Response to editor

Dear Prof. Huffman,

we have the pleasure to submit this revised version of our paper “Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol” (ACP-2014-1007).

Best regards

Elena Barbaro

Comments

The manuscript has made marked improvement from the last time, as suggested by the referees. I would like to see a few additional areas made clearer, however, before publication. I've uploaded a document with some individual/minor comments written in-place, and I've added some more substantive comments separately.
Please process the changes appropriately and upload two versions: one clean manuscript, and a separate file with all changes from the current version with tracked changes so I can review quickly and efficiently. Feel free to add a cover letter with any discussion/explanation necessary.
Non-public comments to the Author:
Please also see the following comments and suggestions.

Comments:

Line 309 - Figure 4 is hard to interpret in relation to your comments in Lines ~309. I see that you are referencing the comparison between Figure 4 and Figure 1, but the sizes of these figures and the complexity of the data in both make it difficult to test your statements here. Could you make this easier for the reader by either integrating the chlorophyll concentration along each of the sample tracks, or something that would take the work away from the reader having to look so hard at this to merely get a rough idea for what you are saying?

To help the reader in understanding the correlation between chlorophyll and amino acid concentration in the MZS aerosol, we have modified the figure 4.

Line 375 - I suggest adding more detail on your interpretation of Figure 3 here. The way you look at Fig. 3 plays heavily into the way you conclude certain ideas here, but it is again hard to piece all of

these details together by simply looking at Figure 3. I suggest adding text to the paragraph here (or close by) to more clearly support your arguments.

Line 379: The text in this area still needs to be refined in relation to the comments from referee #3 (page 8 of your response). This is one example of where the term "enrichment" becomes unclear to me. I agree with referee #3 that the processes may be influenced by primary emission. You site in your response that the Atmospheric Physics book suggests that coarse particles cannot be transported to Antarctica due to their short residence time. This depends on the wind, altitude of particle path, and weather patterns, because there are plenty of consistent observations of large particles being transported 1000's of km. (Obrist, et al. (2008), Atmos. Environ., 42, 7579–7589 as one quick example). I'm not sure what the answer is here, but I'm not confident you can quickly write away all primary emission and influence of coarse particles as simply as referencing this textbook.

We agree with the editor that the text must be improved. We have completely revised these paragraphs and we have added the other hypothesis suggested also by the referee 3. We have moved some sentences in order to clarify our hypothesis; we have re-ordered our argument in what we hope is a more logical sequence. We have described the different percentages of amino acids in the coarse fraction of DC aerosol related to MZS aerosol. Then we have introduced the back trajectories and in the end we have made our hypothesis. Our results are a good starting point for future investigations but at the moment it's quite difficult to define a correct interpretation for the increase of amino acid percentages in the coarse particles.

The final version can be read as:

The mean concentrations of free amino acids in the coarse aerosol particles collected at DC for the two field campaigns were 407 and 421 fmol m^{-3} (see Fig. 5)..At our coastal site, the mean free amino acids concentration in the coarse fraction was 264 fmol m^{-3} (Fig. 2). At DC, the free amino acid concentration in the coarse aerosol, expressed as a fraction percent of the total free amino acids concentration was found to be 13% in 2011-12 and 23% in the 2012-13 campaign. Conversely, during our 2010-2011 sampling campaign at MZS, which is located near the marine aerosol source, we found that only 2% of the total free amino acid concentration was present in the coarse fraction.

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 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 that during the summer, there is a continuous flux of relatively clean air from the upper troposphere with aerosol from high altitude inputs and long range transport (Cunningham and Zoller, 1981; Stohl and Sodemann, 2010).

Cluster means backward trajectories analysis of all the samples collected during both summer campaigns at DC revealed a prominent marine source (Fig. 3). Fig. 3 shows that the 10-days backward trajectories came from the Southern Ocean where there are no land based man made influences.

Fig. 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 mainly in the percentages of amino acids in the coarse fraction. 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 hours (Fig. 3) whilst in 2012-2013 the time range was between 4 and 7 days (Fig. 3).

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 suggest that the amino acids in the aerosol collected at DC can have two possible sources. The first hypothesis is that they were present in primary emitted coarse mode aerosol particles, which come from phytoplanktonic sea spray coarse mode particles (Matsumoto and Ueamatsu, 2005), or from soil dust coarse mode particles (Mace et al., 2003). Particles and their chemical constituents can travel for many weeks in the upper troposphere without being lost, provided they are not subject to wet deposition, or that the compounds are reacting in the aerosol phase. The second hypothesis is that amino acids had a marine source and these aerosols underwent several physico-chemical transformations 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 could either grow during long-range transport, due to condensation of molecules from the gas phase or by collision of small and large particles (coagulation) (Petzold and Karcher, 2012; Roiger et al., 2012). However, these processes are unlikely in Antarctica due to the very clean conditions. The most likely explanation is that the fine fraction has been subjected to other processes that increased the particle size of the aerosol. The most likely remaining 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 specific reason for the increase of amino acids percentage in the coarse particles is not clear, based on the available data. In our future investigations, we will also evaluate the aerosol mass, which is probably a key parameter to measure that will help explain this increase of concentration in the coarse particles.

Line 398 - I'm confused here. I thought you didn't measure aerosol mass here, e.g. Line 384. If you didn't measure total aerosol mass, or in each fraction, how do you know the fractions quoted here? If nothing else, be a little clearer with explanation.

We have calculated the percentage of amino acids in the coarse fraction related to the total concentration detected in the PM10 aerosol. We didn't measure aerosol mass. In order to clarify the concept, we have modified the sentence as follows:

"The mean concentrations of free amino acids in the coarse aerosol particles collected at DC for the two field campaigns were 407 and 421 fmol m^{-3} (see Fig. 5)..At our coastal site, the mean free amino acids concentration in the coarse fraction was 264 fmol m^{-3} (Fig. 2). At DC, the free amino acid concentration in the coarse aerosol, expressed as a fraction percent of the total free amino acids concentration was found to be 13% in 2011-12 and 23% in the 2012-13 campaign. Conversely, during our 2010-2011 sampling campaign at MZS, which is located near the marine aerosol source, we found that only 2% of the total free amino acid concentration was present in the coarse fraction."

