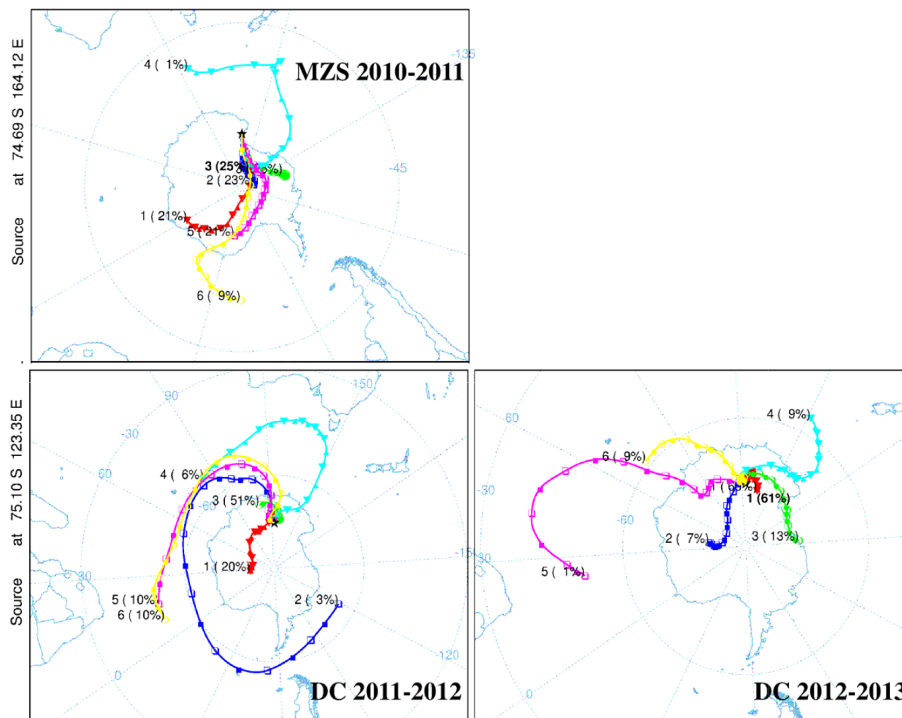


Figure 3. Cluster means backward trajectories analyses at 500 m.a.g.l. at the coastal base “Mario Zucchelli Station” (MZS) during the summer of 2010–2011 and cluster means backward trajectories at the Italian-French base Dome C (DC) during the summers of 2011–2012 and 2012–2013.

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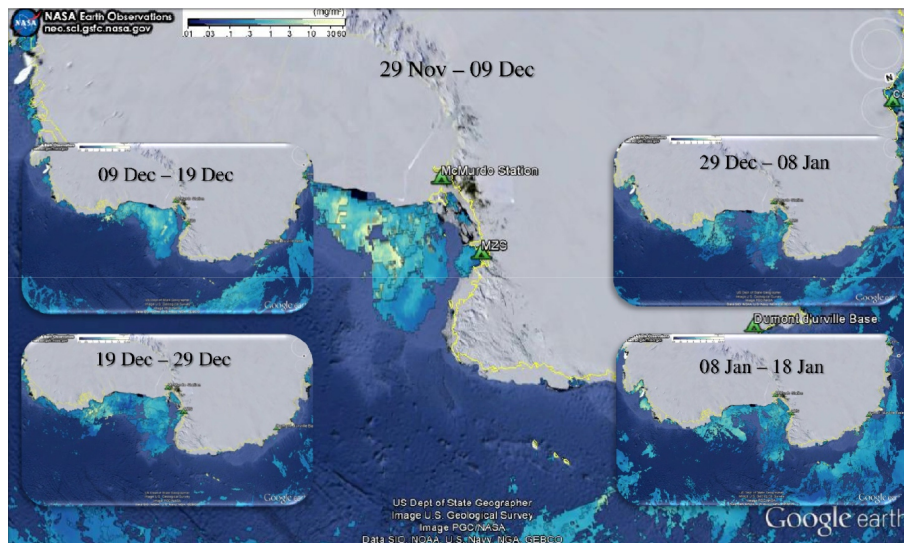


Figure 4. Distribution of chlorophyll concentrations in the Ross Sea for each sampling period obtained through the Aqua/MODIS NASA satellite.

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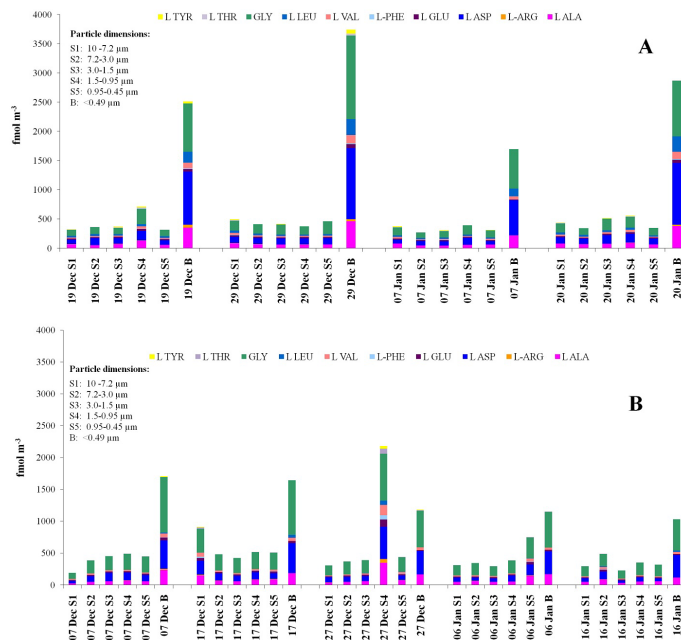


