



Characterization of free L- and D-amino acids in size-segregated background aerosols over the Ross Sea, Antarctica



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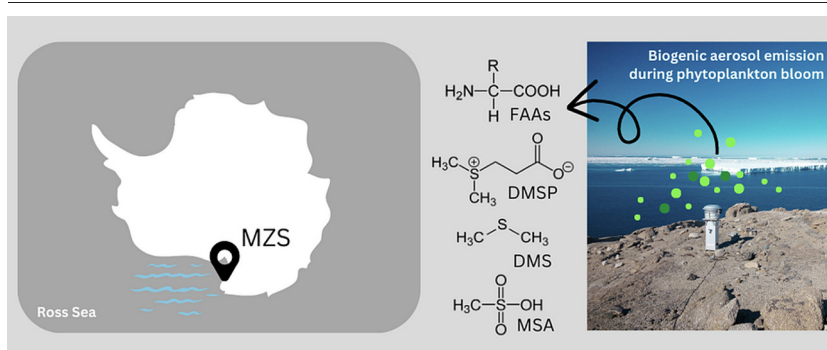
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HIGHLIGHTS

- The article improves the knowledge about the free amino acids' sources in the Antarctic aerosols.
- D/L Ala ratio suggests microlayer as plausible source of airborne free amino acids.
- Local input is shown by the relation between DMSP and coarse D-Ala.

GRAPHICAL ABSTRACT



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ABSTRACT

The study of airborne chemical markers is crucial for identifying sources of aerosols, and their atmospheric processes of transport and transformation. The investigation of free amino acids and their differentiation between the L- and D-enantiomers are even more important to understand their sources and atmospheric fate. Aerosol samples were collected with a high-volume sampler with cascade impactor at Mario Zucchelli Station (MZS) on the coast of the Ross Sea (Antarctica) for two summer campaigns (2018/19 and 2019/20). The total mean concentration of free amino acids in PM₁₀ was 4 ± 2 pmol m⁻³ for both campaigns and most of free amino acids were distributed in fine particles. The coarse mode of airborne D-Alanine and dimethylsulfoniopropionate in seawater showed a similar trend during both Antarctic campaigns. Thus, the study of D/L Ala ratio in fine, coarse and PM₁₀ fractions indicated the microlayer as the local source. This paper demonstrated that free amino acids follow the trend of DMS and MSA release occurred in the Ross Sea, confirming their applicability as markers for phytoplankton bloom also in paleoclimatic studies.

1. Introduction

Primary biological aerosol particles (PBAPs) are relevant in cloud processes and may play an important role in global climate changes

(Després et al., 2012). They can act as condensation or ice nuclei than most other aerosol particles (Abe et al., 2016). An increasing attention of the scientific community is devoted to the cloud condensation nuclei (CCNs) and ice nuclei (INs) formation processes because of the impact of CCNs and INs on radiative forcing is not yet fully understood (Kristensson et al., 2010; Szyrmer and Zawadzki, 1997). Besides, amino compounds through the capability to form CCNs or INs, could

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affect the atmospheric water cycle, and the scavenging of air pollutants (Chan et al., 2005; McGregor and Anastasio, 2001).

Free amino acids (FAAs) are a common source of carbon and nitrogen in both marine and freshwater ecosystems (Berman and Bronk, 2003). These compounds are released from living phytoplankton, either directly or by cellular lysis of senescent algae (Bronk et al., 1994), bacteria activity and biological degradation (Ge et al., 2011). FAAs can also have other sources such as biomass burning emissions (Chan et al., 2005; Feltracco et al., 2019; Zangrando et al., 2016), volcanic emission (Scalabrin et al., 2012) or input from soil (Dittmar et al., 2001). Amino acids exist in two forms, L- and D-enantiomers, with L-amino acids being almost exclusively incorporated into proteins. D-amino acids are produced by biotic racemization (Hernández and Cava, 2016) by algae, bacteria and archaea and constitute a significant fraction of the dissolved organic matter content of oceans (Xu et al., 2017). D-amino acids exist in either free or combined forms, with bacterial and algal peptidoglycan as the most common combined form (Yokoyama et al., 2003). Therefore, the presence of free D-isomers is indicative of a larger proportion of bacteria in aerosols (Wedyan and Preston, 2008).

Owing to Antarctica distance from anthropogenic and continental emission sources, this polar site is an excellent natural laboratory to study the biogeochemical cycles of natural elements. Barbaro et al. (2015) suggested that free amino acids can be used as potential markers for the evolution and fate of marine aerosol, although further investigation was necessary to define the applicability of these compounds. Several studies were conducted in the Arctic aerosol to estimate the relationship of amino acids and phytoplanktonic bloom, also considering the microbiology diversity in the aerosol samples. Feltracco et al. (2021) collected L- and D-amino acids in the Arctic aerosol during the pre-phytoplankton bloom and apex phase, defining how D-amino acids could serve as indicators of developing marine blooms, while L-amino acids might constitute a useful marker for the bloom peak and subsequent post-bloom decline.

Here, the concentrations trend of L- and D- FAAs in aerosol samples collected at Mario Zucchelli Station (MZS) on the coast of the Ross Sea (Antarctica) were investigated during two consecutive summer campaigns 2018–2019 and 2019–2020. The source attribution of FAAs is delineated by considering the particle-size distribution, and also using back-trajectories analysis and satellite Chlorophyll *a* (Chl *a*) concentration. Moreover, the comparison of FAAs trend with those of dimethylsulfoniopropionate (DMSP), dimethylsulphide (DMS) and methanesulfonic acid (MSA) is also evaluated because these species were considered very specific for marine primary production emission. DMS is a secondary product generated via enzymatic cleavage of dimethylsulfoniopropionate (DMSP) (Stefels et al., 2007), while methanesulfonic acid (MSA), is an oxidation product of DMS (Gondwe et al., 2003; Quinn et al., 2002).

