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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Amino acids in Antarctica: evolution and fate of marine aerosols" *by* E. Barbaro et al.

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REF: Referee A: Authors

Response to Anonymous Referee #1

REF: General comments This work presents the results of more than four field studies in the southern hemisphere, targeting the role of amino acids in aerosol loading. The remote nature of this work makes these data especially precious. In the larger context of characterizing marine organic aerosol, these finding are even more valuable. The paper is generally well-written and clear, but I have some recommendations for sections that should be improved. Although numerous, my comments are largely minor in nature; therefore, I recommend this paper for publication with minor revisions. Specific

comments Pg 17081 First two paragraphs: I find this entire section very hard to follow. The use of the phrase, "In the present work," in Line 4 implies that the Dome C data discussed above are from another study. However, I gather they are not. Further, the Dome C station is not the only location where AA were found primarily in the backup filters. According to Figure 2, the MZS samples also showed the highest concentration of AA in the backup filters.

A:We agree with the referee that this section was very hard to follow. I modified the sentences as follows: “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." In this paragraph we wanted to highlight that we observed an increase in the percentage of amino acids fraction in the coarse particles at a long distance from the aerosol source.

REF: Pg 17081 Same section: "This evidence suggests that hydrophobic amino acids present in the coarse particles are less reactive." I don’t see how the data support this conclusion. It might, but it needs to be better explained. Same paragraph: "This indicates that the coagulation processes with the relative increase of Ala concentration in larger particles are probably together with slow oxidation processes." The wording "probably together" is confusing, please reword this sentence.

A:As suggested by referee we clarified this concept by removing the paragraph regarding the Ala. The interesting behavior of this amino acid is now reported after the description of photochemical proprieties of amino acids. We introduced the following sentences: “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

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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”. ”

REF:Conclusions: "This first study on the distribution of Antarctic amino acids permitted to identify the marine source of aerosols and to study the ageing of aerosols." This summary is overstating the findings of this work. I suggest, "This first study on the size distribution of amino acids in Antarctic identified sources of marine aerosols in this region and characterized some transformations taking place as marine aerosols are transported to the interior of the Antarctic continent."

A:We thank the referee for the suggestion and we replaced the sentence.

REF: Conclusions, Line 7: Instead of what?

A: As suggested by the reviewer, we removed “instead” and modified the sentence in order to clarify the main concept.

REF:Figure 2: The inset contains more information than the larger figure and it makes sense to swap the two figures, such that the inset becomes the main figure. Figure 4: The distributions of AA are very hard to compare in this format. It might be useful to see the distributions as fractions of total AA and to have a separate indicator for total AA.

A:One of our main results was the identification of the different particle-size distribution of amino acids in Antarctic aerosols near the source (at the MZS station) and after the long-range transport (at the Dome C station). We prefer to keep the inset of the “zoom without B filters”(fig. 2) because the reader can easily recognize the difference between the different sampling sites (fig 2 and 4). We modified the colors of both figures (2 and 4) in order to help the reader to identify each amino acid, removing the colors that were too similar (such as those before Tyr and Ala). We prefer to maintain this graph layout because it describes the particle-size distribution of the total concentration of

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amino acids while also showing the most abundant amino acids. The minor abundant amino acids significantly contributed only to the total concentrations while the single visualization of these amino acids is not very importantfor the aims of our study.

REF:Figure 6 was generate with a different software package than the others and the text on the axes is blurry.

A:We corrected the resolution and replaced figure 6.

REF:Technical corrections The paper would benefit from editing by a native English speaker. There are numerous awkward sentences and grammatical errors, especially in the second half of the manuscript. A few are itemized below.

A:The manuscript was corrected by an English native speaker.

REF:Pg 17068 Line 2: replace "the latter's" with "their" Lines 17-18: since amino acids are biological material, it would be more accurate to say "intact biological material" Pg 17070 line 1: Type-o, replace De Hann with De Haan Pg 17071 Line 13 : replace "the single amino acid" with "a single amino acid" Line 15: insert "us" after "allowed" Pg 17076 Line 16: in this and other cases, replace "dominant" with "predominant" Line 18: remove the pluralization of "others" Pg 17082 line 12: Omit "the" before Figure 5 Pg 17083 Line 27: replace "better" with "calmer" to be more specific. Pf 17084 Line 6: replace "a strong presence of " with "expansive"

A:We thank the referee and we followed all the above-listed suggestions.

REF: Pg 17070 Line 23: Since Antarctica is a continent, I believe the authors are referring to sources requiring exposed rock or soil. If so, this might be clarified.

A: As suggested, we modified the sentence as follows: "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)."

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REF:Pg 17079 Line 21: "A prominent marine source was revealed by the cluster means backward trajectories analyses analysis of all the samples" It is not clear if the "analyses analysis" is a mistake or just an awkward wording.

A: We corrected the error. The correct sentence is “A prominent marine source was revealed by the cluster means backward trajectories analysis of all the samples collected during both austral summer campaigns”.

REF:Pg 17082 Line 17: "A longer time inland can be improved chemical and photochemical reactions" I’m not sure what this means, but I think it should read, "A longer transportation time from the source to the sampling site allows for more chemical aging, including photochemical reactions, to take place."

