Amino acids in Antarctica: evolution and fate of marine aerosols

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

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Abstract

The chemical composition and size distribution of marine aerosols constitute an important parameter to investigate the their impact on global climate change. Amino acids are an important component of organic nitrogen in aerosols and particles with amino acids are considered good cloud condensation nuclei (CCN) and efficient ice nuclei (IN), with important effects on the radiation balance.

The main aim of this study was to investigate the L- and D- free amino acid composition of Antarctic aerosols in three different areas: two continental bases, Mario Zucchelli Station (MZS) and Concordia (Dome C), and during an oceanographic cruise on the Southern Ocean near the Antarctic continent. The study of size distribution of amino acids in aerosols permitted to characterize the water-soluble organic carbon (WSOC) component of marine aerosols near the source and after long-range transport. Amino acids can be used as markers for biogenic aerosol and these compounds can indicate the prevalence of phytoplanktonic material or bacterial matter through D/L ratio. Moreover, this study permitted to investigate the reactivity of these compounds during long-range transport.

The mean amino acid concentration detected at the Italian coastal MZS was 11 pmol m^{-3}, and a higher percentage of amino acids were present in the fine fractions. The study of amino acid composition in the coastal sampling station allowed us to investigate a marine aerosol produced near the source.

Once produced on the sea surface, marine aerosols undergo several physical and chemical transformations. This was demonstrated by using the samples collected on the Antarctic plateau. In these samples, the lowest amino acid values (0.7 and 0.8 pmol m^{-3}) in aerosols were determined with an enrichment of amino acids percentage in the coarse particles.

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

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1. Introduction

In recent years, the scientific community has shown particular interest in the organic composition of aerosols as the latter contribute to a substantial portion of the marine aerosol mass, especially to the submicron size fraction (Bigg, 2007). The study of marine aerosols is crucial considering their significant contribution to global aerosol load given the ocean's extension with consequent impacts in the Earth climate (O'Dowd and De Leeuw, 2007; Petzold and Karcher, 2012; Boucher et al., 2013). Several studies (Facchini et al., 2008a,b; Rinaldi et al., 2010) demonstrated that the chemical composition of marine organic aerosols is a combination of different primary and secondary sources. Moreover, in the primary emissions *via* bubble bursting processes, the presence of phytoplankton can modulate the chemical and physical proprieties of marine organic 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 constitute an interesting component of the organic nitrogen content of aerosols because they are highly efficient ice nuclei (IN) (Szyrmer and Zawadzki, 1997) and good cloud condensation nuclei (CCN) (Raymond and Pandis, 2003; Huff Hartz et al., 2006; Kristensoon et al., 2010). De Haan et al. (2009) postulated that amino acids can contribute to the formation of new particles in the atmosphere. These compounds can also serve as a source of nutrients for marine ecosystems thanks to their high bioavailability (Zhang et al., 2002).

Several studies determined amino acid concentrations in the condensed phase of aerosols (Gorzelska and Galloway, 1990; Spitzy, 1990; Milne and Zika, 1993; Saxena and Hildemann, 1996; Zhang et al., 2002; Zhang and Anastasio, 2003; Mandalakis et al., 2010;Mandalakis et al., 2011; Ge et al., 2011 and its references), but also in rainwater (Mopper and Zika, 1987; Mace et al., 2003a,b), in fog (Zhang and Anastasio, 2001), and in dew water (Scheller, 2001). In the atmosphere these

Eliminato: Marine aerosols are among the most important natural aerosol systems at the global level, due to the oceans' extent (O'Dowd and De Leeuw, 2007). They play an important role in the Earth system, especially in climate and atmospheric chemistry, as they significantly contribute to the global aerosol burden and influence both direct and indirect radiative forcing as well as a variety of chemical processes (IPCC, 2007).¶
Knowledge of the chemical composition of these particles is crucial to better understand the mechanisms influencing climate change, due to the ability of these particles to act as cloud condensation nuclei. ¶
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Eliminato: As for secondary organic aerosols, their production involves several mechanisms which have not yet been clarified (Vignati et al., 2010;Spracklen et al., 2008;Myriokefalitakis et al., 2010). However, Bates et al. (1992) demonstrated that the production of secondary marine organic aerosols is associated with biologically-driven emissions of organic compounds from phytoplankton. Lim et al. (2010) studied the role of aqueous chemistry in the formation of secondary organic aerosols, describing a number of photochemical reactions that occur in the atmosphere. A detailed understanding of these mechanisms is essential to quantify the role of marine aerosols in the functioning of the Earth system. ¶

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Eliminato: ;Zhang and Anastasio, 2003 compounds 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 ones (Mopper and Zika 1987; Milne and Zika, 1993), and particulate amino acids (solid microorganisms and debris particles inside the liquid aerosol phase) (Kuznetsova et al., 2005).