The Ross Sea is a deep bay of the Southern Ocean in Antarctica, between Marie Byrd Land and Victoria Land. Its nutrient rich water makes it the Southern Ocean's most productive sea, with abundant planktonic life that provides a habitat for benthic, mid-water species and top predators (Cincinelli et al., 2017). Studies of phytoplankton in the Ross Sea have been very intensive in the last decades. Chl *a* usually begins to increase in November when mixed layers in the Ross Sea provide sufficient irradiance for growth (Arrigo and Van Dijken, 2004). In general, the temporal dynamics of phytoplankton assemblages in the Ross Sea are well known. The spring biomass is dominated by *Phaeocystis antarctica* (Arrigo et al., 1999) and after its decline, phytoplankton assemblages are dominated by diverse populations of diatoms, which tend to dominate assemblages in austral summer in the shallower mixed layers and are often associated with sea ice melt (Arrigo et al., 1999).

Despite the growing interest in the plankton dynamics, few studies were conducted to understand its relationship with the airborne organic molecules, especially amino acids. Barbaro et al. (Barbaro et al., 2017; Barbaro et al., 2016; Barbaro et al., 2015) carried out some preliminary studies focusing on long range atmospheric transport (LRAT), bubble bursting events, and the aerosol-snow transfer processes. These studies stated that aerosol collected at MZS was characterized by sea salt input with Na^+ ,

Mg^{2+} , and SO_4^{2-} as the main species. The present study further deepened the previous research and filled the gap about the relationship between FAAs and the consolidated and well-known markers of marine primary productions in order to definitely attribute the source of FAAs in Antarctica.

2. Experimental

2.1. Sample collection

In the framework of the Italian Research Program in Antarctica (PNRA), aerosol sampling was carried out using a multi-stage Andersen impactor (TE-6070, Tisch Environmental Inc., Cleves, OH, USA) placed at Campo Icaro (74° 42' 43"S 164° 07' 00"E), about 2 km south of the Italian MZS (Victoria Land, Antarctica) over two different Antarctic expeditions during the austral summer periods (from 9th Nov 2018 to 26th Jan 2019 and from 18th Nov 2019 to 28th Jan 2020). The sampler accumulated particles with cut-off diameters of 10.0 μm , 7.2 μm , 3.0 μm , 1.5 μm , and 0.95 μm on slotted filters and < 0.49 μm on the backup filters (pre-combusted, 4 h at 400 °C in a muffle furnace). The frequency of sampling was 10 days with a mean total air volume of 15,000 m^3 per sample. Field blanks were obtained using filters installed on the sampler for 5 min with the air pump switched off. Samples and blanks were wrapped in a double layer of aluminium foil and stored at -20 °C until analysis.

Aerosol sampling for ion composition was performed at Campo Icaro (the same site of multi-stage Andersen impactor) for the same time period in the two Antarctic campaign (2018–19 and 2019–20) by a low volume sequential aerosol sampler (Giano – Dado lab srl Milano) equipped with PM_{10} sampling heads operating at constant air flow of 2.3 $\text{m}^3 \text{h}^{-1}$ in accord with the European rule EN12341. Aerosol samples are collected on Teflon filters (PALL, Germany), 47 mm in diameter. Filters are stored in Petri plastic dishes, shipped to Italy, kept at -20 °C until they are cut, extracted, and analysed.

Sea water samples were collected at the sea surface in two sites using Schott bottles for the analysis of DMSP about once a week when the piers were free from sea ice. Sea water samples for DMSP analysis were acidified to $\text{pH} < 2$ to minimize chemical and biological degradation of DMSP during the preservation period. Airborne DMS samplings were performed near the main building of the Italian Antarctic base Mario Zucchelli Station (MZS) at about 5 m distance from the sea at 2 m above the sea level, at sub daily resolution (typically 4 sampling in the 24 h) by filling electropolished stainless steel canister by compressing air at 4 bars within several minutes with a membrane pump (Millipore XX5522050).

2.2. Chemical analysis

Reagents and standards solutions used in this study are reported in the Supplementary Material. The description of the sample's treatment for FAAs determination are reported in four previous studies (Barbaro et al., 2017; Barbaro et al., 2015; Feltracco et al., 2021; Feltracco et al., 2019). Briefly, each half filter was spiked with a mixed solution of 8 labelled FAAs as an internal standard and were then extracted twice for 15 min with ultrapure water in an ultrasonic bath. The slotted filters were extracted with 10 mL of ultrapure water, whilst the back-up filters were extracted with 30 mL. The extracts were then filtered through a 0.45 mm, Ø25 mm polytetrafluoroethylene (PTFE) filter (Lab Logistic Group, Meckenheim, Germany) before analysis. To avoid any contamination from laboratory air particles, samples were handled inside an ISO 5 clean room under a laminar flow bench (class 100). Field blank filters were also treated using the same procedure. All reported values are blank corrected. The method detection limits (MDLs) and method quantification limits (MQLs) of the analytical procedure were determined as three and ten times the standard deviation of the average value of the field blank. The instrumental analysis was performed using an Agilent 1100 Series HPLC System (Waldbronn, Germany) coupled to an API 4000 Triple Quadrupole Mass Spectrometer (Applied Biosystem/MDS SCIEX, Concord, Ontario, Canada). Analytical methods are described by Barbaro et al. (2014).

