

## ***Interactive comment on “Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol” by E. Barbaro et al.***

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Response to Anonymous Referee #1 REF: This study reports on the size resolved measurement of free amino acids in Antarctic aerosol at two different sites, a coastal and an inland station, as well as during a cruise. Higher concentrations of amino acids were found at the coastal station originating from the sea with an enrichment of amino acids in the fine fraction compared to the inland station. Further inland, amino acids were predominantly present in the coarse fraction. The authors attribute these differences to physical and chemical processing of amino acids during atmospheric transport from the sea further inland. During the cruise the highest concentrations

C499

were found which the authors attribute to the presence of intact biological material. The manuscript presents a valuable data set and provides important insights into the chemical and microphysical characteristics of amino acids in aerosol in a sparsely studied environment. I recommend publication after a careful revision of the interpretation of results as outlined below in the “general comments” section. General Comments: In addition to the collected data the authors use back trajectory analysis to interpret their results. Beyond this, they rely heavily on literature for interpretation especially regarding the implications for and of ice nucleation related to the presence of amino acids in the aerosol. The authors present no measurement based evidence nor direct links to previous studies for their speculative interpretation that amino acid containing aerosol transported towards inland Antarctica has undergone ice nucleation and exhibits therefore amino acid enrichment in the coarse fraction. The single reference that is given to support this does not contain information that would directly discuss this process. Since neither evidence by the data nor from literature is provided that the observed amino acids can actually serve as ice nuclei, and since it is not at all clear from the description in the manuscript whether ice-nucleated particles were present in the coarse mode aerosol collected on the filter, I suggest removing the related passages. These are: p. 1284, l. 22-24: “: :this is unlikely: : :”, and p. 1285 l. 5-8: “The most likely process: : :”. Instead it can be said that the specific reason for this enrichment is not clear based on the available data.

AC: As suggested by the referee, we removed the sentences “this is unlikely in Antarctica where the intense cold probably promotes ice-nucleation phenomena, a process that is helped by the presence of amino acids (Szyrmer and Zawadzi, 1997)”. The paragraph is now reads as follows: “These fine aerosol particles can grow during long-range transport, due to condensation of molecules from the gas phase or by collision of small and large particles (coagulation) (Petzold and Karcher, 2012; Roiger et al., 2012). However, this is unlikely in Antarctica due to the very clean conditions. The specific reason for this enrichment is not clear based on the available data.”

C500

REF: Make sure that all references named in the text are present in the bibliography, there are some inconsistencies.

AC: As suggested by the referee, we checked the bibliography, removing some references missed in the manuscript,

REF: p. 1271, l. 21: Not all amino acids enhance the ice nucleating ability of aerosol, I suggest relativizing as follows: “: : : because some of them have been shown to : : :”.

AC: We agree with referee and we modified the sentences as suggested by referee.

REF: p. 1274, last paragraph of the introduction: Include the years when the measurements were conducted.

AC: We introduced the years of sampling.

REF: p. 1274, l. 16-18: Include quantitative evidence that air masses were really not influenced by emissions from the research station.

AC: We have modified the phrase to read “It was chosen because it is located in a valley that is physically separated from the main station area by a hill, to reduce as much as possible eventual pollution from the research station.” As we do not have recent monitoring data from that site.

REF: p. 1277, l. 5-8: The message of this sentence is very difficult to understand. Please make several sentences out of this. In addition, in line 7 the single “s” probably means “used”.

AC: I modified the sentences as follows: “In this work the amino acids were quantified using the isotope dilution method where an isotopically labeled standard was available. For other amino acids, where a labeled standard was unavailable, an internal standard was used to quantify the analytes. A detailed description of which analytes are quantified with which method can be found in Barbaro et al. (2014).”

REF: p. 1278, l. 17: What do you mean by repeatability? Do you mean standard

C501

deviation?

AC: In this case we are using the IUPAC definition of repeatability which from the IUPAC Gold Book is defined as: “The closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and after short intervals of time). The measure of repeatability is the standard deviation qualified with the term: ‘repeatability’ as repeatability standard deviation. In some contexts repeatability may be defined as the value below which the absolute difference between two single test results obtained under the above conditions, may be expected to lie with a specified probability.” (from <http://goldbook.iupac.org/R05293.html>) In the manuscript we used the phrase “The repeatability is determined as the relative standard deviation of the analytical results for the 5 spiked filters.” This phrase on repeatability follows IUPAC guidelines to avoid confusion with reproducibility which is defined as: “The closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or after different intervals of time). The measure of reproducibility is the standard deviation qualified with the term ‘reproducibility’ as reproducibility standard deviation. In some contexts reproducibility may be defined as the value below which the absolute difference between two single test results on identical material obtained under the above conditions, may be expected to lie with a specified probability. Note that a complete statement of reproducibility requires specification of the experimental conditions which differ.”

REF: p. 1282, l. 4: Specify which temperatures you refer to: air, sea surface etc.?

AC: I added “air” before “temperature”

REF: p. 1284, l. 21: insert “or” in “due to condensation of molecules from the gas phase or by collision of small and large particles: : :”. And continue as follows: “However, this is unlikely in Antarctica due to the very clean conditions.” Remove the following

C502

sentence “This is unlikely: : :”.