Several sources can affect the content of atmospheric dissolved free amino acids. Amino acids can be detected in volcanic emissions (Mukhin et al., 1978; Scalabrin et al., 2012), but biomass burning was also suggested as a possible source of WSOC (Mace et al., 2003a; Chan et al., 2005). The different types of amino acids in continental particles are thought to be produced by plants, pollens and algae, but also by fungi and bacteria spores (Milne and Zika, 1993;Scheller, 2001; Zhang and Anastasio, 2003; Mace et al., 2003a). The continental contribution was evaluated by Mace et al. (2003b), who distinguished the biogenic amino acids present in fine particles from the amino acids contained in anthropogenic coarse particles. Many amino acids are produced by anthropogenic sources such as 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. Near the inhabited continents, several sources could produce amino acids in the particle phase, although soil and desert dust are probably the most important sources of high amino acid concentrations

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; Wedyan and Preston; 2008; Mandalakis et al., 2011) but few studies were 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 penguins as a source of amino acids in the aerosol of Bird Island in the South

Eliminato: Amino acids, being an important portion of organic aerosols, can influence the cloud formation or act as ice-forming nuclei due to their hygroscopicity (Szyrmer and Zawadzki, 1997;Wedyan and Preston, 2008). De Hann et al. (2009) have postulated that amino acids can contribute to the formation of new particles in the atmosphere. These compounds can also serve as a source of nutrients for marine ecosystems thanks to their high bioavailability (Zhang et al., 2002). ¶

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Atlantic Ocean. To our knowledge, the present paper is the first investigation that considers 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 acid are peptidoglycans, the main structural components of bacterial cell walls (Voet and Voet, 1999).

Chiral information can reveal the primary and secondary origins of aerosol components as demonstrated in several recent studies (Kuznetsova et al, 2005; Wedyan and Preston, 2008; Nozière et al., 2011; Gonzàlez et al., 2011; Gonzàlez et al., 2014). Amino acid enantiomeric ratios can be used as powerful markers for characterizing nitrogen 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). The combined amino acids are more influenced by bacterial sources while this contribution is relatively small for free amino acids. The presence of free D-isomers is a significant index of a great proportion of bacteria in aerosols where photosynthesizing organisms are not present (Wedyan and Preston, 2008).

The aim of this study is to investigate the occurrence and concentration levels of dissolved free L- and D-amino acids in the Antarctic aerosols and to estimate how these compounds produced from seawater surface were distributed in the size-segregated aerosols, as well as their composition and distribution after long-range atmospheric transport. Amino acids can be involved in cloud formation act as ice-forming nuclei (Raymond and Pandis, 2003; Huff Hartz et al., 2006; Kristensoon et al., 2010; Szyrmer and Zawadzki, 1997) and affect the atmospheric balance (Chan et al., 2005). Amino acids can be used as markers for biogenic aerosols and their different compound reactivity may be useful for determining the age of the aerosol (Scalabrin et al., 2012). The enantiomeric D/L ratio of amino acids in aerosols can help to trace the origin of biogenic aerosols, indicating the prevalence of phytoplanktonic material or bacterial matter (Kuznetsova et al., 2005).

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Due to their distance from anthropogenic and continental emission sources, polar regions are excellent natural laboratories to conduct studies on the behavior, evolution and fate of marine aerosols. In Antarctica, long-range atmospheric transport of anthropogenic pollutants is minimal because the continent is surrounded by the Southern Ocean, where natural sources such as seawater provide the main contributions to marine aerosols (Bargagli, 2008). Aerosol measurements in Antarctica provide information on the concentrations and behavior of aerosols, such as particle formation and growth, with minimal interference from anthropogenic sources (Bargagli, 2008;Bourcier et al., 2010).

Four different Antarctic austral summer campaigns were conducted to pursue our investigation: in two consecutive field campaigns, aerosols were collected on the Antarctic plateau near the Italian-French base of Concordia Station (Dome C); one sampling period was carried out at the Italian coastal base MZS; finally, shipboard aerosols were sampled on the R/V Italica on the Southern Ocean, near Antarctica.

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

2. Experimental section

2.1 Sample collection

Aerosol samplings were carried out during four different Antarctic austral summer campaigns, in the framework of the “Progetto Nazionale di Ricerche in Antartide” (PNRA). The sampling sites are shown in figure 1.

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Five aerosol samples were collected at the Italian base MZS from 29 November 2010 to 18 January 2011. The sampling site was at the Faraglione Camp (74° 42′ S – 164° 06′ E), about 3 km south of the MZS in Victoria Land. The site is a promontory at 57 m asl. It was chosen because it is located in a valley that is separated from the main station area by a hill, and pollution from the research station is therefore negligible.

At the Italian-French base Dome C, four aerosol samples were collected from 19 December 2011 to 28 January 2012; finally, five airborne samples were obtained from 07 December 2012 to 26 January 2013. The sampling site was in the East Antarctic plateau (75° 06’ S – 123° 20’ E), about 1 km south-west of the Dome C buildings, upwind of the dominant wind (from south-west).

Aerosol samples in terrestrial bases (MZS and Dome C) were collected using a TE-6070, PM10 high-volume air sampler (average flow 1.21 m^3 min^{-1}) provided with a Model TE-235 five-stage high-volume cascade impactor (Tisch Environmental Inc., Cleves, OH) equipped with a high-volume back-up filter (Quartz Fiber Filter Media 8” x 10”) and with a 5.625" x 5.375" Slotted Quartz Fiber for collecting particle size range in the following range: 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 campaign lasted 10 days, with a total air volume of ~15,000 m^3 per sample.