A:We agree with the referee and we modified the sentence as follows: “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)”.

REF: Pg 17085 Line 2 and other cases: the authors are switching from past to present tense inconsistently. The air masses "came" from inland in this case, but likely do not always.

A: The manuscript was corrected by an English native speaker.

REF: Pg 17085 Lines 7 and 11: the word "relevant" is misused here. I believe the authors mean "significant," "noteworthy," or "detectable."

A:The word "relevant" was replaced with "detectable".

âĂČ Response to Anonymous Referee #2

REF: This paper reports some measurements of free amino acids in Antarctica (a coastal and a continental site) and at sea in a nearby region. The results contain

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some interesting information, which is why, in principle, this paper could potentially be published in this journal. However I have serious problems with many aspects of this paper. First, the scientific objectives and scientific questions addressed are unclear as the few arguments given in the text to justify this study are inadequate or inaccurate. At the minimum the authors should provide solid arguments on 1) why they focus on amino acids and no other compounds, 2) why they analyse they enantiomeric composition rather than their total concentration, and 3) why this study was performed in the Antarctica region. Second, numerous statements in the paper (and not the least in the abstract) are false and directly contradict the current knowledge in atmospheric chemistry, in particular on the potential role of amino acids in cloud formation and on the chemical reactions occurring in aerosols. These statements are disturbing and further question the scientific relevance of this study. Therefore they have to be corrected. Another important problem is the references, which are often inadequate or insufficient, as clearly emphasized by the comment from J. Schmale that directly relevant works on the same topic are not even quoted. This is not acceptable and has also to be corrected. Last but not least, essential information on the analytical procedure, in particular on the detection sensitivity of the different enantiomers of amino acids, is missing making it impossible to judge the validity of the results themselves. Unless all these major issues are addressed, I can not accept this paper for publication. Only once the changes requested below are made and the truly interesting information in this work is properly discussed, this paper can be considered for publication.

A: We prepared a new version of our manuscript, clarifying some key points and concepts such as the aim and importance of our research on Antarctic aerosols. We improved the references as also suggested by referee 3 and by J. Schmale. The information about the analytical procedure was also completed. We hope that this re-ordering of the work makes it clearer.

REF: 1. General objective of the study and main results Even after several readings of this manuscript I can not find (in particular in the abstract and introduction) the argu-

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ments justifying the objective of this study and clearly stating the scientific questions that are to be answered. This is a major problem to understand the relevance of the measurements, analyses, and of the study itself. The abstract and introduction provide some explanations but those are, at best, vague or, at worse, false and contradict the current knowledge in atmospheric science. For instance the abstract begins by a series of statements that are nearly all false: - "the chemical composition and size distribution of marine aerosols is an important parameters for global climate change": False, the IPCC 2013 reports does not indicate that marine aerosols are more important than other aerosols on that aspect.

A: As suggested by referee 3, we reduced this paragraph but we also introduced the following sentence: "The study of marine aerosols is crucialconsidering 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; Boucher et al., 2013)." The aim is to highlight the importance of marine aerosols, the main subject of our study. We agree with referee 2. The IPCC 2013 reports does not explicitly indicate that marine aerosols affect climate change but it affirms that "aerosol particles interact with solar radiation [. . .]". We reformulated our previous version, which was probably imprecise. Several studies [1; 2; 3; 4; 5] reported that "the marine environment represents one of the largest natural aerosol sources." and that "marine aerosol systems are important as they exert a significant influence on the Earth's radiative balance [. . .].".If aerosols particles affect the Earth climate and marine aerosolscontribute significantly to the global aerosol load,then marine aerosols do have an impact on the climate.

REF: - "Amino acids are important components of organic nitrogen in aerosol and have the ability (: : :) to act as Cloud Condensation Nuclei: : :" Doubly false: the main organicnitrogen components in aerosols are organonitrates. Amino acids are only present intrace concentrations, hardly exceeding the mM range. I am quite sure that the review by Ge et al., 2011 quoted in introduction does not present amino acids as a majoraerosol component. Furthermore there are no studies indicating that amino

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acids are good CCN and the articles quoted in support of this are inadequate: Szrymer, 1997is a study of ice nuclei, not CCN, and Wedyan, 2008 is not a CCN study. In fact, amino acids are not expected to be good CCN because they are neither surfactants nor significantly more hygroscopic than inorganic salts or other organic compounds,such as sugars.

A: We substituted the term “important” with “interesting”. The term “important” was not meant to indicate that amino acids are present in the atmosphere in particularly high concentrations but merely to underline the relevance of studying these compounds. We also introduced an explanation about the relevance of amino acids, reporting that they are very efficient ice nuclei and good cloud condensation nuclei. We agree with referee 2 that the previous references were inadequate and added four new references[6; 7; 8; 9] to studies that demonstrate that amino acids act as cloud condensation nuclei and ice nuclei.Szyrmer and Zawadzki[6] report that “ some amino acids were discovered to possess ice-nucleting ability” and Kristensson et al. [9]that “ particles containing amino acids [. . .] are good cloud condensation nuclei”. The sentence is now formulated as follows: “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) good cloud condensation nuclei (CCN) (Raymond and Pandis, 2003; Huff Hartz et al., 2006; Kristensoon et al., 2010).”