Per Referee #3 Comment: Please add the Kristenson et al. 2010 article you reference in your response, but not the others. This is the most directly applicable and circumvents some of the contentious comments from previous referees.

We agree with the referee 3 and the editor and we added this sentence: "Recently Kristensoon et al., (2010) investigated the ability of some amino acids (e.g. glycine or leucine) to act as cloud condensation nuclei (CCN), they found that particles containing amino acids at "atmospherically relevant mixture ratios" are good CCN."

Line 118: In response to a referee you changed a line to say that your "aim is to study aerosol particle formation and growth in Antarctica". This seems over-reaching, since you don't actually measure this process. The concentrations of amino acids might contribute to these processes, but you would have to scale back the goal sentence appropriately, e.g. "Our aim is to study concentrations of airborne amino acids, which may be related to aerosol growth in Antarctica in some circumstances."

We agree with the editor and we changed the sentences as suggested.

Additional Minor comments:

Abstract, Line 37: May be better to consider using something like the terminology "found in higher concentration" rather than enriched, which may be ambiguous here.

As suggested, we modified as follows: "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 have higher concentrations of amino acids compared to the coastal site. ."

Page 10 – Several places you write "errors %" or something similar, but these should all be streamlined to be "percent error". Look through and change to be consistent and accurate.

We have changed "error %" and other similar phrases with "percent error.

Page 12, Paragraph starting Line 280 – It was unclear to me where the samples were taken. Were these water samples?

We have clarified the type of samples (aerosol samples) collected above the Oceans and in the Arctic station. You can read: "The mean total concentration of free 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 a mean free amino acid concentration of 10.7 pmol m-3 in aerosol samples above the Pacific Ocean, while Gorzelska and Galloway (1990) and Wedyan and Preston (2008) observed means of 3 pmol m-3 and 20 pmol m-3 respectively in the Atlantic Ocean. Scalabrin et al. (2012) determined a mean concentration of 2.8 pmol m-3 using the same aerosol sampling method reported here at an Arctic coastal station."

Line 384 – "aerosols mass" should be "aerosol mass"

We modified "aerosols mass" with "aerosol mass".

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

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Keywords: amino acids, Antarctica, LC-MS/MS, marine aerosols.

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 and 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 have higher concentrations of amino acids compared to the coastal site. The amino acid composition in the aerosol collected at Dome C had also changed compared to the coastal site, 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 (as microorganisms or plant 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 world-wide 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 extent 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 depends on 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 proprieties 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 some of them have been shown to enhance the ice nucleating ability of atmospheric particles (Szyrmer and Zawadzki, 1997). Recently Kristensoon et al., (2010) investigated the ability of someamino acids (e.g. glycine or leucine) to act as cloud condensation nuclei (CCN), they found that particles containing amino acids at "atmospherically relevant mixture ratios" are good CCN. These compounds can also serve as a source of nutrients for marine ecosystems due 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; Spitzy, 1990; Milne and Zika, 1993; Saxena and

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231 Hildemann, 1996; Zhang et al., 2002; Zhang and Anastasio, 2003; Mandalakis et al., 2010;
232 Mandalakis et al., 2011; Ge et al., 2011 and its references), in rainwater (Mopper and Zika, 1987;
233 Mace et al., 2003a,b), fog (Zhang and Anastasio, 2001), and in dew water (Scheller, 2001). They
234 can be present as dissolved combined amino acids (proteins and peptides) (Kuznetsova et al., 2005;
235 Ge et al., 2011), dissolved free amino acids from the hydrolysis of the combined amino
236 acids(Mopper and Zika 1987; Milne and Zika, 1993), and particulate amino acids (from solid
237 microorganisms and debris particles inside the liquid aerosol phase) (Kuznetsova et al., 2005).
238 Several emission sources can affect not only the total concentration of dissolved free amino acids in
239 the atmosphere, but also the amino acid composition of the aerosol. Amino acids have been
240 detected in volcanic emissions (Mukhin et al., 1978; Scalabrin et al., 2012), biomass burning has
241 also been suggested as a possible source of amino acids as part of the WSOC content (Mace et al.,
242 2003a; Chan et al., 2005). The different amino acids found in continental particles are thought to
243 have been originally produced by plants, pollens and algae, as well as fungi and bacterial spores
244 (Milne and Zika, 1993; Scheller, 2001; Zhang and Anastasio, 2003; Mace et al., 2003a) and can be
245 found in high concentrations in soil and desert dust. The continental contribution was evaluated by
246 Mace et al. (2003b), who found that biogenic amino acids were present in the fine particles and that
247 coarse particles contained amino acids from mainly anthropogenic sources. The anthropogenic
248 sources currently identified are tobacco smoke (Ge et al., 2011), incinerators, waste collection
249 centers and sewage treatment plants (Leach et al., 1999). Zhang and Anastasio (2002) identified
250 livestock farming as the main source of amino acid ornithine in Californian aerosols. Matsumoto
251 and Uematsu (2005) describe how long-range transport influences the concentration of amino acids
252 in the North Pacific Ocean, while an evident marine source was verified by Weydan and Preston
253 (2008) in the South Atlantic Ocean. Several studies investigated the free dissolved amino acids in
254 marine aerosols (Gorzelska and Galloway, 1990; McCarthy et al., 1998; Mace et al., 2003;
255 Matsumoto and Uematsu, 2005; Kuznetsova et al., 2005; Wedyan and Preston; 2008; Mandalakis et
256 al., 2011) but few studies have been conducted in the polar regions. Schmale et al. (2013) conducted