Amino acids were also determined in seven other samples retrieved from the Ross Sea (Antarctica) on the R/V Italica from 13 January to 19 February 2012 (table S1).

During the oceanographic cruise, airborne aerosols were collected by means of a circular quartz fiber filter (quartz fiber filter (QFF) (SKC Inc., Eighty Four, To-13 model)) using a TE 5000 High Volume Air Sampler (Tisch Environmental Inc., OH) in order to determine the TSP (total suspended particulate) fraction, where the particles had a diameter above 1µm.To avoid contamination from the ship’s exhaust, air samples were automatically controlled by a wind sector, in order to start sampling only when the relative wind direction changed from -135° to 135°C of the bow, and when the relative wind was above 1 m s^{-1}. Collection was scheduled to last about five days, but this time frame was subject to variations, due to the wind selector and to cruise events.

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The airborne sampling volumes varied between 511 and 2156 m^3. The track chart is reported in SupplementaryFig. S1.

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

2.2 Sample processing

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

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

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

2.3 Instrumental analysis

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

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Chromatographic separation was performed using a 2.1x 250 mm CHIROBIOTIC TAG column (Advanced Separation Technologies Inc, USA) with a mobile phase gradient elution consisting of ultrapure water with 0.1% formic acid (eluent A) and methanol with 0.1% formic acid (eluent B). The binary elution gradient program at a flow rate of 0.2 mL min^{-1} was used as follows: 0-15 min, isocratic elution with 30% of eluent B; 15-20 min, gradient from 30 to 100% B; 20-25 min washing step with 100% of eluent B; 27-30 min, equilibration at 30% eluent B. The injection volume was 10 µL.

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

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

2.4 Back-trajectory calculation and satellite imagery

Backward air trajectories arriving at MZS, Dome C and R/V Italica were computed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion models(Draxler and Rolph, 2013). The meteorological data used for computing all the backward trajectories were the NCEP/NCAR Global Reanalysis Data. For MZS data, a vertical velocity model was used as vertical motion while an isoentropic model was employed for the analysis of Dome C air masses, as suggested by Stohl et al (2010).

240 hours normal back-trajectories beginning at 500 m above ground level (agl) at MZS and Dome C were calculated during each sampling campaign period. Four runs were computed for every sampling day starting every six hours and the resulting multiple trajectories were aggregated into 6 groups in order to highlight major patterns in the origin of air masses reaching sampling sites. For the oceanographic cruise, trajectory matrices were performed in order to simulate the ship's itinerary. In this case, for each 24-h sampling event, 5-day backward trajectories were computed.

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

3. Results and Discussion

3.1 Free amino acid determination in the coastal area

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

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

The total concentration of amino acids, calculated from the sum of their six size distributions in all aerosol samples, have a median value of 5 pmol m^{-3} and an average value of 11 pmol $m^{-3,}$ due to the higher amino acid concentration in the first sample (29 November-9 December), as shown in Fig. 2.

The average concentration of amino acids determined in this study was very similar to those found in the literature for marine aerosols in remote areas. Matsumoto and Uematsu (2005) reported an average free amino acid concentration of 10.7 pmol m^{-3} in the Pacific Ocean, while Gorzelska and

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Galloway (1990) and Wedyan and Preston (2008) observed a mean of 3 pmol m^{-3} and 20 pmol m^{-3} respectively in the Atlantic Ocean. Scalabrin et al. (2012) determined an average concentration of 2.8 pmol m^{-3} using the same sampling method at the Arctic coastal station.

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

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In the present work, 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 presented similar compositions in all the samples, with average percentages of 9% for Glu, 7% for Ala, 5% for Thr, 4% for Asp, 2% for Val while 1% for other amino acids (Phe, Tyr and Pro).

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The first sample collected between 29 November and 09 December had a higher concentration of Arg (74%), while Gly was 11%. In contrast, in the other samples, Gly was the predominant compound, with a percentage between 48 to 56%, while arginine was about 18%.

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Scheller (2001) demonstrated that high quantities of Arg were closely linked with plant growth, but the cluster means backward trajectories (Supplementary Fig. S2) conducted for our samples show that air masses come from open-sea regions (1 %) and principally from the internal Antarctic continent (99 %), both characterized by their lack of vegetation. These considerations suggest that local marine influence was the main source of amino acids in MZS and that the concentration of atmospheric amino acids was linked to the primary production in the sea, as also confirmed by other studies(Meskhidze and Nenes, 2006;Vignati et al., 2010; Yoon et al., 2007; Mueller et al., 2009).

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

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

Meteorological conditions play an important role in the processes of aerosol formation. Indeed, the first sampling period (29 November-09 December) was characterized by temperatures ranging between -10°C and -1.5°C, while in the next sampling period, the temperature was always above-2°C (PNRA-ENEA, 2014). Studies conducted on the sea 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. In such conditions, near-surface turbulence was increased, leading to an increase of material in the microlayer, where bubbles also actively contributed as transport mechanisms. Leck and Bigg (2005) showed that the main occurrences of fine aerosol formation in the atmosphere were observed during periods of lead melting and refreezing. Our first sample was collected when the pack ice was melting and refreezing, and indeed we observed the highest concentration of total amino acid in the fine aerosols.