In the Chemistry Department of University of Florence laboratories, the PM_{10} filters are analysed by ion chromatography (IC). The $\frac{1}{4}$ filter is extracted in ultrapure water ($> 18 \text{ M}\Omega$) in ultrasonic bath at room temperature, then the solution is injected by an autosampler in three IC (ThermoFisher Dionex) for the determination of cations, inorganic anions and MSA (Becagli et al., 2022a).

Airborne DMS measurements were achieved in the MZS laboratories, by using a gas chromatograph equipped with a flame photometric detector (HP6890, 393 nm), while the analysis of seawater DMSP was accomplished at the Korea Polar Research Institute (KOPRI) laboratories. Analysis conditions for both analytes are reported elsewhere (Becagli et al., 2022b),

2.3. Back trajectories calculation, wind roses and satellite-derived Chl *a*

120 h (5 days) back trajectories were calculated every 6 h at 60 m a.s.l., which corresponds to the elevation of the sampling site, to evaluate the long-range transport (Fig. S1, Supplementary Material). The NOAA HYSPLIT trajectory model from the NOAA ARL was applied, using the GDAS one-degree meteorological database (<https://www.ready.noaa.gov/archives.php>). The trajectories were then displayed as frequency. Meteorological data from meteorological station managed by the Antarctic Meteo-Climatological Observatory (Eneide), were used to produce wind roses using Origin 2018 (Northampton, MA, USA). A 1-day Chl *a* concentration from the Level-2 MODIS Aqua data sets were obtained with OCI Algorithm and displayed with SeaDAS 8.1.0 (NASA, seadas.gsfc.nasa.gov) (Fig. S2). The Chl *a* data product provides an estimate of the near-surface concentration of Chl *a* using an empirical relationship derived from in-situ measurements of chlorophyll-*a* and remote sensing reflectance (Rrs) in the blue-to-green region of the visible spectrum.

3. Results

Eleven FAAs (Glycine (Gly), L-Alanine (L-Ala), D-Alanine (D-Ala), L-Arginine (L-Arg), L-Glutamic acid (L-Glu), L-Hydroxyproline (L-Hyp), L-Phenylalanine (L-Phe), L-Proline (L-Pro), L-Tyrosine (L-Tyr), L-Threonine (L-Thr) and L-Valine (L-Val)) had blank corrected concentrations higher than the MDLs (Table S1). The total mean concentration of FAAs in PM_{10} (calculated as the sum of all the stages) was $4 \pm 2 \text{ pmol m}^{-3}$ for both campaigns. Concentrations ranged from 2.0 to 6.7 pmol m^{-3} . Samples collected from 21st of December 2018 to 1st of January 2019, 8th–18th and 18th–28th of December 2019 had the highest concentrations, with total amino acids concentrations in PM_{10} twice as high as those collected in the other periods (Table S1). The mean value of the total dataset is very similar

than those obtained during the 2010–2011 sampling campaign (Barbaro et al., 2015) and slightly higher to those obtained in the 2014–2015 sampling campaign (Barbaro et al., 2017) at the same sampling site. Furthermore, the concentrations found in these campaigns were again lower compared to the values determined in the Arctic aerosol in spring 2015 (Feltracco et al., 2019).

Surprisingly, in both campaigns the predominant compounds were L-Ala (47.9–54.4 %) and Gly (23.3–28.6 %) (Fig. 1). The concentration of L-Ala ranged between 0.7 and 3.5 pmol m^{-3} and Gly between 0.6 and 1.6 pmol m^{-3} . While the high abundance of glycine is due to its very low reactivity and because it is generally considered an indicator of long-lived aerosol (Matsumoto and Uematsu, 2005; McGregor and Anastasio, 2001), airborne L-Ala has never been found as most abundant amino acid in Antarctic aerosol. This could be due to the L-Ala in seawater synthesis in seawater by the enzyme aspartate decarboxylase in the metabolic processes of prokaryote diatoms (Bromke, 2013a). Furthermore, high levels of L-Pro were found in both campaigns (9.6 %, 0.3 pmol m^{-3} and 9.5 %, 0.4 pmol m^{-3}). Proline was found in a concentration range of $0.3\text{--}10 \text{ pmol m}^{-3}$ in the Antarctic aerosol during an oceanographic cruise on the Southern Ocean onboard the R/V *Italica* (Barbaro et al., 2015). In general, the highest FAAs concentrations were detected in the fine particles ($<0.95 \mu\text{m}$) in the first campaign, accounting for 57 % of the total sum of FAAs, while a shift towards the coarse particles ($>0.95 \mu\text{m}$) occurred in the second campaign, with fine particles accounting for 46 %. Fig. 2 shows the relative abundance in size distribution for both campaigns. The figure shows how fine particles represent for L-Glu only the 20 % and 7 % of PM_{10} , differing significantly from the other compounds. There are no other FAAs that show a similar distribution. The closest one is L-Val with 44 % and 36 % of fine particles. Other percentages of FAAs were homogeneously distributed in both campaign (3 % for L-Tyr, 2 % for L-Thr, L-Glu, L-Phe and 1 % L-Arg, L-Val and < 1 % for L-Hyp). The low relative abundance of D-amino acids (1 %) slightly differs compared with those found in Arctic aerosol, where D-Ala and D-Asp accounted together for 14 % (Feltracco et al., 2019). No D-amino acids were detected previously in coastal zones in Antarctica (Barbaro et al., 2017, 2015). This suggests a lack of soil humic substances around the selected sampling site (Dittmar et al., 2001) or a very low rate of racemization of Alanine (Kimber et al., 1990).