257 a complete study on the characterization of Sub-Antarctic marine aerosols and they identified
258 hatching penguins as a source of amino acids in the aerosol of Bird Island in the Southern Atlantic
259 Ocean. To our knowledge, this paper is the first to investigate the different compositions and
260 particle-size distributions of amino acids in Antarctic aerosols.
261 Chirality is an important feature of amino acids and the homochirality of life on Earth occurs
262 because L-amino acids are the only enantiomers used during the biosynthesis of proteins and
263 peptides (Cronin and Pizzarello, 1997). The principal biochemical source of D-amino acids are
264 peptidoglycans, the main structural components of bacterial cell walls (Voet and Voet, 1999).
265 Chiral information can be useful in revealing the primary and secondary origins of aerosol
266 components as demonstrated by several recent studies (Kuznetsova et al, 2005; Wedyan and
267 Preston, 2008; Noziére et al., 2011; Gonzàlez et al., 2011; Gonzàlez et al., 2014). Amino acid
268 enantiomeric ratios can be powerful markers for characterizing nitrogenous materials (McCarthy et
269 al., 1998). Kuznetsova et al. (2005) indicated that the relative enrichment in L-amino acids may
270 result from planktonic particles that concentrate at the sea surface while D-enantiomers come
271 predominantly from bacteria (Wedyan and Preston, 2008). Therefore the presence of free D-isomers
272 is indicative of a larger proportion of bacteria in aerosols (Wedyan and Preston, 2008).
273 The aims of this study are to investigate the occurrence and concentration levels of dissolved free L-
274 and D-amino acids in the Antarctic aerosols, to determine how these compounds produced from the
275 seawater surface are distributed in size-segregated aerosols, and to study their compositional and
276 distribution changes after long-range atmospheric transport.
277 Due to their long distance from anthropogenic and continental emission sources, polar regions are
278 excellent natural laboratories for conducting studies on the behavior, evolution and fate of marine
279 aerosols. In Antarctica, long-range atmospheric transport of anthropogenic pollutants is minimal
280 because the continent is surrounded by the Southern Ocean. This means that natural sources are the
281 main contributors to atmospheric aerosols (Bargagli, 2008,Bourcier et al., 2010). Our aim is to
282 study concentrations of airborne amino acids, which may be related to aerosol growth in Antarctica

in some circumstances. Our investigation was carried out over three different Antarctic summer campaigns, including two consecutive field campaigns (2011-2012 and 2012-2013) on the Antarctic plateau at the Italian-French base of Concordia Station (DC). One sampling period (2010-2011) was carried out at the Italian coastal base MZS and finally, aerosols were sampled from the R/V Italica on the Southern Ocean, between Antarctica and New Zealand (2012).

Eliminato: Our aim is to study aerosol particle formation and growth in Antarctica because there is minimal interference from confounding anthropogenic sources.. ¶ ¶

2. Experimental section

2.1 Sample collection

Aerosol sampling was carried out over three different Antarctic expeditions during the austral summer period, in the framework of the "Progetto Nazionale di Ricerche in Antartide" (PNRA). The sampling sites are shown in Fig. 1, obtained using Google Earth maps.

During the first expedition one sampling campaign collected five aerosol samples from the Italian base MZS from 29th November 2010 to 18th January 2011. The sampling site was at the Faraglione Camp (74° 42′ S – 164° 06′ E), about 3 km south of MZS in Victoria Land. The site is a promontory at 57 m asl. It was chosen because it is located in a valley that is physically separated from the main station area by a hill, to reduce as much as possible eventual pollution from the research station.

During the second expedition four aerosol samples were collected from the 19th December 2011 to 28th January 2012 at the Italian-French base Concordia Station located at Dome C (DC) on the East Antarctic plateau (75° 06' S – 123° 20' E), and seven other samples retrieved from the Ross Sea (Antarctica) on the R/V Italica during the oceanographic sampling campaign from 13 January to 19 February 2012 (Fig 1).

In the third expedition, five aerosol samples were obtained from 07th December 2012 to 26th January 2013 at Dome C. The sampling site at Dome C during both expeditions was located about 1 km south-west of the Concordia Station buildings, upwind of the 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 m^3 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" x 10") and a 5.625" x 5.375" slotted quartz fiber filter for collecting particle size fractions in the following ranges: 10.0 – 7.2 µm, 7.2 – 3.0 µm, 3.0 – 1.5 µm, 1.5- 0.95 µm, 0.95 – 0.49 µm, < 0.49 µm. The sampling period for each sample was 10 days, for a total air volume of ~15,000 m^3 per sample.

During the oceanographic cruise, airborne aerosols were collected onto circular quartz fiber filters (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 >1µm. 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 aswell as cruise events. Due to these events the actual aerosol sampling volumes varied from between 511 and 2156 m^3. The sea voyage track chart is reported in Fig. 1.

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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

337 protocol is summarized below and was applied to the identification of amino acids in Antarctic
338 samples.
339 Each quartz fiber filter was cut in half using stainless steel scissors that were previously washed
340 with methanol. Filters were broken into small pieces using clean tweezers, and were placed into
341 50mL conical flasks. Slotted quartz fiber filters from the cascade impactor and circular quartz fiber
342 filters from the TSP samplers were treated in the same way. They were spiked with 100 µL of ^{13}C
343 isotopically-labelled amino acid standard solutions (with concentrations ranging between 2 and 3
344 µg mL^{-1}), they were then ultrasonically extracted twice for 15 minutes in an ice bath with 5 mL and
345 then 2 mL of ultrapure water. The extracts were combined and filtered through a 0.45 µm PTFE
346 filter in order to remove particulate and filter traces before instrumental analysis.
347 The larger high volume back-up filters were spiked with 400 µL of internal standard solution and
348 were extracted with 25 mL then 5 mL of ultrapure water in an ultrasonic ice bath as described
349 above.

350 **2.3 Instrumental analysis**

351 The enantiomeric determination of free L- and D-amino acids by HPLC-MS/MS has been described
352 in detail by Barbaro et al. (2014). This instrumental method has been applied to the aqueous extracts
353 of the aerosol samples collected during this study.
354 An Agilent 1100 Series HPLC Systems (Waldbronn, Germany; with a binary pump, vacuum
355 degasser, autosampler) was coupled with an API 4000 Triple Quadrupole Mass Spectrometer
356 (Applied Biosystem/MSD SCIEX, Concord, Ontario, Canada) using a TurboV electrospray source
357 that operated in positive mode by multiple reaction monitoring (MRM).
358 Chromatographic separation was performed using a 2.1x 250 mm CHIROBIOTIC TAG column
359 (Advanced Separation Technologies Inc, USA) with a two mobile eluents. Eluent A is ultrapure
360 water with 0.1% v/v formic acid and eluent B is ultra pure methanol with 0.1% v/v formic acid.