REF: -Abstract: “In order to understand which physical and chemical transformations occur during transport processes, aerosol samples were collected during four campaigns”: This statement gives at least a hint on the goal of the study. Unfortunately the “transformations” are very vague and should be specified. And this statement does not explain why amino acids can answer these questions and have been studied, and why the study had to be done in Antarctica.

A: We removed this sentence in order to clarify the main aim of our work. The sentence now goes as follows: "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

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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."

REF: The introduction contains further such false statements: - p. 17068, li 23/24: (Marine aerosols): play an important role in the Earth system(: : :) as they significantly contribute to the global aerosol burden:". This could notbe more wrong, as marine aerosols have very small concentrations and sizes and therefore a minimal contribution to the global aerosol burden.

A: Petzold and Karcher[10] reported that "the ocean is one major source of natural aerosols with an estimated annualemission of 1 000 to 10 000 Tg (= 1012 g = 1 megaton) of material". This affirmation suggests that marine aerosols are among the main contributors to the global aerosol burden. The physical and chemical proprieties of marine aerosols were thoroughly investigated by the O'Dowd's group. A very interesting article published on Nature [1] illustrated that sea-salt aerosols dominate the whole size fraction with a 74% contribution to the accumulation mode mass. We therefore disagree with referee 2, because experimental data [10] confirm that some marine aerosol particles are produced with a diameter above of 1μm (coarse fraction). As reported in previous comments, we modified this paragraph in order to reduce this section in favor of a more detailed description of amino acid aerosol particles and their sources.

REF: - p 17069, li1-3: actually, the current consensus in the atmospheric community is thatthe chemical composition of aerosols does not affect their CCN properties. If the authors want to make this statement they need to support it with some solid literature.

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A: We removed this paragraph in order to reduce the first section. We agree with referee 2 that this sentence was imprecise. We would understand the chemical composition of aerosol because “the ability of an aerosol particle to take up water and subsequently activate, thereby acting as CCN at a given supersaturation, is determined by its size and composition” (IPCC 2013, Chapter 7).

REF: Introduction: There are many other such examples (see point 2 below) and it is impossible to listthem all. But, in summary, the absolute minimum that needs to be justified in theabstract and introduction of this paper are:

A: As suggested by referee 2, we reformulated the goals of our study and answered the questions as follows.

REF: - why studying amino acids and not other compounds ? A: “Amino acids can be involved in cloud formation or act as ice-forming nuclei (Raymond and Pandis, 2003; Huff Hartz et al., 2006; Kristensoon et al., 2010; Szyrmer and Zawadzki, 1997) and affect 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, 2012).”

REF: - why measuring their enantiomeric composition and not their total concentrations ?

A: "The enantiomeric D/L ratio of amino acids in aerosols might help to trace the origin of biogenic aerosols, indicating the prevalence of phytoplanktonic material or bacterial matter (Kuznetsova et al., 2005)."

REF: - why this investigation had to be performed in the Antarctica region and nowhere else?

A: “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

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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)."

REF: Here are some aspects that would be very interesting to discuss and might justify the relevance of this study: - a unique feature of amino acids, that can provide unique information on aerosols, is they chirality. Unfortunately this is not discussed anywhere in this paper. For information on how chiral information can reveal the primary or secondary origin of aerosol components, please see the following papers: - Nozière, B. et al., Atmospheric chemistry in stereo: A new look at Secondary Organic Aerosols from isoprene, Geophys. Res. Lett., 38, L11807, doi:10.1029/2011GL047323, 2011. - González, N.J.D., et al., New method for resolving the enantiomeric composition of 2-methyltetrols in atmospheric organic aerosols, J. Chromato. A, 1218, 9288, 2011. - González, N.JD., et al., Primary and secondary organics in tropical rainforest aerosols: Chiral analysis of 2-methyltetrols in the Amazon, Env. Sci. Proc. Impacts, 16, 1413 – 1421, 2014. In particular, it would be highly interesting to explain that the amino acids measured in this study are largely from biological origin, as shown by their large enantiomeric excesses, and to discuss the potential reasons for the small, rather unexpected, racemic fractions, as amino acids are known to be present as only one enantiomer in the natural environment: microbial processing or racemisation by abiotic reactions in aerosols. Note however that amino acids can potentially be racemized in the natural environment and in aerosols (in which case this has to be justified), but certainly not "produced" by abiotic reactions in aerosols, as written p 17080 li 17/18 in the text (but I hope this is a misunderstanding of the term "ageing" – see point 2 below). Another interesting property of amino acids is that they are efficient catalysts for ionicorganic reactions, as shown by: - Nozière, B., et al., The Formation of Secondary Light-Absorbing "fulvic-like"Oligomers: A Common Process in Aqueous and Ionic At-

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mospheric Particles ?, Geophys.Res. Lett., 34, L21812, doi:10.1029/ 2007GL031300, 2007. - Nozière, B., and A. Córdova,A Kinetic and Mechanistic Study of the Amino Acid-Catalyzed Aldol Condensation of Acetaldehyde in Aqueous and Salt Solutions, J. Phys.Chem. A, 112, 2827, 2008. These studies were later continued by the De Haan group, which focused mostly onaerosol formation rather than on chemical mechanisms. Note, however, that in the reactions studied by Noziere et al., amino acids are catalysts, thus not consumed in the reactions and their enantiomery is conserved (this is also demonstrated in numerouspapers in organic chemistry). The small condensation pathways forming imidazoles reported by the De Haan group are minor (< 1 % of the total reaction for instance in the case of glyoxal), thus hardly constitutes a "scavenging process" for amino acids asindicated p.17080 li 26.