As mentioned above, DMS and MSA were used as specific markers of phytoplankton bloom to better understand the sources of airborne amino acids. DMS ranged between below the detection limit and 802 pptV with a mean value of 40 pptV, while MSA in the PM_{10} ranged between 1 and 797 with a mean value of 86 ng m^{-3} . Discussion about DMS and MSA atmospheric processes and trend was discussed elsewhere (Becagli et al., 2022a).

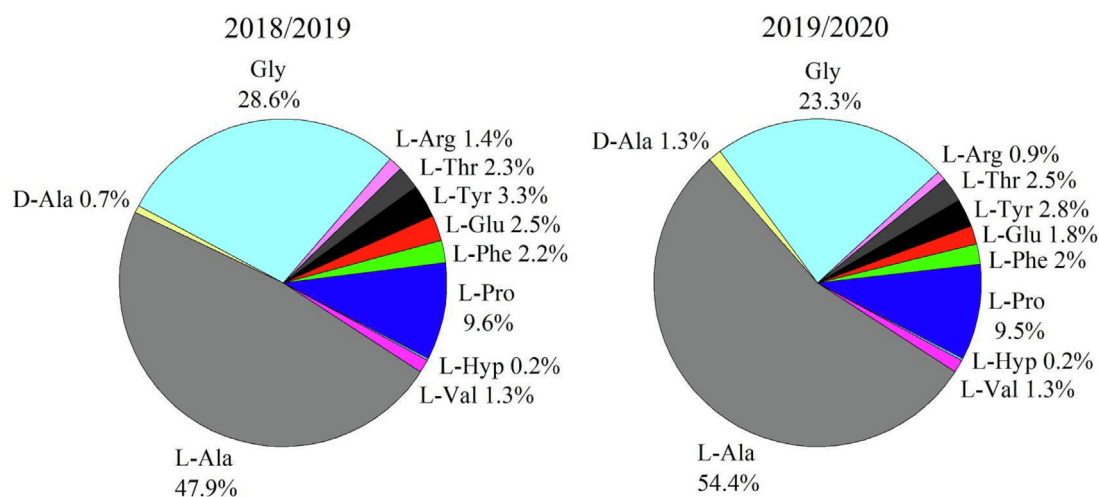


Fig. 1. Mean relative abundances of amino acids in the two sampling campaigns.

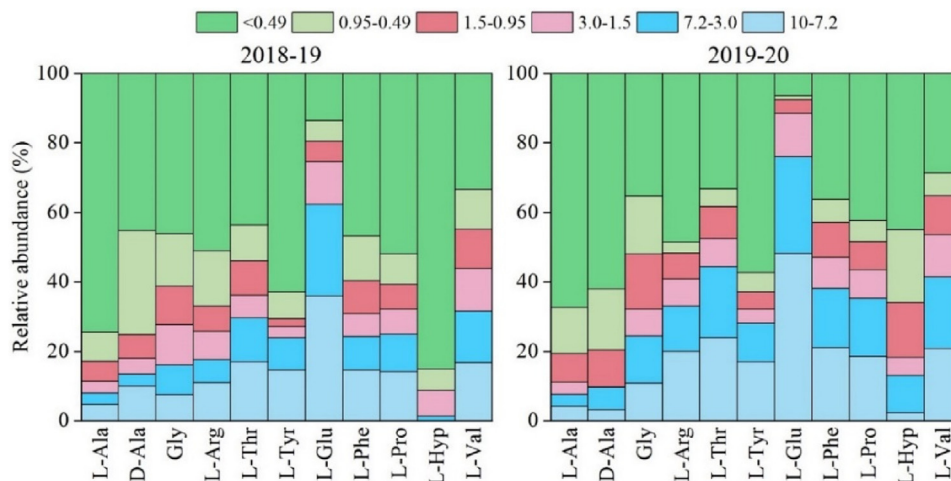


Fig. 2. Relative abundance of size distribution variation of detectable free amino acids of the two sampling campaigns.

4. Discussion

4.1. The variability of FAAs in aerosol over the Ross Sea

Several studies established that the main source of FAAs in the polar regions is the phytoplankton bloom (Barbaro et al., 2015; Feltracco et al., 2021, Feltracco et al., 2019) with a local contribution due to bubble bursting processes, despite the contribution of biomass burning events may not be totally excluded (Chan et al., 2005; Feltracco et al., 2020). Thus, a more detailed study regarding the behaviour of L- and D- amino acids and their relationship with other phytoplankton bloom markers in Antarctica is mandatory to better understand the applicability of these tracers in paleoclimatic studies.

A typical phytoplankton spring bloom from December to end of January was observed in nearby polynya of Ross Sea over the sampling periods, nevertheless some differences can be clearly visible with the DMS and MSA trend (Fig. 3). Despite MSA (together with SO_4^{2-}) is the main products from the oxidation of DMS (Barnes et al., 2006; Read et al., 2008), the trends of MSA differed from those of DMS, especially in the first campaign. This different pattern of MSA and its precursor was studied in a previous paper (Becagli et al., 2022a) and was attributed to difference sources of air masses delivering gaseous DMS from the near polynya and MSA that, in case it does not overlap the DMS concentration pattern, arises from source areas far from the sampling site. Notable differences between MSA and DMS levels were also observed in the regions of Antarctic peninsula and Arctic Svalbard due to source region-dependent oxidation processes (Jang et al., 2022; Park et al., 2021). Assays of Chl a provide a useful information on the spatial and temporal variability of phytoplankton biomass in the Ross Sea and allows us to determine the composition and ecological status of the phytoplankton community (Zangrando et al., 2016). Our evaluation about the evolution of Chl a was achieved with satellite measurements (Fig. S2) that pointed out the complexity of spatial variations of Chl a. The satellite derived Chl a is in accordance with the values of DMS found in the field with the phytoplankton blooms that occur rapidly over the course of 2 weeks in mid-November in both campaigns, with strong Chl a production mainly in front of McMurdo Station, with a minor and more sporadic release in the Ross Sea.