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 to30% eluent B. The injection volume was 10 µL.

In this work the amino acids were quantified using the isotope dilution method where an isotopically labeled standard was available. For other amino acids, where a labeled standard was unavailable, an 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, the validation was carried out by spiking five cleaned quartz filters (for each type of filter) with 100 µL of a solution containing all the native L and D amino acids (with concentrations ranging between 2 and 4 µg mL^{-1}) and 100 µL of a solution containing all the isotopically-labeled ^{13}C amino acids (concentrations ranging between 2 and 3 µg mL^{-1}). The filters were subsequently extracted as described above in section 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 ×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 percent 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 percent errors 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 percent 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 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.

2.5 Back-trajectory calculation and satellite imagery

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Backward air trajectories arriving at MZS, Dome C and R/V Italica were computed using a 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 while an isoentropic model was employed for the analysis of DC air masses, as suggested by Stohl et al (2010).

240 hours of 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 agl (above ground level), 100 m, 500 m and 1000 m at MZS and DC to evaluate how the trajectories varied with height. The results are shown in Supplementary Fig. 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 agl 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 a121 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 (Supplement Fig. S4-S6), thus confirming the stability of the HYSPLIT calculations.

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.

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

443 **3. Results and Discussion**

444 **3.1 Free amino acid determination in the coastal area**

445 Nine L-amino acids (L-Ala, L-Asp, L-Arg, L-Glu, L-Phe, L-Pro, L-Tyr, L-Thr) and Gly had blank
446 corrected concentrations higher than the MDLs (Supplementary Tables S2 and S3), while all D-
447 amino acids had values below the MDLs, probably due to a negligible presence of bacteria in the
448 aerosol source (Kuznetsova et al., 2005; Wedyan and Preston, 2008). The total concentration of
449 amino acids, calculated as the sum of their six size distributions in all aerosol samples, has a median
450 value of 5 pmol m^{-3} and a mean value of 11 pmol m^{-3}, due to the higher amino acid concentrations
451 in the first sample (29 November-9 December), as shown in Fig. 2.
452 The mean total concentration of free amino acids determined in this study was very similar to those
453 found in the literature for marine aerosols in remote areas. Matsumoto and Uematsu (2005) reported
454 a mean free amino acid concentration of 10.7 pmol m^{-3} in aerosol samples above the Pacific Ocean,
455 while Gorzelska and Galloway (1990) and Wedyan and Preston (2008) observed means of 3 pmol
456 m^{-3} and 20 pmol m^{-3} respectively in the Atlantic Ocean. Scalabrin et al. (2012)determined a mean
457 concentration of 2.8 pmol m^{-3} using the same aerosol sampling method reported here at an Arctic
458 coastal station.
459 Higher mean concentrations of amino acids were found in the Mediterranean. Barbaro et al. (2011)
460 determined a mean value of 334 pmol m^{-3} in the Venice Lagoon (Italy); Mandalakis et al.
461 (2010,2011) found 166 pmol m^{-3} and 172 pmol m^{-3} in two studies in the Eastern Mediterranean
462 around Greece, respectively. In the Southern hemisphere, Mace et al. (2003b) performed several
463 studies on the coast of Tasmania (Australia), and found mean free total amino acid concentrations
464 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, and 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 09 December had 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 percentage between 48 to 56%, while Arg was present as18% 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 1% of the air masses come from open-ocean areas whilst the major part (99%) principally come from the interior of theAntarctic continent, areas that are characterized by alack 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; Müller 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 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-09 December) was characterized by temperatures ranging between -10°C and -1.5°C, while in the successive sampling periods, the air 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. Fig. 2 shows that 98%of the total free amino acids are generally found in the fine particles (<1µm, 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 is consistent with 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 had not yet been studied.

Fig. 5 presents 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 (Supplementary 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}for2012-2013 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; Barbaro et al., 2011; Mandalakis 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 1.5-0.95 µm). After evaluating the wind rose plots 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 (Supplementary Fig. S7).

The meanconcentrations of free amino acids in the coarse aerosolparticles collected at DC for the two field campaigns were 407 and 421fmol m^{-3} (see Fig. 5). At our coastal site, the mean free amino acids concentration in the coarse fraction was264 fmol m^{-3} (Fig. 2). At DC, the free amino acid concentration in the coarse aerosol, expressed as a fraction percent of the total free amino acids

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concentration was found to be 13% in 2011-12 and 23% in the 2012-13 campaign. Conversely, during our 2010-2011 sampling campaign at MZS, which is located near the marine aerosol source, we found that only 2% of the total free amino acid concentration was present in the coarse fraction.

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 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 that during the summer, there is a continuous flux of relatively clean air from the upper troposphere with aerosol from high altitude inputs and long range transport (Cunningham and Zoller, 1981;Stohl and Sodemann, 2010).

Cluster means backward trajectories analysis of all the samples collected during both summer campaigns at DC revealed a prominent marine source (Fig. 3). Fig. 3 shows that the 10-days backward trajectories came from the Southern Ocean where there are no land based man made influences.

Fig. 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 mainly in the percentages of amino acids in the coarse fraction. 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 hours (Fig. 3) whilst in 2012-2013 the time range was between 4 and 7 days (Fig. 3).

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 suggest that the amino acids in the aerosol collected at DC can have two possible sources. The first hypothesis is thatthey were present in primary emitted coarse

Eliminato: were characterized by a prevalence of free amino acids in the fine fraction, witha notable increase of amino acids percentage (related to the total amino acids concentration detected in the PM_{10}aerosol samples) enrichment of amino acids in the coarse particles (13% of the total in 2011-12 and 23% of the total in 2012-13 campaigns) compared to coastal aerosol. In fact, during our 2010-2011 sampling campaign at MZS, which is located near the marine aerosol source,we observed only 2% of total free amino acids in the coarse particles.

Eliminato: 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 theintense cold over the plateau and presence of amino acids in the aerosol particles (Szyrmer and Zawadzki, 1997).