The local marine source of the aerosols collected in the coastal station MZS was also confirmed by the distribution of amino acids in the different particle fractions. Fig. 2 shows that the highest concentration of amino acids (11342 fmol m^{-3} as mean value, 98%) was generally observed in fine particles (<1µm), while a much lower average value of 265 fmol m^{-3} (2%) for total amino acid concentration was observed in the coarse fraction (>1 µm). Our experimental evidence corresponds to the enrichment of WSOC (e.g., amino acids) in sea spray submicron particles described by O'Dowd et al. (2004) and Keene et al.(2007). WSOC were present in all aerosol size fractions, but the greatest enrichment was associated with the smallest size fraction (0.1-0.25 µm) (Keene et al., 2007;Facchini et al., 2008b;Modini et al., 2010). The correlation between the increased enrichment

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of aerosol organic fraction and the decrease in particle dimension is in agreement with the thermodynamic prediction of bubble bursting processes under conditions in which the ocean surface layer becomes concentrated with surfactant material, which, in addition to inorganic salts, can be incorporated into sea spray drops (Oppo et al., 1999).

3.2 Free amino acid determination in remote continental area

Dome C Station is an ideal site for studying the chemical composition of "background" aerosols, andseveral studies (Fattori et al., 2005; Jourdain et al., 2008; Becagli et al., 2012; Udisti et al., 2012) were carried out to investigate the distribution of inorganic compounds and of a few organic molecules (e.g., methansulfonic acid). However, the amino acids pattern had not been studied yet.

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

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

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

The total average concentrations of these amino acids above MDLs, obtained from the sum of the amino acid concentrations in all stage sampled, were respectively 0.8 pmol m^{-3} and 0.7 pmol m^{-3}for the 2011-2012 and 2012-2013 austral summer Antarctic fields (Fig. 4). To our knowledge, these mean concentrations were the lowest concentrations detected in all investigated areas (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), confirming that this type of aerosol characterization describes the amino acid concentration in very remote "background aerosols".

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Spostato in giù [7]: This location is ideal for studying the chemical composition of "background" aerosols.

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Eliminato: The study of "background aerosols" is very important to estimate the impact of anthropogenic sources on the atmosphere and to study the natural phenomena that occur in atmospheric aerosols. Dome C Station is situated on the ice sheet in the Eastern Antarctic plateau, where the only possible anthropogenic contamination can come from the station itself, the airplane and the traverse used to supply it. This location is ideal for studying the chemical composition of "background" aerosols. ¶
In this remote area, our samples were collected during two consecutive austral summer field campaigns (19 December 2011 - 28 January 2012 and 07 December - 26 January 2013) in order to evaluate the size-distribution of amino acids concentration and the variability between two different years.¶
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The background profile of amino acids was altered by the higher concentrations in the coarse fraction 1.5-0.95 µm of the sample collected from 27 December 2012 to 06 January 2013 (Fig. 4B). Having evaluated the wind roses for each sample in the two summer field campaigns, we consider that these samples were the only ones to be contaminated by human activities at the Dome C station (Supplementary Fig. S3).

A prominent marine source was revealed by the cluster means backward trajectories analysis of all the samples collected during both austral summer campaigns (Supplementary Fig. S4 and S5). During the Antarctic austral summer, the surface inversion over the polar ice cap is relatively weak and aerosols produced on the ocean's surface and transported through the upper troposphere can be easily mixed down to the surface(Cunningham and Zoller, 1981). There are also some mechanisms of transport from the lower stratosphere to the upper troposphere near the coast of the Antarctic continent. The materials returning to different sources can be mixed into the upper troposphere, and this air generally descends over the polar plateau, thanks also to the cooling of the latter's surface. During the summer, there is a continuous flux of air from the upper troposphere(Cunningham and Zoller, 1981;Stohl and Sodemann, 2010).

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

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This enrichment of amino acids in the percentage of coarse fraction can be due to long-range transport where the increase in the dimension of these particles can be improved by the presence of amino acids, as these compounds are considered efficient IN (Szyrmer and Zawadzki, 1997).

The composition of aerosols may change during long-range transport due to photochemical, chemical and ionic reactions (Milne and Zika, 1993; Noziére et al., 2007; 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 ammonium, 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 the oxidation process, which is a removal mechanism for hydrophobic organic compounds, is slower in larger carbonaceous aerosols.

The aerosols collected at Dome C station were characterized by the prevalence of amino acids in the back-up filters (<0.45 µm), but the amino acid fraction in the coarse particles represented a higher percentage (13-23%) than that of the aerosols generated near the source. In fact, during our 2010-2011 sampling campaign at MZS station, located near the aerosol source, we observed only 2% of amino acids in the coarse particles.