All detected FAAs increased during the two main DMS and MSA peak in both Antarctic Campaign in both coarse and fine particles, suggesting a direct input from phytoplankton climax phase. Wind roses and frequency of back trajectories (Fig. S1 and S3) show how the observed profiles are often the results of the confluence of katabatic flows from the Reeves and Priestley glaciers (Bromwich et al., 1993; Vignon et al., 2019) passing over the polynya of Terra Nova Bay before to reach the sampling site. The formation of blooms over this polynya causes various processes of particle formation with more type of biomasses available for aerosolization. This

process makes the amino acids more prone to aerosolization if emitted as fine particles (O'Dowd et al., 2004; Quinn et al., 2014), rather than their direct emission through sea spray.

Becagli et al. (2022a) showed how in the same period the maximum of DMS during first campaign was related to the phytoplankton senescent phase following the bloom of *Phaeocystis antarctica* that occurred in the polynya area when sea ice became to disappear. Furthermore, in January 2019 MSA reached its maximum value, while atmospheric DMS remained low, due to its fast biological turnover in sea water in this period. Despite these discrepancies between DMS and MSA, FAAs underwent both the seawater biological activities detected by sulphur compounds. The presence of free amino acids in coarse particles at the same time of higher concentration of DMS suggests that the portion of the polynya close to the sampling site is plausibly the main source of FAAs, but the latter may have undergone also LRAT, considering their presence in fine mode. On the contrary, DMS appears to be emitted only close to the sampling site (Becagli et al., 2022a). Interest deserves the second campaign, the coarse mode of L- and D-amino acids is well related with the peaks of DMS and MSA from 8th to 18th December 2019 (second campaign), then a shift towards fine particles was observed, showing an increase during immediately after (18th–28th December). This delay should be attributed to two phenomena: 1) an emission from ocean's surface where particles are transported to Antarctic plateau with the return of such particles due to katabatic flow; 2) an emission due to LRAT with a different phytoplankton bloom compared to that of the Ross Sea. L-Pro and L-Hyp followed the same temporal trend, due to the possible photochemical origin of L-Hyp from L-Pro, as also reported elsewhere (Stadtman and Levine, 2003). The main source of L-FAAs could be driven by L-Pro and L-Arg, considering that L-Pro can be emitted by spores from seawater (Fischer et al., 2004) and L-Arg is involved in the diatom urea cycle (Bromke, 2013b). Gly and L-Ala were also strongly related in both campaign ($R^2 = 0.8$ and 0.6 , respectively): this interesting behaviour confirms the hypothesis of limited atmospheric reactivity as proposed by Maria et al. (2004), who suggested that Gly, together with L-Ala, can undergo the LRAT, as a result of the slow oxidation rates.

D-amino acids, including D-Ala, are essential components of peptidoglycan in many bacterial cell walls and can breakdown existing biofilms (Yu et al., 2020). D-Ala was also often found in marine diatoms (Yokoyama et al., 2003) and is an unambiguous tracer for microbial degradation (Dittmar, 2004). Considering the presence of D-Ala in the bacterial biomass (Dittmar, 2004), during the cell wall breakdown it can be released in seawater and thereafter in the atmosphere through bubble bursting phenomena. In general, D-enantiomers tend to be accumulated during dissolved organic matter degradation because of the key role of bacteria (Park et al., 2022). Furthermore, it is well known that dinoflagellates are one of the major DMSP-producing phytoplankton group also in Antarctica (Caruana and Malin, 2014) and during the period of dinoflagellate bloom, the