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Spostato in su [2]: During the Antarctic summer, the surface inversion over the polar ice cap is relatively weak and aerosols produced on the ocean's surface can betransported through the upper troposphere to the Antarctic plateauwhere they are easily mixed down to the surface(Cunningham and Zoller, 1981). There are also some transfermechanisms from the lower stratosphere to the upper troposphere that occur near the coast of the Antarctic continent. Aerosol from different sources mixesinto the upper troposphere, and this air descends uniformly over the Antarcticplateau 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).

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mode aerosol particles, which come from phytoplanktonic sea spray coarse mode particles (Matsumoto and Ueamatsu, 2005), or from soil dust coarse mode particles (Mace et al., 2003). Particles and their chemical constituents can travel for many weeks in the upper troposphere without being lost, provided they are not subject to wet deposition, or that the compounds are reacting in the aerosol phase. The second hypothesis is that amino acids hada marine source and these aerosols underwent several physico-chemical transformations 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 could either grow during long-range transport, due to condensation of molecules from the gas phase or by collision of small and large particles (coagulation) (Petzold and Karcher, 2012;Roiger et al., 2012). However, these processes are unlikely in Antarctica due to the very clean conditions. The most likely explanation is that the fine fraction has been subjected to other processes that increased the particle size of the aerosol. The most likely remaining 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 specific reason for the increase of amino acids percentage in the coarse particles is not clear, based on the available data. In our future investigations, we will also evaluate the aerosol mass, which is probably a key parameter to measure that will help explain this increase of concentration in the coarse particles.

The chemical composition of aerosols may change during long-range transport due to photochemical, chemical and ionic reactions (Milne and Zika, 1993; Noziére 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

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Spostato in su [1]: The concentration of free amino acids in the coarse particles of aerosols collected at DC had meanvalues of 407 and 421fmol m^{-3} (see Fig. 5) for the twofield 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, witha notable enrichmentof amino acids in the coarse particles (13% of the total in 2011-12 and 23% of the total in 2012-13) 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 transportpromoted by theintense cold over the plateau and presence of amino acidsin the aerosol particles (Szyrmer and Zawadzki, 1997).

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. Fig. 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.

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 phenomenon, Ala significantly contributes to the amino acid content in these "remote aerosols" as it does not degrade during long range transport.

Fig. 6 shows that the main difference between the two campaigns is mainly in the percentage of hydrophilic and neutral amino acids present. A longer transportation time from the source to the sampling site would allow chemical transformation through photochemical reactions to take place, decreasing the concentration of hydrophilic amino acids thus modifying the composition so that the

Spostato in su [3]: Fig. 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 campaignsis mainlyin the percentages of hydrophilic and neutral amino acids present. We suggest that the transport processes of the air masseswerethe main cause of these variationsasthe time spent inland by the air masses in the 2011-2012 summer was about 36 hours (Fig. 3) whilstin 2012-2013 the time range was between 4 and 7 days (Fig. 3).

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741 more stable Gly (a neutral component) becomes the main compound (Fig. 6). In the 2012-2013
742 summer, the time spent inland by the air masses ranged from between 4 and 7 days whist in the
743 2011-2012 summer it was only 36 hours.
744 Looking at the acid-base proprieties of the amino acids, some differences can be observed between
745 two different types of aerosol. As described above, the predominant amino acid in the MZS aerosols
746 was Arg, which contributed considerably to the percentage of basic compounds (53%). The pH
747 neutral components represented an important percentage (40% and 68% for coastal and inland
748 aerosols respectively). Gly is mainly present in large quantities in these aerosols because of its very
749 low atmospheric reactivity (half life of 19 days) (McGregor and Anastasio, 2001) and its presence is
750 usually considered an indicator of long-range aerosol transport (Milne and Zika, 1993; Barbaro et
751 al., 2011). The acid compounds (Asp and Glu) contribution was quite different in the aerosols from
752 the two different stations: with a low percentage in the coastal samples at MZS (7%) that was in
753 contrast with the higher content in the aerosols from DC (33% and 26% respectively for the two
754 consecutive field campaigns). This result can be explained by a study conducted by Fattori et al.
755 (2005) on the DC aerosol, where high acid content was found. High concentrations of hydrochloric,
756 nitric and sulfuric acids were found in the aerosol fine fraction, promoting numerous series of acid-
757 base atmospheric reactions that neutralize the basic compounds. In the atmosphere, amino acids are
758 present in very low quantities so it is thought that they do not influence the pH of aerosols.
759 However, the pH of aerosols, can influence the chemical form of the amino acids present.

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760 **3.3 Free amino acids during an oceanographic cruise**

761 Measurements of free amino acids were carried out on aerosol samples collected on the Southern
762 Ocean onboard the R/V Italica from 13th January to 19th February 2012. Aerosols were sampled
763 using a TSP sampler that collects particles with a diameter above 1 µm. The first and second
764 samples covered the track between New Zealand (from Lyttelton harbor) and MZS (Antarctica),
765 and the sixth and last samples were collected during the return journey between Antarctica and New

767 Zealand. Samples 3, 4 and 5 were collected on the Ross Sea near the Antarctic continent (Fig. 1).
768 Five L-amino acids (L-Asp, L-Arg, L-Glu, L-Phe, L-Pro) and Gly were present in the samples,
769 while other L- and D-amino acids had concentrations below MDLs (Supplementary Table S1). The
770 total concentrations of free amino acids varied between 2 and 12 pmol m^{-3}.
771 The first and last samples had the highest concentrations of free amino acids (Fig. 7), and their
772 relative sampling periods were characterized by temperatures ranging between -1°C and 18°C
773 (sample 1), in contrast, temperatures during the remaining sampling periods were always below -
774 1°C, with a lowest value of -8°C (sample 4). Higher temperatures can facilitate metabolic processes
775 and accelerate atmospheric chemical reactions, as well as promote bubble bursting from the sea
776 surface. This is probably the main source of amino acids in our on-ship samples. This is also
777 supported by the back-trajectory analysis (Supplementary Fig. S8a-g), that demonstrate only a
778 marine influence for that period. The concentration of amino acids was strongly influenced by sea
779 conditions during sampling. The field report (Rapporto sulla campagna Antartica, 2012), noted that
780 during navigation from New Zealand to the ice-pack region, the winds were always above 30 knots,
781 with maximum values of 60 knots with wave heightsof12 meters. This probably explains the higher
782 total concentration of free amino acids in the first two samples (12 pmol m^{-3}). Along the same track,
783 but under calmer sea conditions (sample 7), we observed a slight reduction in the total concentration
784 of free amino acids (8 pmol m^{-3}).These values were very similar to those reported by Matsumoto
785 and Uematsu (2005) in the Pacific Ocean and to those reported by Gorzelska and Galloway
786 (1990)and Wedyan and Preston (2008) in the Atlantic Ocean. The lowest concentrations were
787 observed in samples 2 and 6, probably due to the fact that they were collected far from Oceania and
788 from the Antarctic coast, in an area characterized by expansive pack ice and by temperatures below
789 -1°C, where the bubble bursting process was reduced.
790 The samples collected near the Antarctic coast (samples 3,4 and 5) were the most interesting ones
791 because the results could be compared with the amino acid values detected in the coastal station
792 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 µm 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 concentration was lower than that measured in the cruise's aerosols (3.5 pmol m^{-3}). So we suspect that the aerosols with a diameter above 10 µm, that were collected with theTSP sampler but not the cascade impactor, could be the main source of the difference in amino acid concentration values in the samples collected on the R/V Italica.