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

Fig. 5 shows that hydrophilic components were predominant in marine aerosols released into the atmosphere, while hydrophobic compounds considerably increased in the aerosols collected at the continental station. The low abundance of hydrophobic amino acids in coastal aerosols was

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Spostato in giù [1]: This evidence suggests that hydrophobic amino acids present in the coarse particles are less reactive. Our hypothesis is confirmed by the behavior of Ala. Ala is classified as hydrophobic (Pommie et al., 2004) and its average concentration for the coarse fraction at Dome C was 70 fmol m^{-3}, the same value quantified in the coarse fraction in the MZS samples. This indicates that the coagulation processes with the relative increase of Ala concentration in larger particles are probably together with slow oxidation processes. Thanks to this phenomenon, Ala significantly contributes to the amino acid content in these “background aerosols”. ¶

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observed also by Mandalakis et al. (2011), and is probably caused by their lower tendency to dissolve in the aqueous particles contained in coastal aerosols. This classification permits to hypothesize that a higher content in hydrophilic amino acids can reflect a higher water content in the aerosols. This is a very important indication, because amino acids can be involved in cloud formation, behaving as ice-nuclei activators and affecting the balance of atmospheric radiation (Szyrmer and Zawadzki, 1997; Mandalakis et al., 2011).

The comparison between the concentrations of hydrophobic Ala in the two sampling sites(MZS and Dome C) highlighted a very similar average concentration (70 fmol m^{-3}) in the coarse particles. This interesting behaviormay confirm the hypothesis of limited atmospheric reactivity proposed by Maria et al. (2004), indicating a larger 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 “background aerosols”.

Fig. 4 shows that the concentration of amino acids for the 2011-2012 austral summer Antarctic campaign was higher than the values reported for the 2012-2013 Antarctic campaign, and Fig. 5 underlines that the main difference between the two campaigns resides in the percentages of hydrophilic and neutral amino acids. We suggest that the transport processes of air masses was the main cause of these variations because the time spent inland by these air masses in the 2011-2012 summer was about 36 hours (Supplementary Fig. S4) while in 2012-2013 the time range was between 4 and 7 days (Supplementary Fig. S5). A longer transportation time from the source to the sampling site allows for a chemical transformation through photochemical reactions to take place, decreasing the concentration of amino acids and modifying the composition where the more stable Gly (neutral component) becomes the main compound (Fig. 5).

With regard to the acid-base proprieties of amino acids, some differences can be observed between two different types of aerosols. As described above, the predominant amino acid in the MZS aerosols was Arg, which considerably contributed to the percentage of base compounds (53%). Neutral components, which represented an important percentage (40% and 68% for coastal and

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internal aerosols respectively), were heavily influenced by the presence of Gly. This amino acid is commonly present in large quantities in the aerosols because of its very low atmospheric reactivity (half time of 19 days) (McGregor and Anastasio, 2001) and is usually considered an indicator of long-distance aerosol transport (Milne and Zika, 1993; Barbaro et al., 2011).

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The acid compounds (Asp and Glu) content showed a mismatch between aerosols in the two different stations: the negligible percentage in the coastal MZS (7%) was in contrast with the important content in the aerosols of Dome C (33% and 26% respectively for the two consecutive field campaigns). This evidence can be explained using a study conducted by Fattori et al. (2005) in the Dome C aerosol, where high acidity content was verified. High concentrations of hydrochloric, nitric and sulfuric acids composed the aerosol fine fraction, promoting numerous acid-base atmospheric reactions with neutralization process but also with an increase in the acid component as demonstrated in our studies. In the atmosphere, amino acids are present in small quantities and it can be thought that they do not influence the pH of aerosols. Aerosols, however, can influence the chemical form of amino acids.

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3.3 Free amino acids during an oceanographic cruise

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

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

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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 (Supplementary Table S2).

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

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

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The concentration of amino acids was strongly influenced by sea conditions during the sampling.

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

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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.

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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, and where the bubble bursting process was reduced.

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

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

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

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

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

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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 (typical diameter 15-120 µm) could not be evaluated because the sampler eliminated the particles above 10µm. This is probably the reason why Pro concentration was always below MDLs.

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Asp was detected in only one sample (sample 5), with a concentration of 502 fmol m^{-3}. This value is very similar to those measured in the two field campaigns above the Antarctic plateau, considering only the slotted filter above 1 µm (446 e 382 fmol m^{-3} respectively for the austral summer field campaigns 2011-12 and 2012-13). The back-trajectory analysis (Supplementary Fig. S6e) demonstrated that, in the air mass coming from the plateau, aspartic acid was a predominant component of amino acid content.

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

The neutral components (77%) gained influence in the shipboard data (particles with diameter >1 µm). Gly was the predominant component, with concentrations ranging between 1.5 and 4.1 pmol m^{-3}. A very low percentage of hydrophobic amino acids (2%) characterized the aerosols collected on the ship, probable due to the major incidence of the local source in the amino acid content.