A: We must thank referee 2 for the suggestion and we improved the introduction with a new section about the chirality of amino acids. We also introduced the suggested references to exemplify the importance of chiral information as aerosol marker. The sentence "The composition of aerosols may change during long-range transport, due to the production and destruction of species via photochemical reactions." (p 17080 li 17/18) was reformulated to clarify the concept. In the old sentence the racemization process was not considered. The sentence would affirm that several chemical transformations take place in the atmosphere, involving the formation and destruction of numerous different species. Amino acids have different stabilities in the atmosphere and some can be degraded by chemical agents (âĂćOH, O3, etc) [11]. The racemization process is too slow and it is used for dating study in paleoclimatology [12]. We agree with the referee that D-amino acids certainly not "produced" by abiotic reactions in aerosols. The sentence now goes as follows: "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)." and represents an introduction to the next discussion.

REF: Finally, one last main objective of this study, or at least main points of conclusion

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that should be emphasized are - the presence of all these biological amino acids in regions with (apparently) littlebiological activity - although is it worth emphasizing that microbial activity is very much present even in such extreme environments. An important discussion would thus be,based on the back trajectories, whether they are locally produced or transported fromwarmer regions,

A: We introduced the following passage in the conclusions: “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 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.”. In fact, the presence of free L-amino acids in the Antarctica reflects a specific planktonic origin while Gly and Ala are proposed as biogenic long-range markers.

REF: - their presence in fine particles, while a common assumption is that biological materialis mostly present in large aerosols fraction.

A: The water soluble compounds (WSOC) in the fine particles of marine aerosols was already demonstrated by O’Dowd’s group [1]. This is the first study on the identification of dimensional distribution of amino acids in the marine aerosols near the sources and, as suggested by referee 2, this aspect was underlined in the conclusions. Microorganisms can be a source of free amino acids in the coarse particles as demonstrated during the cruise sampling.

âĂČ REF: 2. Links with other atmospheric chemical questions As emphasized above, a number of disturbing statements contradicting the current understanding of atmospheric processes are present throughout the paper. Several of them have been identified above on the topic of: - the importance of marine aerosols for climate, - the

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importance of amino acids as CCN. A: As suggested by referee 2 in previous comments, we considered these questions and modified the introduction in order to clarify the concepts.

REF: Other important ones concern aerosol processes: - “ageing” or “aging” refers exclusively to chemical transformations in aerosols, not to physical transformations. Thus a statement such as in p.17080 li 17/18 “the enrichment in the coarse fraction can be explained by the ageing of the aerosols” is chocking because it suggests that amino acids can be quantitatively produced by abiotic reactions in aerosols, which is absurd (thermodynamically). I am guessing that the authors mean some kind of physical transformation affecting the size of the particles, but they need to explain this better.

A: We agree with the referee that ageing is a chemical processes and that the term was inappropriately used. We removed this term from the manuscript, clarifying the sentence in pg 17080 li17/18 as follows: “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).”

REF: - the Lim et al paper on photochemical reactions in water quoted in introduction (p17069, li 17/18) applies to cloud chemistry (very diluted concentration of organics in water), not to aerosol chemistry.

A: We agree with referee 2 and we removed the sentences “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.” as indicated also by referee 3 that suggested to reduce the introduction about the marine aerosols.

REF: - regarding the discussion or aerosols reactions, p. 17080 li 18-29, the reactivity of amino acids stated in some of the references cited was demonstrated with gas-phase OH radicals, which is hardly relevant in aerosols. And the occurrence of OH

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radicals and radical oxidation reactions in the aerosol bulk was never demonstrated. Furthermore, photo-induced processes are not the only type of chemical reactions in aerosols, as supported by the many recent works on ionic reactions, in particular those involving amino acids and quoted above (Noziere et al papers). As explained above the imidazole formation reported in a later study from De Haan group is only a minor pathway.

A: In p. 17080 li 18-29, we preferred to remove the reference to McGregory and Anastasio [11] because they describe the photochemical transformations of amino acids in fog waters. The photochemistry of amino acids in aerosols was examined in depth by Milne and Zika [13] and the occurrence of OH radicals in aerosols was demonstrated in literature as well as cited in reference books about aerosol science. For example, Seinfeld and Pandis[14] affirm that "the key to understanding tropospheric chemistry begins with the hydroxyl (OH) radical. Because the OH radical is unreactive toward O2, once produced, it survives to react with virtually all atmospheric trace species". We agree with the referee that photo-induced processes are not the only type of chemical reactions in aerosols and we also considered the ionic reactions in our discussions. "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)."