The back-trajectory analysis (Supplementary Fig. S8C-E) demonstrated that the air masses came from inland Antarctica, where no vegetation is present. The biological material present in the atmosphere with a size > 10 µm includes pollens which typically vary between 17-58 µm, fungal spores between 1-30 µm, and algal spores between 15-120 µm. Instead bacteria have a diameter between 0.25-8 µm, and viruses have diameters that are typically less than 0.3 µm (Jones and Harrison, 2004). For this reason, we propose that the biological materials influenced the concentration of the total free amino acids in the shipboard aerosols.

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 in aerosols. In the MZS aerosols, the presence of spores could not be evaluated because the sampler did not sample the particles >10µm. This is probably the reason why the Pro concentration was always below MDLs at MZS.

818 Asp was detected in only one sample (sample 5), with a concentration of 502 fmol m^{-3}. This value is
819 very similar to those measured in the two field campaigns on the Antarctic plateau (DC),
820 considering only the slotted filter stages above 1 µm (446 e 382 fmol m^{-3} respectively for the l
821 summer field campaigns of 2011-12 and 2012-13). The back-trajectory analysis (Supplementary
822 Fig. S8E) demonstrated that this air mass came from the plateau, where aspartic acid was a
823 predominant component of the amino acid content.
824 In the aerosols collected during the cruise, the Arg concentration was very low because the
825 sampling conducted on board R/V Italica during the summer of 2012 excluded fine particles,
826 whereas Arg was one of the most abundant compounds observed in the coastal station found in the
827 fine fraction.
828

829 **4. Conclusions**

830 This first study on the size distribution of amino acids in Antarctica has identified possible sources
831 of marine aerosols in this region and has characterized some chemical and physical transformations
832 that take place during transport to the interior of the Antarctic continent.
833 Marine emissions of fine particles occurred *via* bubble bursting processes on the surface of the
834 Southern Ocean. The mean total amino acid concentration detected at MZS was 11 pmol m^{-3}, with a
835 higher percentage of amino acids found in the fine fraction. The aerosol samples collected at Dome
836 C had the lowest amino acid values (0.7 and 0.8 pmol m^{-3}) and the coarse particles were found to be
837 enriched with amino acids compared to the coastal site. Numerous chemical and photochemical
838 events may have contributed to a decrease in the concentration in amino acids in the fine fraction,
839 and the chemical reactions were faster for hydrophilic compounds than for hydrophobic ones, as
840 suggested by an observed Ala enrichment.
841 The presence of only the L-enantiomers of free amino acids in Antarctic aerosols suggests that
842 marine particles were the main sources of free amino acids in this area and that these compounds

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844 can be modified when transported to the interior of the continent. Gly and Ala, are the most stable
845 compounds, and may be used as biogenic markers of long-range marine aerosols. The back-
846 trajectory analysis demonstrated that the differences in the transport time of air masses inside
847 Antarctica can result in modifications to the percentage of amino acids in the coarse particles.
848 The study of aerosols with diameters>10 µm indicated that bubble bursting processes can also emit
849 microorganisms that are composed of a higher number of neutral amino acids.
850

851 **Author contributor**

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

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871 *activities in Antarctica.*

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Figure captions

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.

Figure 2. Amino acid size distribution in the samples collected during the summer of 2010-11 at Mario Zucchelli Station (Antarctica).

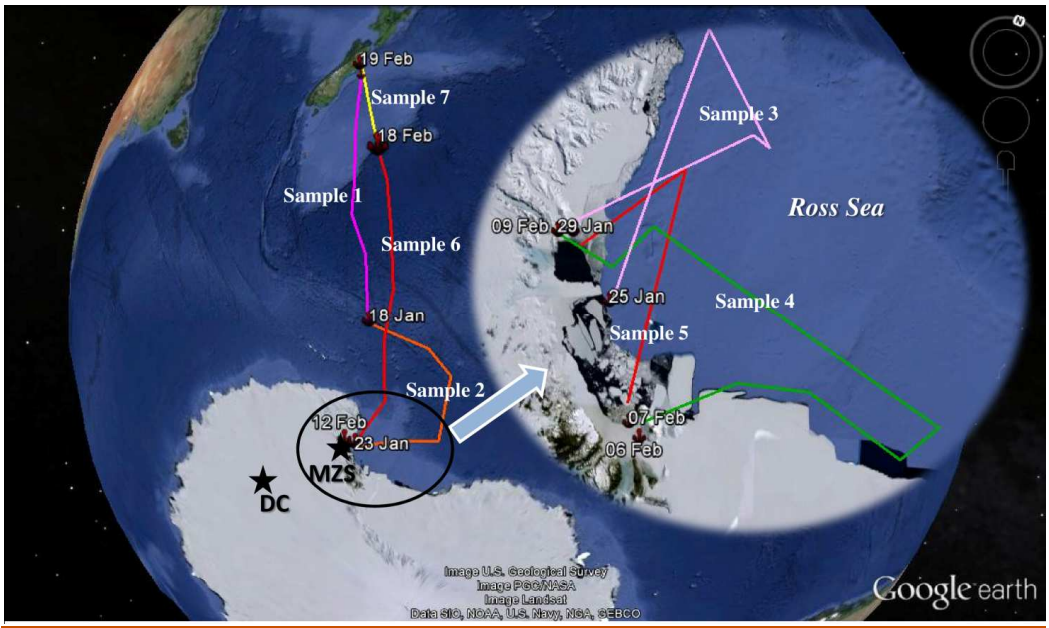
Figure 3. Cluster means backward trajectories analyses at 500 m aglat the coastal base “Mario Zucchelli Station” (MZS) during the summer of 2010-2011 and cluster means backward trajectories at the Italian-French base Dome C (DC) during the summers of 2011-2012 and 2012-2013.