4. Conclusions

This first study on the size distribution of amino acids in Antarctica identified sources of marine aerosols in this region and characterized some chemical and physical transformations taking place during the 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. An increase in the percentage of amino acid fraction in the coarse particles was observed during the long-range transport as verified at Dome C station. Numerous chemical and photochemical events may contribute to decreasing the concentration in amino acids in the fine mode, and the chemical reactions were faster for hydrophilic compounds than for hydrophobic ones, as suggested by Ala enrichment in the aged aerosols.

The only presence of L-enantiomers of free amino acids in Antarctic aerosols suggests that planktonic particles (Kuznetsova et al., 2005) were the first sources of free amino acids in this area

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and that these compounds can be modified while transported inside the continent. Gly and Ala, the most stable compounds, may be used as biogenic markers of long-range marine aerosols. The back-trajectory analysis demonstrated that the difference in the transport time of air masses inside Antarctica can modify the percentage of amino acids in the coarse particles.

The study of aerosols with diameters>10 µm indicated that bubble bursting processes can also emit microorganisms composed by a higher number of neutral amino acids.

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

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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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Acknowledgments

This work was financially supported by the Italian Programma Nazionale di Ricerche in Antartide (PNRA) through the project "Studio delle sorgenti e dei processi di trasferimento dell'aerosol atmosferico antartico" (2009/A2.11). The research was also supported by funding from the National Research Council of Italy (CNR) and from the Early Human Impact ERC Advance Grant from the European Commission's VII Framework Programme, grant number 267696, contribution n° 12.

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The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for providing the HYSPLIT transport and dispersion model and/or READY website (http://www.ready.noaa.gov) used in this publication.

The authors thank ELGA LabWater for providing the PURE-LAB Option-R and Ultra Analytic, which produced the ultra-pure water used in these experiments.

In conclusion we wish to thank Prof. A. Ceccarini (University of Pisa, Italy), Dr. M. Bonazza (University of Trieste, Italy), Dr. S. Illuminati (Polytechnic University of Marche – Ancona, Italy) and Dr. E. Padoan (University of Torino, Italy) for their help and cooperation during the sampling 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.

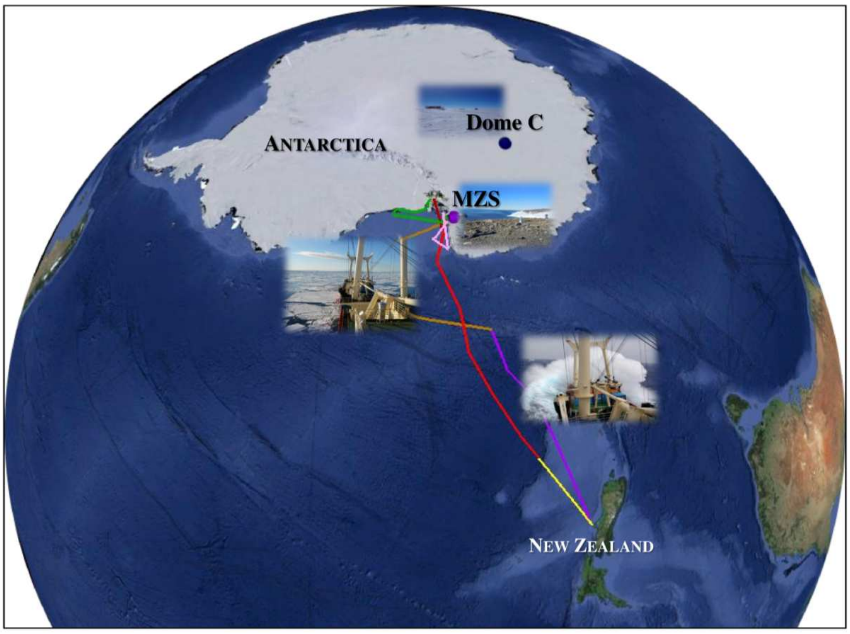
Figure 2. Amino acid size distribution in the samples collected during the austral summer 2010-11 at the Mario Zucchelli Station (Antarctica).

Figure 3. Distribution of chlorophyll concentrations in the Ross Sea for each sampling period obtained through Aqua/MODIS NASA satellite.

Figure 4. Size distributions of amino acids concentration in the samples collected during the austral summer 2011-12 (A) and during the austral summer 2012-13 (B) at the Italian French base “Concordia Station” (Dome C).

Figure 5. Comparison between theme an percentages of hydrophilic, neutral and hydrophobic contributions of the aerosols sampled at the Mario Zucchelli Station and at Dome C.