REF: - there seems to be the beginning of a discussion on the acid-base properties of amino acids p.17082, li 1 and following. This could be interesting but the reasoning and conclusions are very difficult to follow in the text. Just to be clear (because it is not obvious in this paper), amino acids are weak bases and would only contribute to increase the pH of aerosols - however they are in such small quantities that they are unlikely to have any effect at all, especially when mixed with strong acids.All these statements need to be removed, re-phrased, or at the very least much better justified.

A: We modified the arrangement of the paragraphs in order to facilitate their understanding. This discussion on the acid-base propriety was introduced to explain how

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the chemistry of aerosols in different sampling sites influences the chemistry of amino acids. As suggested by referee 2, in order to clarify this discussion we introduced the following sentence: “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.” âĂČ REF: 3. Literature As mentioned above, a large part of the literature cited is inadequate, as clearly confirmed by the comment from J. Schmale. Therefore, in addition to adding the Schmale paper to the literature list - as well as ALL other relevant studies (for instance those quoted above), please correct the following points: - unless otherwise specified by the journal, literature should always be quoted by increasing chronological order, i.e., the oldest papers first, which are the precursor studies and deserve proper credit for it. In particular, when quoting measurements of amino acids in rainwater and aerosols, the papers from the Zika group in the 1990’s should be quoted first (and there are several of them).

A: As suggested by referee 2, we corrected the chronological order of our references in the text.

REF: - for the sake of objectivity, ALL references regarding the climate contribution of aerosols should be taken from the IPCC 2013 report, not from random studies taken out of context or older reports, which, obviously, have been updated by the 2013 report.

A: We agree with the referee and we modified the sentence in order to better describe what the IPCC 2013 reports reported. We added this reference in the text.

REF: - It is also VERY surprising that ALL the literature cited in introduction on marine aerosol (p.17069 li 6-20) is from the 2000’s. Surely, there must be reference papers on this topic before that.

A: In the introduction, we added several references published before 2000.

REF: - in particular, the papers cited on p.17069,li 13/14 to support secondary aerosol formation studies are inadequate are they are modelling papers, not experimental stud-

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ies determining which mechanisms take place in marine SOA formation. There are other occurrences in the paper where modelling papers are used to justify mechanistic questions

A: As suggested also by referee 3, we reduced the introductive section about marine aerosols in order to better focus the introduction on the importance of amino acids in aerosols. As suggested by referee 2, the unsuitable references were removed.

REF: – this has to be corrected everywhere.

A: The use of modeling papers are minimized within reason.

REF:- as mentioned above, the Lim et al paper quoted in introduction (p 17069, li 17/18) discusses the wrong kind of chemistry for this study: cloud chemistry instead of aerosol chemistry. But there are many other papers that discuss aerosol chemistry, either based from field observations or from laboratory studies, that could be quoted instead.

A: As indicated in our previous comment to referee 2, we removed this reference from our paper.

REF: - as mentioned above the Szyrmer and Wedyan papers quoted in introduction do not demonstrate the CCN efficiency of amino acids.

A: We agree with the referee that Szyrmer et al. [6]do not demonstrate that amino acids are good CCN: they demonstrate the efficiency of amino acids as ice nuclei. We corrected this error and added the correct references where amino acids are indicated as good CCN[7; 8; 9].

REF: Beyond the introduction (which, alone, contain most of the above problems !) I strongly encourage the authors to carefully check their literature list as, shall a second review be requested, it will be very thoroughly examined.

A: As suggested by the referee we improved our literature review, and hope that the

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new introduction provides a better focus on the scientific issue at stake. âĂČ REF:4. Description of the analyses The samples collection and analyses are the part of the study on which I have the least problems with. Yet some essential information for the validity of the results is missing in the description of the analytical method, in particular the determination of the detection sensitivities of each enantiomer of the amino acids. We recently demonstrated in one of our studies that the detection efficiencies of compounds of very similar structure could be very different, thus it would be essential to know if the concentrations here have been determined from a single standard or using authentic standard of each amino acid. Furthermore, we have also established that the detection sensitivity of different enantiomers of the same compounds could also be significantly different (up to a factor 5), independently of the column used or detection technique (MS or other), and probably due to the ionization technique. If it was assumed that both enantiomers have the same detection sensitivity, such differences could result in the small racemic fractions reported in this work. Also, unless I am mistaking, I have not seen any mention that "blank" filters were analysed by the same procedure, to check for potential artefacts. Thus, in order to trust the results of this work it is essential to explain the analysis in more detail.

A: The instrumental method LC-MS/MS was described in our recent paper [15]. In our research [15], we demonstrated that each enantiomer has different detection sensitivities and reported the instrumental detection limit for each compound. The development of a method is not the aim of the present paper because we want to focus only on the environmental aspects. Quantification of amino acids was performed using authentic D and L amino acids (see section "Reagents and standard solutions" in Supporting Material). The pre-analytical procedure for the analysis of aerosol samples was validated through the estimation of the trueness, repeatability and efficiency (yield%) for each amino acid. The procedural detection limits were calculated as three times the standard deviation of the average values of the field blank (n=3). We agree with referee 2 that we forgot to insert the blank amount of amino acids in the table. We introduced these values in tables S2, S3 and S4. The amino acids concentration on the sam-

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ples was calculated by subtracting these blank amounts and by considering the values above the method detection limits (MDL).