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

Figure 5. Size distributions of amino acid concentrations in the samples collected during the summer of 2011-12 (A) and during the summer of 2012-13 (B) at the Italian French base “Concordia Station” (Dome C).

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.

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.



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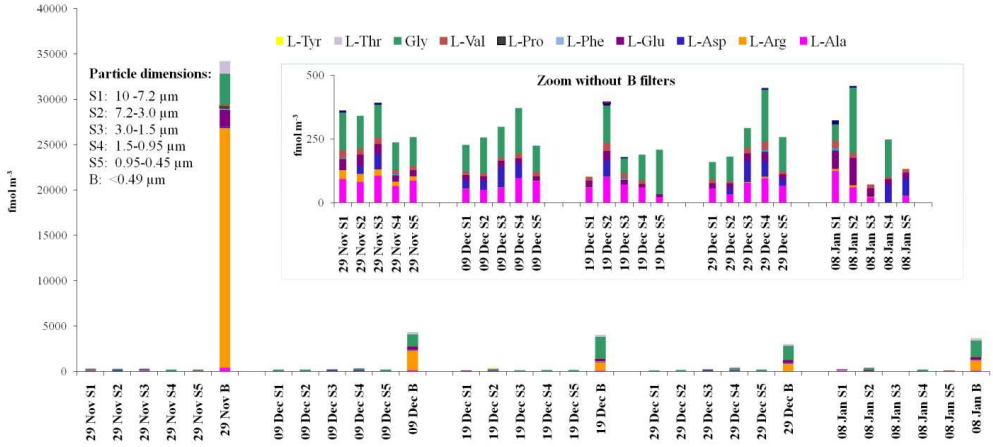

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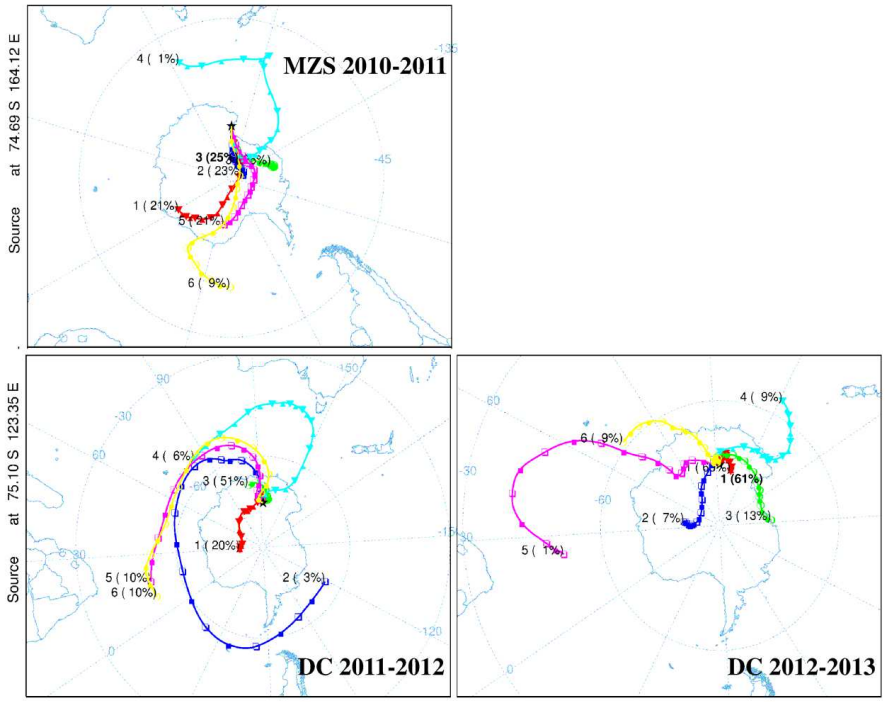

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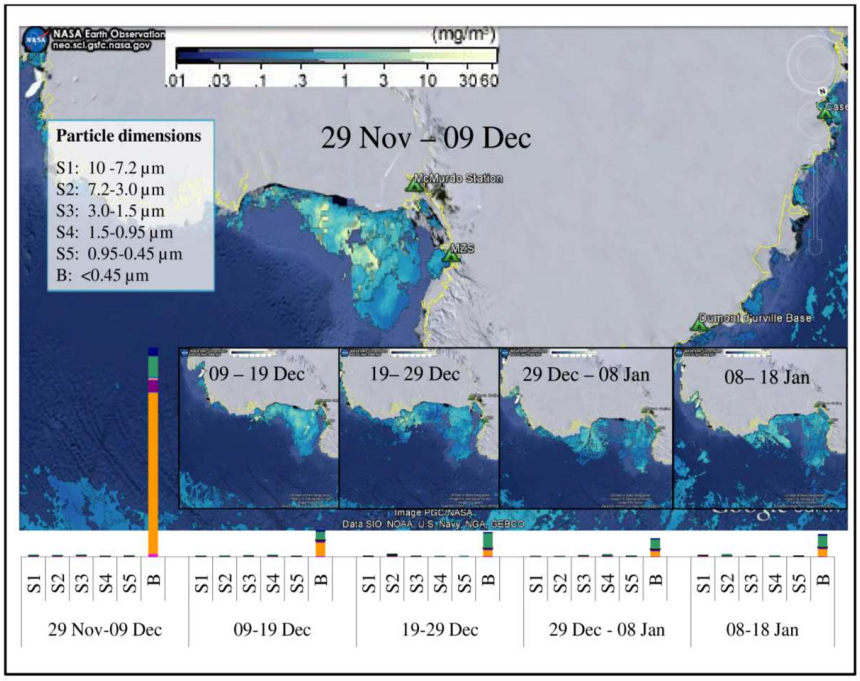