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



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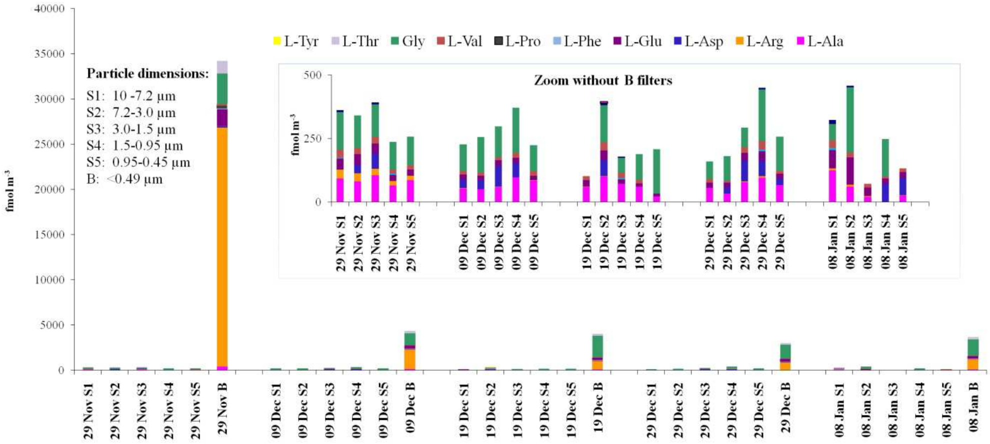

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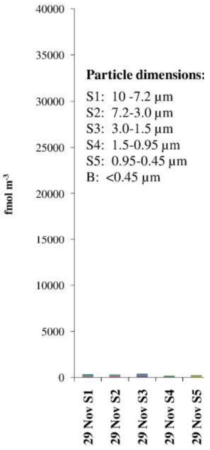

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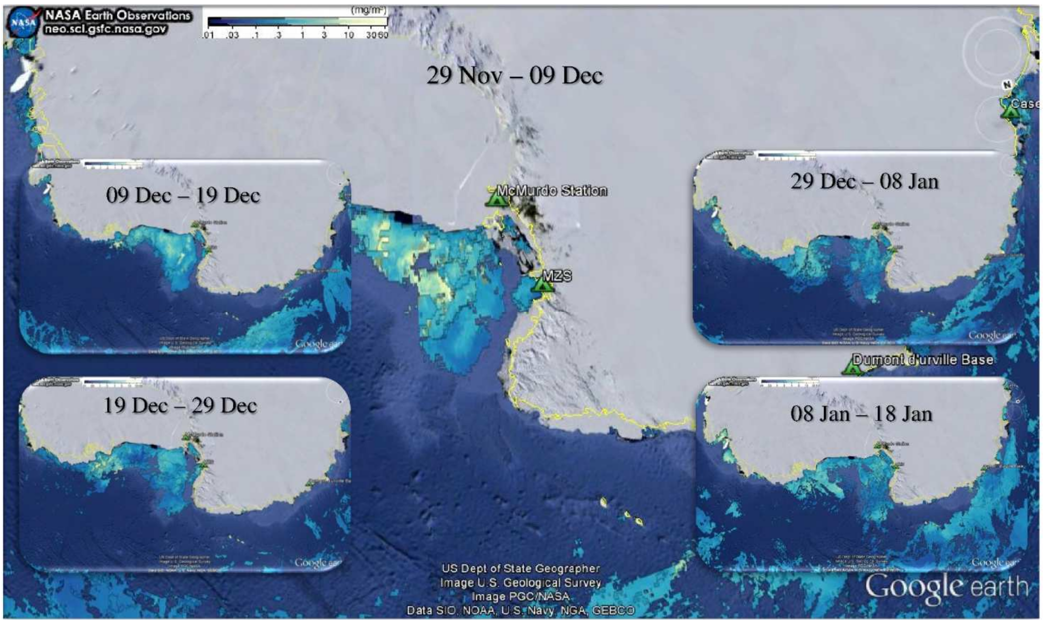

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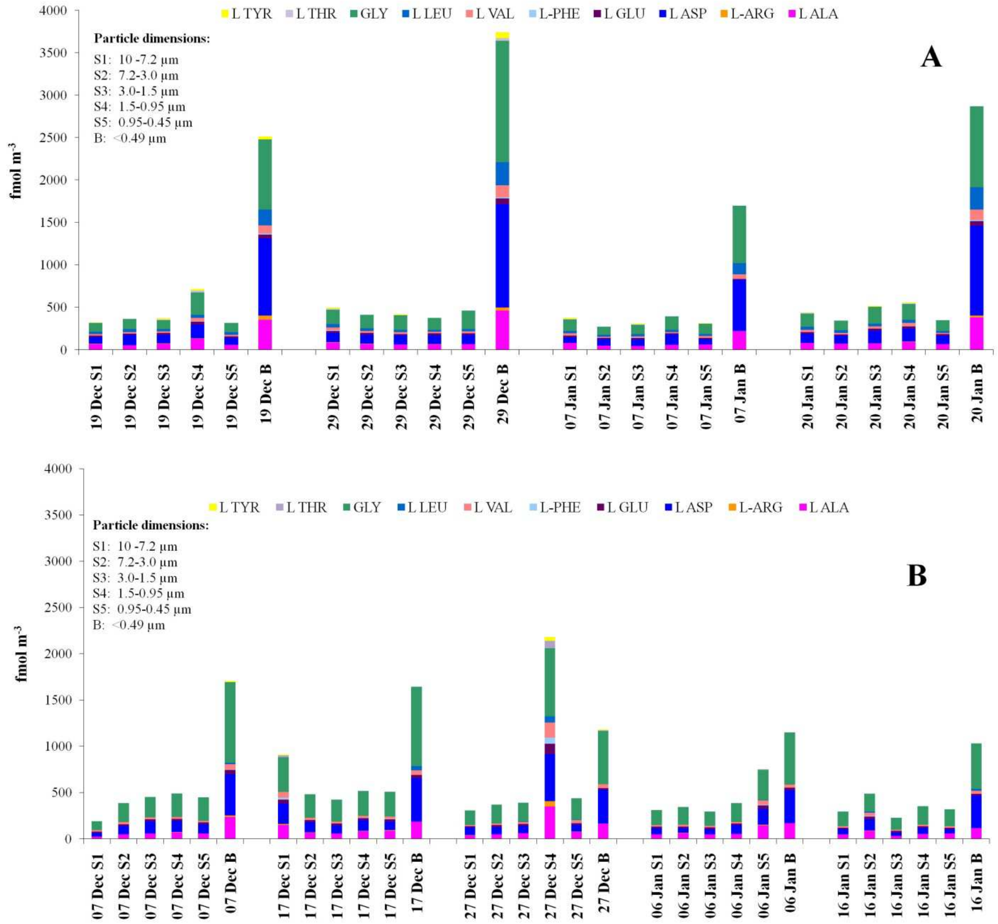