âĂČ Response to Anonymous Referee #3

REF: The study is very important, since it reports on the availability of amino acid compounds in aerosol particles at Antarctica and the southern Ocean, which has never been reported before. The disposition of the paper is very clear. However, the paper needs significant language improvements, and the text needs to be more coherent and the “flow” of the text needs to be improved. A native English speaker must be consulted. Also, some major changes, for example in the abstract, introduction, and some speculative information need to be addressed as explained below before this paper can be accepted for publication.

A: As suggested by referee 3, we inspected the whole manuscript, clarified several points in the abstract and introduction, and removed the speculative information. The manuscript was corrected by an English native speaker.

REF: Abstract page 17068 Lines 4-6: This part of the sentence should be changed. The CCN activity refers to the amino acid part of the aerosol particle, while in reality the entire aerosol particle activates and not only the amino part (language correction in other words).

A: We agree with the referee and we modified the sentence as follows: “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."

REF: Lines 7-9: This is a non-specific statement of the objectives. What is the role of amino acids in this statement, what does four austral summer campaigns got to do with aerosol transformations, and what is the real objective?

A: As suggested by the referee we removed the sentence in lines 7-9. We clarified

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the main aim of the study and modified the sentence as follows: “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.”

REF: Line 10: “the Italian coastal base”. Which Italian coastal base? I suggest to give the name of the station in the abstract, or where it is positioned.

A: We added the name of the Italian coastal base “Mario Zucchelli Station” in the abstract.

REF: Lines 11-12. “The main components were in fine fractions, establishing a local marine source.” What is the reason to attribute the source as a local marine source, just based on the fine fraction (this is not 100% sure, please avoid writing that it is a local marine source)? This sentence also needs to be changed due to errors in the language.

A: The reasons for this source attribution are explained in section 3.1. The high percentage of amino acids in the fine fraction is one of the main reasons of local source as demonstrated also by O’Dowd et al. [1]. Briefly, others reason are the high concentration of arginine, the study of back-trajectories, the comparison of MODIS data. We agree with the referee that the meaning of the sentence can be misleading and we modified the sentence as follows: “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

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sampling station allowed us to investigate a marine aerosol produced near the source."

REF: Lines 12-16: I am sorry: The reader does not understand what the coarse fraction has got to do with the background values of amino acids (this is written later in the text, but cannot be understood on its own here)?

A: As suggested by referee 3, we reformulated these sentences: "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."

REF: Lines 17-19: What do you mean with biological?

A: As suggested by referee 1, we introduced the adjective "intact". The presence of microorganisms is better explained in section 3.3.

REF: Lines 11-16: Please avoid to include the speculation about the photochemical transformation and coagulation as reason for the change in amino acid composition.

A:We wrote this sentence: "Once produced on the sea surface, marine aerosols undergo several physical and chemical transformations". This is not a speculation, but an observation confirmed by several studies [2; 3].

REF: Introduction page 17068-17069 Lines 21-25 (page 17068), and lines 1-23 (page 17069). In my opinion, the authorsmention in too much length the general formation and properties of marine aerosols.This section could be shortened substantially in favor for a more detailed descriptionof amino acid aerosol particles and their sources, which the authors do later in the introduction.

A: We reduced this section as suggested by referee 3 and modified some sentences as also indicated by referee 2. The section is now composed of only two paragraphs in order to extend the description of amino acids proprieties, different sources and chirality.

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REF: Introduction page 17069 Line 25: Please mention in what form the amino acids appear in the aerosol form; dissolved combined amino acids (proteins and peptides) (Kuznetsova et al., 2005; Geet al., 2011), dissolved free amino acids from the hydrolysis of the combined ones(Mopper et al. 1987; Milne et al. 1993; Sommerville et al., 2001), and particulate amino acids (solid microorganisms and debris particles inside the liquid aerosol phase)(Kuznetsova et al., 2005).

A: We thank referee 3 and added the suggested description.

REF: Lines 25-27. Many more studies have reported amino acid concentrations. Pleaserefer to the review by Ge et al. (2011) instead.

A: We improved the description of amino acid sources with new references.

REF: Line 29: Please consider also to refer to other references on the CCN activity of amino acid particles, e.g. Huff-Hartz et al., 2006; Kristensson et al., 2010; Raymond and Pandis 2002. These references will show that in general, they are not very effective CCN. However, the small amounts normally found in aerosol samples (maximum fewweight percent, Ge et al., 2011) will not decrease the CCN activity of aerosol particlesin a major way (Kristensson et al., 2010).

A:We thank referee 3 for the comment . We replaced the wrong references with the reference suggested by the referee. As discussed in our previous answer to referee 2, we understood that amino acids are good CCN and IN as demonstrated in literature [6; 7; 8; 9]. Ge et al. [16] concluded that "[..] All these studies imply a significant role of amino acids in CCN activation".