AC:I modified the paragraph as suggested by referee and now it is: “These fine aerosol particles can grow during long-range transport, due to condensation of molecules from the gas phase or by collision of small and large particles (coagulation) (Petzold and Karcher, 2012; Roiger et al., 2012). However, this is unlikely in Antarctica due to the very clean conditions. The specific reason for this enrichment is not clear based on the available data.”

REF: p. 1286, l. 3-5: Again, not all amino acids enhance ice nucleating abilities. In addition, hydrophilicity is not a necessity for a particle to ice-nucleate. A wettable particle can do so as well (e.g. mineral dust). I suggest deleting the sentence “This is a very important indication: : :” since it does not support your conclusion regarding the water content of the aerosol.

AC:As suggested by referee I removed the sentence.

REF: Technical Comments: p. 1270, l. 4: introduce an “and” between “: : : organic nitrogen in aerosols, and particles containing amino acids: : :” p. 1274, l. 14: delete “the” before “the 29 November” p. 1275, l. 5: no capitals in “Slotted Quartz Fiber filter” p. 1277, l. 16: continue the sentence “To ensure that: : : this evaluation was carried out: : :”. p. 1277, l. 24: insert a “,” between “filters, respectively.” p. 1278, l. 5: delete “%” p. 1280, l. 20: include “,” before and after “respectively” p. 1280, l. 21: replace “an” by “a” p. 1280, l. 25: move “respectively” to the end of the sentence. p. 1281, l. 2: replace “find” by “found” p. 1281, l. 8: replace “while” by “and” p. 1281, l. 9: replace “is” by “it” p. 1281, l. 10: remove “concentrations a high” p. 1281, l. 12: remove “proportional” p. 1281, l. 16: remove “the” in “that the 1 %” p. 1283, l. 7: replace “shows” by “presents” to avoid repetition p. 1286, l. 27: replace “internal” by “inland” p. 1287, l. 2: replace “composition” by “contribution” p. 1287, l. 8: remove “a” in “promoting a numerous series” p. 1287, l. 15: remove “the” in “the 13 January” p. 1288, l. 3: replace “where” by “that” p. 1289, l. 25: replace “come” by “came” p. 1290,

C503

l. 2: remove the parenthesis p. 1290, l. 10, remove “were”

AC: I modified each point of technical comments as suggested by anonymous referee 1. Æ

Response to Anonymous Referee #2

REF:Review on manuscript acp-2014-1007 “Free amino acids in Antarctic aerosol: potential markers for the evolution and fate of marine aerosol” by E. Barbaro et al. This manuscript is much better than the previous version. The discussion is much clearer and the authors made some efforts to take into account the referee’s comments. In particular, it is now clearly explained that the reported amino acid concentrations are corrected for blank values. The method paper Barbaro et al. Anal. Bioanal. Chem. 2014 is also available, and I was able to check that the analytical procedure is fine. I only have one last question on the discussion, that might need to be clarified: when comparing the amino acid loadings measured in this study and at other locations in previous works (section 3.1), or between aerosol size fractions (section 3.2) is the total aerosol loading somehow taken into account ? Because larger amino acids concentration per volume of air could just be due to larger aerosol masses, not necessarily to higher amino acid concentrations in the particles. In particular, is it clear that the “enrichment” of the coarse fraction in amino acids (and corresponding “depletion” of the fine fraction) discussed in Section 3.2 corresponds really to higher amino acid concentrations in the particles and not just to a higher aerosol mass in the coarse fraction (which is usually the case) ? An easy way to answer would be to measure the sampled aerosol mass (= weight the filters before and after sampling) and express the amino acid concentrations per mass of aerosol sample instead of m<sup>3</sup> of air. Alternatively, the mass in each aerosol fraction could have been measured by a SMPS instrument sampling next to the filter collection : : : If this has not been taken into account, it might be worth considering in the discussion. Other than that, the manuscript seems fit for publication.

C504

AC: We thank the referee for this suggestion and we agree that the amino acids concentration for aerosol mass is more significant. We will consider the SMPS instrument for our next sampling campaign. In our studies, we considered the contribution of amino acids per volume and we did not measure the mass of aerosol in all sites. We have the data of aerosol collected at MZS (unpublished data), obtained by weighing the filters before and after sampling, but the data of other sites was not available. The lack of aerosol mass data for the aerosol samples collected at Dome C and during the oceanographic cruise are due to the high electrostatic charge and low humidity at Concordia making weighing to such precision virtually impossible. You can also imagine the problems in weighing to five significant figures a filter on a ship traversing the Southern Ocean. To clarify the enrichment of amino acids in the coarse fraction, we will investigate the aerosol mass in future expeditions, and we thank the referee for this suggestion. We also introduced in the manuscript the sentence: "In our future investigations, we will also evaluate the aerosols mass, which is probably a key parameter to measure that will help explain this enrichment.". The comparison with other locations in previous works was done by considering the data for sampling volume.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 1269, 2015.