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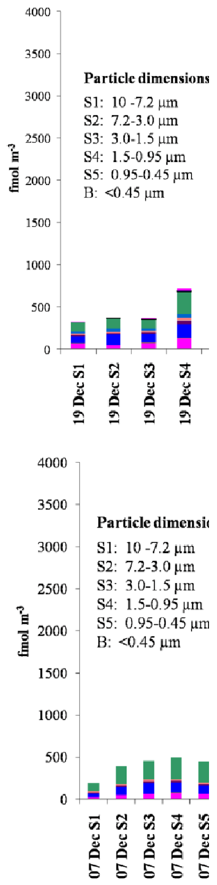

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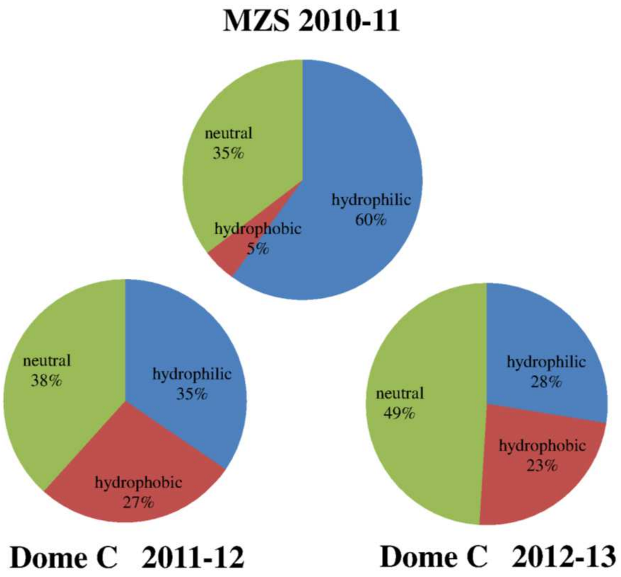

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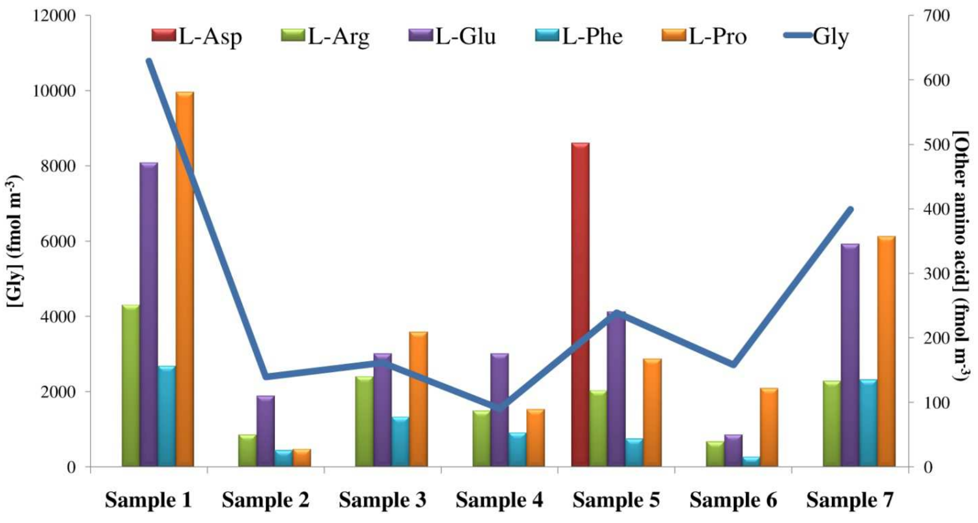

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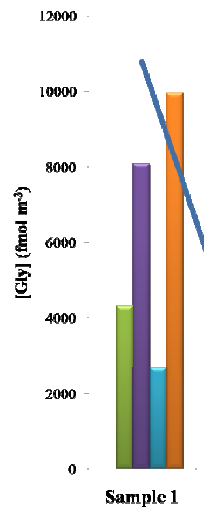

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