Figure 5. Size distributions of amino acid concentrations in the samples collected during the summer of 2011–2012 (a) and during the summer of 2012–2013 (b) at the Italian French base “Concordia Station” (Dome C).

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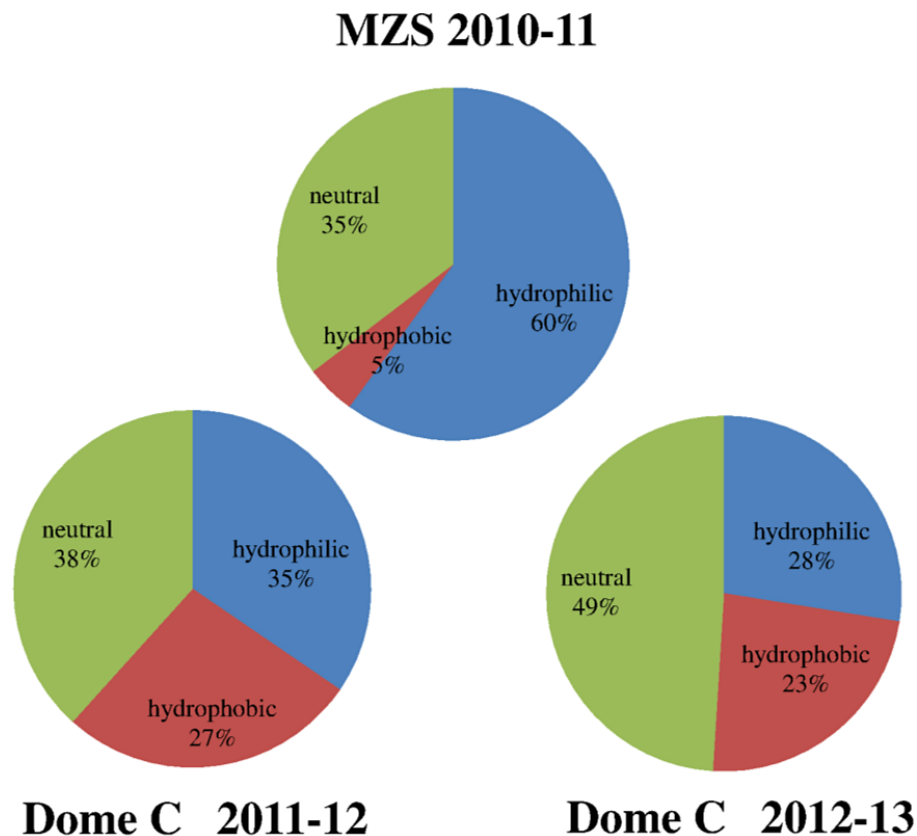


Figure 6. Comparison between percentages of hydrophilic, neutral and hydrophobic amino acid contributions of the aerosols sampled at the “Mario Zucchelli Station” and at Dome C.

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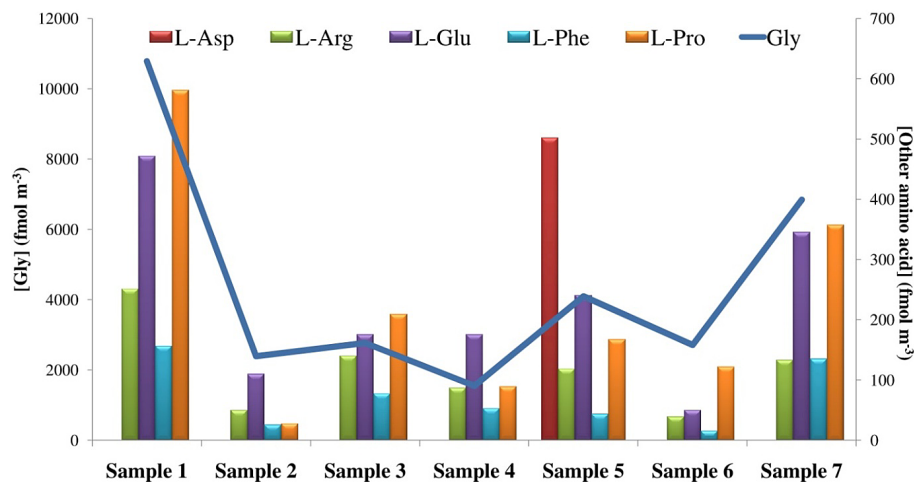


Figure 7. Amino acid distribution in the aerosols sampled on the R/V *Italica* during the oceanographic cruise on the Southern Ocean during the summer of 2012.