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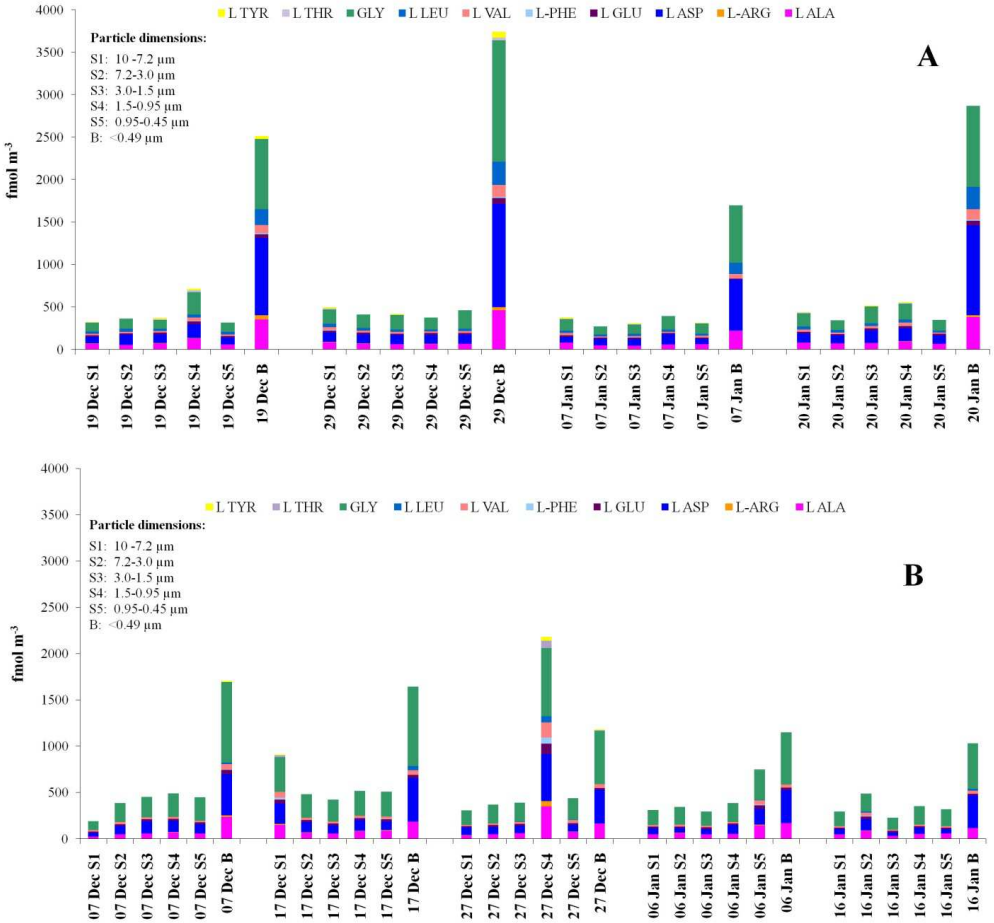

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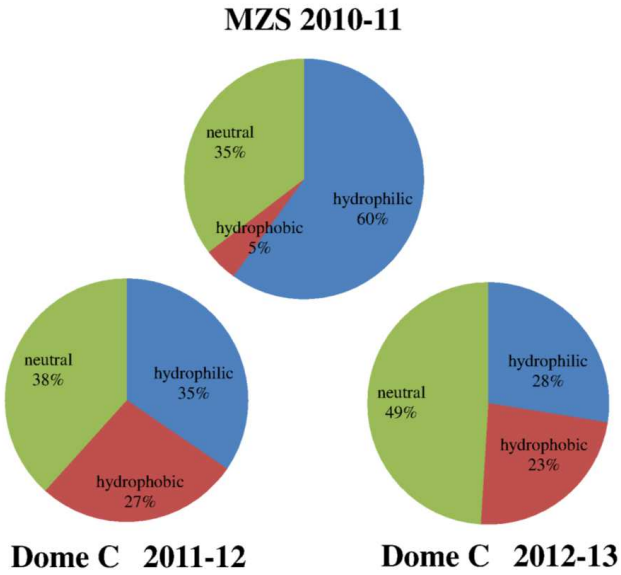

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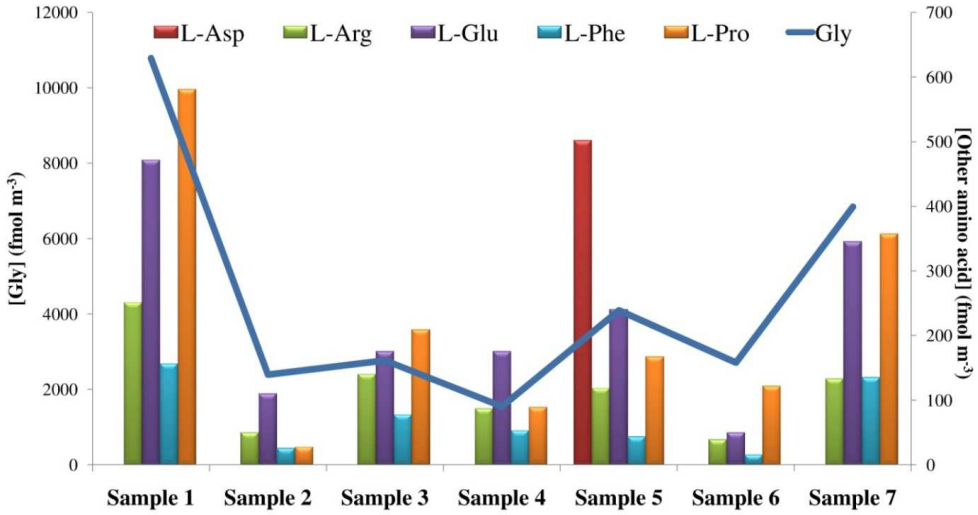

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