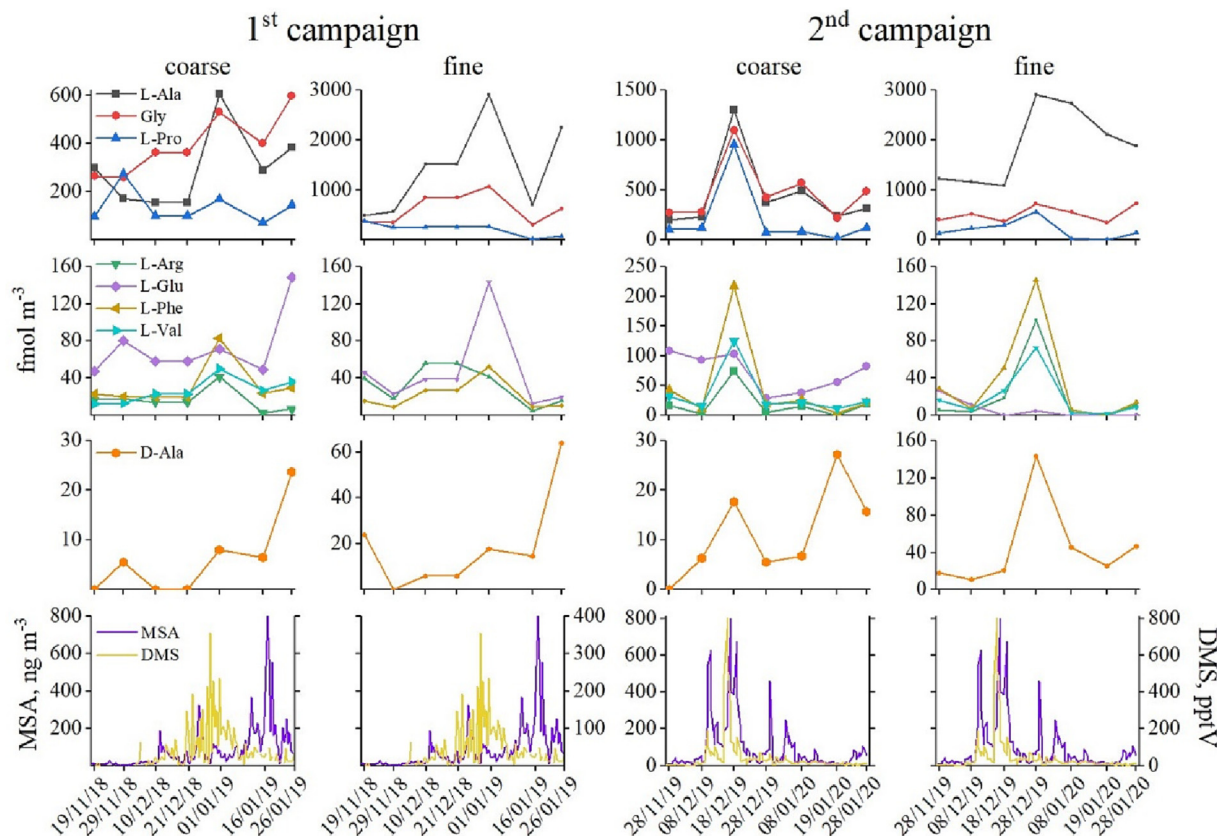


Fig. 3. Free amino acids PM_{10} concentration trend ($fmol\ m^{-3}$) in coarse and fine particles for both campaigns. The concentration data are reported in the plot in correspondence of the last day of aerosol sampling. At the bottom, the DMS (pptV) and MSA ($ng\ m^{-3}$) trend are reported.

Bacteroidetes, *Proteobacteria*, and *Actinobacteria* prevailed in bacterial communities (Bashenkaeva et al., 2017) and they were associated with D-amino acids in an Arctic fjord (Feltracco et al., 2021). As highlighted in Fig. 4, the coarse fraction of D-Ala and sea water DMSP have a similar trend during the Antarctic campaigns, suggesting a common source. The bloom of dinoflagellate releases D-Ala in seawater through the breakdown of bacterial cells with the consequent sea to atmosphere transfer (Bashenkaeva et al., 2017). Gly and L-Ala show also a slight relation, but the highest correspondence between the two markers is reached using the coarse fraction of D-Ala instead of fine fraction, confirming its local source.

A marine source for other FAAs with a relative abundance <3 % such as L-Tyr, L-Thr, L-Phe, L-Arg, L-Val and L-Hyp was suggested by particle size distribution mostly in the fine fraction (<1 μm) of our samples confirming suggestions from previous studies (Barbaro et al., 2017; O'Dowd et al., 2004).

4.2. D/L Ala as useful ratio for source identification

D-Ala was the only D-FAAs detected in this study. This contribution differs significantly if compared with the presence of Arctic airborne D-FAAs collected at Ny-Ålesund, Svalbard Island, where Feltracco et al. (Barbaro et al., 2015; Feltracco et al., 2021, Feltracco et al., 2019) detected several other D-enantiomers like D-Ser, D-Thr, D-Phe, D-Val. Such differences are associated to the sources, with biomass burning being one of the most important sources of FAAs in the Arctic aerosols. D/L Ala in samples collected during this study (Fig. 5) were within the range previously measured in seawater (Dittmar et al., 2001; Fitznar et al., 1999; Kuznetsova et al., 2005). Slight differences were detected between fine and coarse D/L ratio in the samples collected in 19/11/18, 29/11/18, 28/12/19. Furthermore, the sample collected the 19/01/20 showed the highest value of D/L ratio in

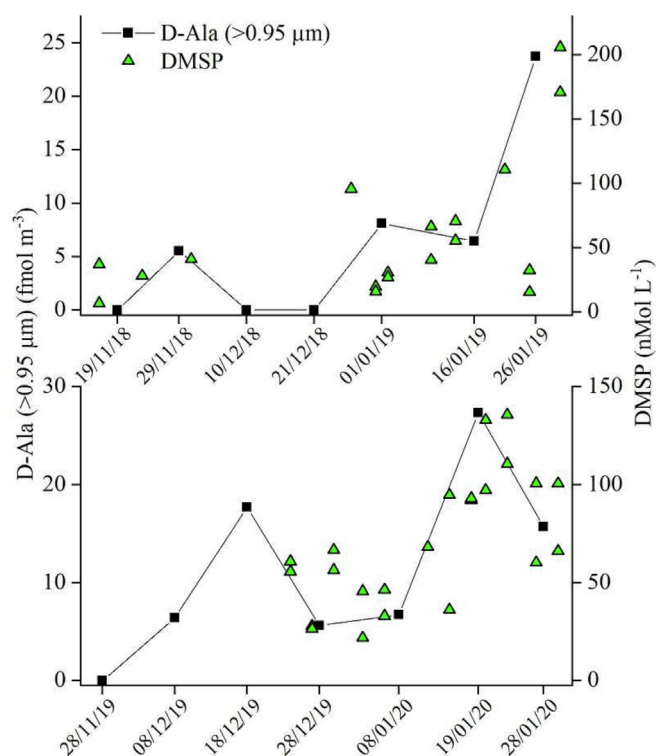


Fig. 4. Time series of measured airborne D-Ala (coarse fraction, >0.95 μm) and DMSP in seawater.