REF:Introduction page 17070 Line 6-12: Many more references are important, which report the measurements ofamino acid composition of aerosol particles. Maybe you should focus on those ones reporting the marine or Antarctic and sub-Antarctic measurements, and skip the discussionon the continental amino acids (lines 13-22)? However, you can mention (asyou already have done) that even at remote marine locations,

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continental amino acids can be major sources of amino acids in marine aerosols (Matsumoto and Ueamatsu,2005). The marine and sub-antarctic references are for example: McCarthy et al.1998, Wedyan and Presteon 2008, Mace et al. 2003, Matsumato and Ueamatsu,2005, Gorzelska and Galloway, 1990, and the one suggested by one of the referees;Schmale et al., 2013.

A: As suggested by referee 3 we modified the introduction about amino acids and added the reference to the studies about amino acids in marine aerosols. We must thank referee 3 for this comment and also J. Schmale for her interactive comment. The reference to her very interesting paper was introduced in our article. The literature provides few studies about amino acid determination in polar regions, and our research is the first investigation of Antarctic aerosols.

REF: Lines 27-28: Do you have a reference to strengthen this statement about the importance of marine aerosols in the southern ocean?

A: As suggested by referee 3, we added the reference to Bargagli, 2008. He reports that "Given the large expanse of oceans with respect to landmasses in the Southern Hemisphere, Antarctic aerosol is usually dominated by sea-salt particles, marine biogenic and volcanic emissions, and small amounts of soil dust".

REF: Lines 23-28, and Lines 1-2 (page 17071). I find it hard to understand what you are trying to mediate in these sentences. Please clarify.

A: We clarified our aim to investigate amino acids in Antarctic region as follows: "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 mini-

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mal interference from anthropogenic sources (Bargagli, 2008; Bourcier et al., 2010)."

REF: Introduction page 17071 Lines 3-19. The aims are stated in a somewhat incoherent way. Would it be possible to make it more coherent? Maybe it is also somewhat vague. Would it be possible to specify instead exactly what you were doing?

A: As also suggested by referee 2, we improved the definition of our aims by answering the three questions suggested by referee 2: why study amino acids, why measure their enantiomeric composition and why perform this investigation in Antarctica?

REF: Experimental section pages 17072-17075 Please put the text about station measurements on page 17072, lines 28-29, and page 17073, lines 1-6 directly after the station description at line 6 on page 17072. All the periods of station measurements should be mentioned together, and then you should mention the ship cruise at the end. And why is the DOME C measurements mentioned twice in the experimental section? Please make this more coherent.

A: We corrected the experimental section, adding the station description after the sampling data.

REF: Page 17072: Please mention that you are doing TSP measurement for the ship cruise. And, why do you mention in several places that the sampling is of particles larger than 1 um diameter? Shouldn't the TSP measurements also include the submicron fraction?

A: We specified that the sampling carried out during the ship cruise involved collecting the TSP fraction, where particles have a diameter above 1 μm. The TSP sampler is composed of two different sampling supports: a circular filter and a polyurethane foam (PUF). The circular quartz filter collects the TSP fraction with a pore size of 1μm, while the PUF samples the volatile and semi-volatile compounds, and particles with a diameter below 1 μm.

REF: Page 17073: Please avoid using emotional expressions like "precious".

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A: We corrected the emotional expression "precious" and replaced it with "rare and expensive".

REF: Page 17075: Mean-clustered trajectories? What is this? Please explain.

A: A full explanation of this modeling techniques is available in reference[17]. In order to better explain the cluster mean trajectories, we introduced the following sentence: “Four runs were computed for every sampling day starting every six hours and the resulting multiple trajectories were aggregated into 6 groupsin order to highlight major paths in the origin of air masses reaching sampling sites.”

REF: In general, please discuss which amino acids compounds you are sampling in the experimental section. For example, you do not mention if it is dissolved combined or dissolved free amino acids that you are measuring, or if you also measure solid amino particles inside liquid aerosol particles.

A: As suggested by referee 3, we introduced in the experimental section the adjective “free” before “L- and D-amino acids in the aerosol samples”. The adjective “free” is present in each sub-section title of the section “Results and Discussion”.

REF: Many, like me who are not familiar with the sampling techniques do not have the competence to conclude which types of compounds you are measuring. And, please also discuss if your sampling method is “soft” or “destroying” the chains, dissolves the solid amino acids, or hydrolyses the combined amino acids into free amino acids. The aerosol sampler permits to collect the particulate matter without modifying the aerosol composition. Each sampler used preserves the representativeness of the sample.

A: The combined amino acid fraction is generally obtained through hydrolysis adding 6N HCl for 24-24 h at 110°C. In our work, we analyzed only the free fraction of amino acids contained in the aerosol particles.

REF: Results and discussion page 17075. You mention L-, and D-amino acids in the results section. For those not familiar with the chirality of these compounds, please

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explain in the introduction that the L-types come predominantly from phytoplankton material in the oceans, and the D-types come predominantly from bacteria (Kuznetsova et al., 2005).

