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

Anonymous Referee #2

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General comment

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 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 their 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)

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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.

Detailed comments

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 arguments 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.
- “Amino acids are important components of organic nitrogen in aerosol and have the

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ability (...) to act as Cloud Condensation Nuclei...” Doubly false: the main organic nitrogen components in aerosols are organonitrates. Amino acids are only present in trace 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 major aerosol component. Furthermore there are no studies indicating that amino acids are good CCN and the articles quoted in support of this are inadequate: Szrymer, 1997 is 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.

- “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.

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 not be more wrong, as marine aerosols have very small concentrations and sizes and therefore a minimal contribution to the global aerosol burden.

- p 17069, li1-3: actually, the current consensus in the atmospheric community is that the 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.

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

- why studying amino acids and not other compounds ?
- why measuring their enantiomeric composition and not their total concentrations ?
- why this investigation had to be performed in the Antartica region and nowhere else ?

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 their 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.J.D., 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

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misunderstanding of the term “ageing” – see point 2 below).

Another interesting property of amino acids is that they are efficient catalysts for ionic organic reactions, as shown by:

- Nozière, B., et al., The Formation of Secondary Light-Absorbing “fulvic-like” Oligomers: A Common Process in Aqueous and Ionic Atmospheric 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 on aerosol 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 numerous papers 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 as indicated p.17080 li 26.

Finally, one last main objective of this study, or at least main points of conclusion that should be emphasized are

- the presence of all these biological amino acids in regions with (apparently) little biological 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 from warmer regions,

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

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These points, alone, would justify the publication of this work. Thus clarifying the main objectives/conclusions and address them would considerably improve this paper and its chances to be published.

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 importance of amino acids as CCN.

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.

- the Lim et al paper on photochemical reactions in water quoted in introduction (p 17069, li 17/18) applies to cloud chemistry (very diluted concentration of organics in water), not to aerosol chemistry.

- 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 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

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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.

- 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.

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).

- 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.

- 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.

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- in particular, the papers cited on p.17069, li 13/14 to support secondary aerosol formation studies are inadequate as they are modelling papers, not experimental studies 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 – this has to be corrected everywhere.

- 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.

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

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.

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

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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.

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