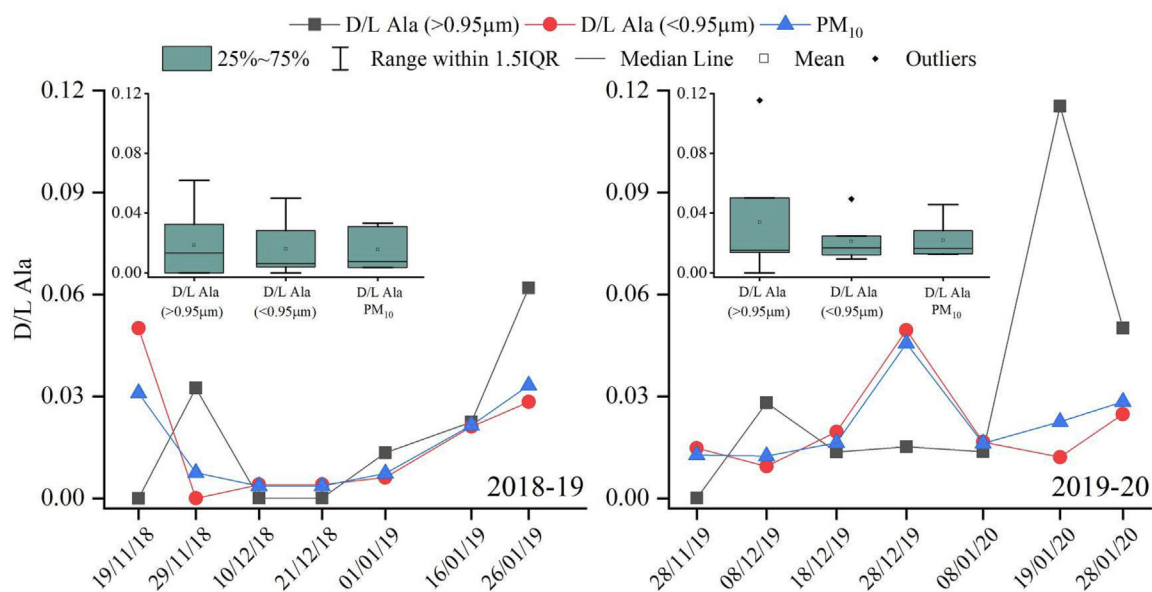


Fig. 5. D/L Ala ratio in the fine, coarse and PM₁₀ particles (line + symbol graph). A boxplot is displayed for each sampling campaign.

coarse particle, with the ratios that still remain very low. This may be attributed to a mixed source related to aerosolization during bubble bursting process of both subsurface water and microlayer (Kuznetsova et al., 2005). Kuznetsova et al. (2005) showed that in all amino acid fractions of microlayer samples, D/L ratios were usually lower than or comparable to ratios in subsurface water, with D/L Ala always below 0.6. Considering the low values obtained from our samples, FAAs were likely sprayed from the Ross Sea microlayer. It should keep in mind that teichoic acids, which are rich in D-alanine, are major components of the cell wall membrane complex in a large number of gram-positive bacteria (Perego et al., 1995). Thus, gram-positive bacterial isolates in the Ross Sea were assigned to five phylogenetically different taxa, *Actinobacteria* predominating (Io Giudice et al., 2007).

4.3. The L-Glu size distribution over the Ross Sea

Even though L-Glu is capable of producing a marked effect on atmospheric new particle formation (Liu et al., 2022), the size distribution of L-Glu differed significantly from the other L-FAAs, being present in fine particles (<0.95 µm) only for 21 % and 6 % of PM₁₀ in the two sampling campaigns, respectively. This divergence is also clearly visible on the hierarchical cluster analysis performed using Ward method (Fig. 6A and B) in which L-Glu is aggregated with other FAAs with high Euclidean

distance (>1), suggesting a different source or behaviour during the atmospheric transport. This trend is enhanced in the second campaign (Fig. 6B) where L-Glu were more distributed towards the coarse particles. The fractions variability (Fig. S4) is not correlated with winds coming from the open sea (Fig. S3), so exceptional bubble bursting processes can be excluded for L-Glu.

From their formation during metabolism, Glu, Gln, Pro and Arg belong to the so-called “glutamate family”. They have 2-oxoglutarate as their common precursor (Scheller, 2001). Arginine, within its four amino groups, is richest in nitrogen and is formed from glutamate via Ornithine. In previous studies (Fischer et al., 2004; Scheller, 2001) large quantities of free arginine were often accompanied in dew samples of Germany by large amounts of free proline and glutamic acid. We found a high correlation between L-Pro and L-Glu in PM₁₀ in the first campaign ($R^2 = 0.9$) that suggest they are formed on the same metabolic pathway, as mentioned elsewhere (Scheller, 2001). No correlation has been found between L-Pro and L-Glu in the second campaign, with L-Glu being more distributed in the coarse mode rather than the other FAAs. Considering that coarse particles are mostly emitted to the atmosphere during mechanical processes from both natural and anthropogenic sources, an explanation of the presence of L-Glu in coarse particles might be the result of its condensation onto larger existing aerosol particles or of particle coagulation, especially during long-range transport due to the confluence of katabatic flows (Feltracco