A: As also suggested by referee 2, we added in the introduction a specific section about the chirality of amino acids.

REF: Please also explain in the Instrument analysis section that you are analyzing both types.

A: "The enantiomeric determination of L- and D-amino acids in the aerosol samples was conducted using a method previously developed by Barbaro et al. (2014)."

REF: I recollect that L-types dominate in coastal-near environments (Kuznetsova et al., 2005), and that D-types are found at off-shore marine environments. I don't think that bacterial amino acids are below detection limit at off-shore locations. Please consult: McCarthy et al., 1998, and Wedyan and Preston, 2008 again. Please discuss the potential difference between you not finding D-amino acids, and the other studies finding these D-types.

A: We modified the introduction of the manuscript as suggested by referees 2 and 3. In these new paragraphs, we explained in more detail that D-free amino acids are a significant index of a great proportion of bacteria in the aerosols where photosynthesizing organisms are not present [18]. Our experimental data demonstrated that the free D-amino acids were below the detection limits, confirming that a major source of amino acids was the phytoplanktonic origin [19].

REF: Result chapter 3.1 Page 17076, Line 1: Please explain what the first sample is.

A: We introduced data about the first sample.

REF: Result chapter 3.2 Page 17078. First paragraph of section 3.2. Consider to remove it entirely. All the stations and ship cruises in this study are remote. This does not have to be mentioned here again. Page 17078, second paragraph of section 3.2.

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In general you are repeatedly mentioning in the introduction of several result sections which periods you are measuring at the different sites. This has been communicated once before, and is clearly seen in Figure 2, why you can remove this text, and also in other places where it is not needed.

A: As suggested by referee 3, we removed the first and second paragraphs to avoid repetitions in the manuscript.

REF: Page 17079. “very aged “background aerosols”. Should rather be “very remote”?

A: We corrected the error and replaced "very aged" with "very remote".

REF: Page 17080-17081. Very rarely do particles from the fine mode grow into the coarse mode, especially if most of the fine mode particles are found well below 1 um diameter. This happen only if the coagulation is very strong (high particle concentration), or if the condensation growth is strong (many condensing vapors). But, the remote areas of the southern ocean, does not really allow for this. Since, coarse mode amino acid aerosol particles sometimes have a continental origin, couldn’t this be the explanation (if you look further back in time on the trajectories to find a continental origin)? Or if you are sampling large marine particles during conditions of favorable sea spray production of coarse mode particles at the same time as micrometer sized amino acid debris solid particles are also collected? Please consider to change this entire discussion. Please mention in the results and discussion section, how large fraction of the WSON the amino acid compounds take up, or the fraction of the total aerosol mass when comparing with other studies reporting measurements of the total mass or WSON mass at Antarctica.

A: The key point of our discussion is reported as follows: “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 ability of amino acids (Szyrmer and Zawadzi, 1997). The concentration of amino acids in

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the coarse particles of aerosols collected at Dome C had average values of 420 fmol m-3 (Fig. 4) for both field campaigns, while our coastal data had a mean concentration of 264 fmol m-3 (Fig. 2). This enrichment of amino acids in the percentage of coarse fraction can be due to the 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)." Referee 3 hypothesized that amino acids in coarse particles may have a continental origin but this theory is not possible because the coarse particles have a lifetime of 1 or 2 days, as reported in figure 3.8 of the book "Atmospheric physics" [10]. We calculated the 240 hours back-trajectories and the air masses in sampling during the 2011-2012 summer spent inland about 36 hours (1.5 day) while 4-7 days during the sampling in the 2012-2013 summer. In both cases, the coarse particles generated by a continental source were already removed by physical processes (for example by sedimentation). Fine particles (<1μm) have a lifetime of 1 month and can be subjected to different physical and chemical processes. The reduction of amino acid percentage in the fine mode can be due to the chemical, photochemical and ionic transformations of amino acids in the atmosphere while an increase of amino acid in coarse fraction can be due to ice-nucleation. The formation of ice nuclei is increased by the presence of amino acids[6]. We agree with referee 3 that coagulation occurs with high particle concentration and the condensation growth with many condensing vapor and that these conditions are not present in the Antarctic plateau. However, these conditions can occur during the long-range transport. Moreover, ice crystals are nearly always present in the atmospheric boundary layer over the Antarctic Plateau [20] and amino acids can improve the ice formation. The aerosols sampler collected all kinds of solid particles, both aerosols and ice crystals of different dimensions, and the ice particles can contain a higher concentration of amino acids. This observation may indeed confirm the proprieties of amino acids as efficient IN.

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REF: Conclusions Please avoid to discuss the coagulation and photochemical transformation with regards to the ageing of compounds in the aerosol particles, since theis is almost ruled out (see previous comments), and since it is only a speculation. Please focus instead on the results that are certain (the average and median concentration of amino acids in the particles, and the range of concentrations, from minimum to maximum, and the difference in composition and concentration between the coastal, dome c, and ship board measurements). Please leave the speculation for the discussion section.

A: We completely revised the manuscript, removed the speculation and specified the main aim of this important study.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C7598/2014/acpd-14-C7598-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 17067, 2014.