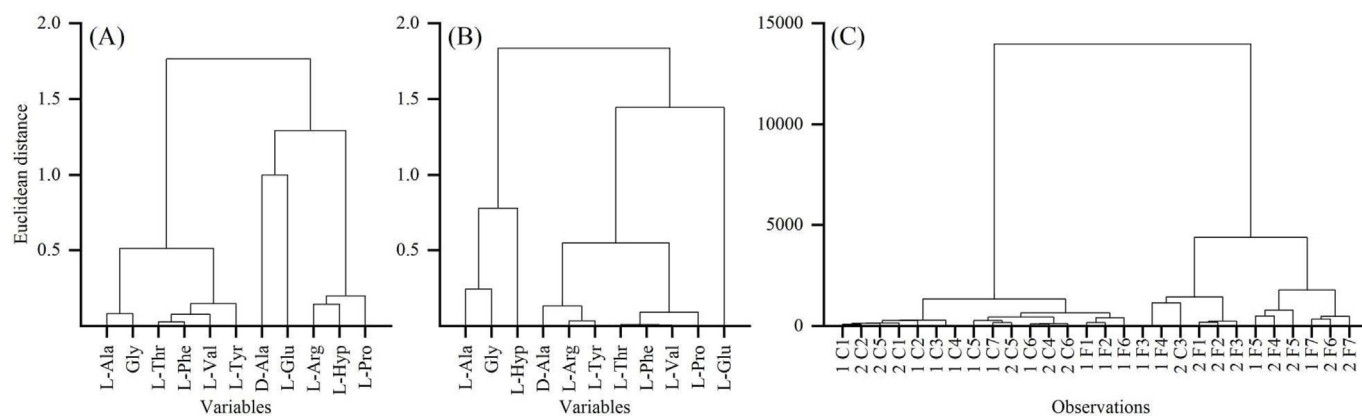


Fig. 6. Hierarchical cluster analysis performed using Ward method. Cluster (A) refers to 2018–19, (B) 2019–20 considering all the six size fractions. Fig. 6C shows the cluster analysis using coarse (C) and fine (F) particles of first (1) and second (2) Antarctic campaign.

et al., 2018; Herckes et al., 2006). Although the sources of the amino acids in aerosols have not yet been sufficiently clarified, significant contributions of aspartic acid and glutamic acid to the airborne combined amino acids in have also been reported in some previous studies (di Filippo et al., 2014; Matsumoto et al., 2023). Here, L-Glu has been found as free form and it is possible that those proteins were broken up into FAAs (Abe et al., 2016).

Another example of the source difference between coarse and fine particles is provided by Fig. 6C, in which the fine particles of both campaigns are all aggregated on the left and coarse particles are grouped on the right. The only exception is given by “2 C3” sample (18/12/19). That period showed a low presence of FAAs in fine particles (mean value of 31 % of the total PM₁₀) that tends to bring together these coarse particles with fine particles of both campaigns.

5. Conclusions

In order to clarify the compound composition of the free amino acids in aerosols, size-segregated measurements were conducted at Mario Zucchelli Station, Antarctica. Two sampling campaigns were studied to understand the impact of Antarctic seas to the atmospheric aerosol. These samples provide information on concentration trends along the two sampling periods and size-distribution. Back-trajectories analysis, DMSP, DMS and MSA were used to describe the geographic origin of the air masses and to explain how phytoplankton blooms influenced the FAAs concentration in the atmosphere. Furthermore, enantiomeric D/L ratios of those FAAs was used to trace the source of proteinaceous matter.

FAAs fit with DMS trends, suggesting that they could serve as indicator of developing biological activity in the Antarctic marine ecosystem. Whereas DMS and MSA are strongly subject to several oxidation processes, sometimes their trend can be differentiated to each other, as happened in the first sampling campaign. These results confirm that FAAs are reliable tracers of phytoplankton bloom, especially considering glycine and alanine, the most stable amino acids in the atmosphere. Thus, the relation between DMSP and D-Ala suggest that the latter could serve as indicators of developing marine blooms, especially if associated with bacterial enrichment. Considering the low values of D/L Ala ratio obtained from our samples, FAAs were sprayed mostly from the Ross Sea microlayer. Amino acids may be used to study past changes in Antarctic bloom timing and duration in paleoclimatic archives such as ice cores.

CRedit authorship contribution statement

Matteo Feltracco: Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization. **Roberta Zangrando:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Review & Editing. **Elena Barbaro:** Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing. **Silvia Becagli:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Project administration. **Ki-Tae Park:** Data Curation, Formal analysis, Writing - Review & Editing. **Marco Vecchiato:** Writing - Review & Editing. **Laura Caiazzo:** Investigation, Data Curation, Writing - Review & Editing. **Rita Traversi:** Conceptualization, Methodology, Validation, Formal analysis, Writing - Review & Editing. **Mirko Severi:** Conceptualization, Methodology, Validation, Formal analysis, Writing - Review & Editing. **Carlo Barbante:** Writing - Review & Editing, Supervision. **Andrea Gambaro:** Conceptualization, Writing - Review & Editing Supervision.

Data availability

The meteorological data is available at <https://www.climantartide.it/dataaccess/aws/index.php?lang=en&aws=Eneide>. The observed Chlorophyll *a* concentration map is available at oceancolor.gsfc.nasa.gov/atbd/chlor_a/. The Gridded Meteorological Data Archives (GDAS) for back trajectories analysis is available at ready.noaa.gov/archives.php.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.163070>.

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