

Interactive comment on “Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets” by Nadja Triesch et al.

Matthew Pendergraft (Referee)

mpenderg@ucsd.edu

Received and published: 19 June 2020

acp-2019-976 Submitted on 23 Oct 2019 Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets Nadja Triesch, Manuela van Pinxteren, Anja Engel, and Hartmut Herrmann

Generally, a referee comment should be structured as follows: an initial paragraph or section evaluating the overall quality of the preprint ("general comments"), followed by a

C1

section addressing individual scientific questions/issues ("specific comments"), and by a compact listing of purely technical corrections at the very end ("technical corrections": typing errors, etc.).

In your evaluation, please take into account the different aspects mentioned on the ACP website at: [https://urldefense.com/v3/__https://www.atmospheric-chemistry-and-physics.net/peer_review/review_criteria.html__;!!Mih3wA!RVxwT_2zwS6jjcQw8KkE9dEEIKCg3c8NhYkfhXujSgZ0_c9y\\$](https://urldefense.com/v3/__https://www.atmospheric-chemistry-and-physics.net/peer_review/review_criteria.html__;!!Mih3wA!RVxwT_2zwS6jjcQw8KkE9dEEIKCg3c8NhYkfhXujSgZ0_c9y$)

General Comments

This paper describes the measurement of free amino acids in seawater (microlayer and underlying water), aerosol, and cloud water at Cape Verde Island. The types and abundances of individual amino acids present in different sample types are compared. Enrichment factors are calculated for amino acid concentrations between the microlayer and underlying water, and between the water and aerosol. The contribution the amino acids make to the pools of organic carbon and total dissolved nitrogen in water and aerosol are presented.

The work largely presents an inventory of amino acids for this location and the given sample types. The concerted measurement of amino acids in underlying seawater, microlayer, aerosol, and cloud water are novel. The authors also mention that these are the first reported free amino acids concentrations for marine clouds. Enrichment factors between seawater and aerosol are useful for comparison but I urge the authors to elaborate a little on the caveats of their use in an open system, namely that it is unlikely that a high fraction of the aerosol (and cloud droplets) measured came from the location of the measured seawater (and even less likely they emerged from those waters when the water was sampled). Concentrations in the atmosphere are also subject to ageing. This differs from other work on sea spray aerosol in closed systems where all particles are emitted from the contained source waters and minimal ageing occurs on the nascent particles (at least upon collection).

C2

This work could be strengthened by: 1. elaborating on the significance of amino acids in the ocean and atmosphere and how the scientific community benefits from their inventory. 2. investigating the drivers of their observations by further relationships amongst their datasets and incorporating other datasets, e.g. Did variations in measured aerosol volume drive variations in amino acid concentrations? Did primary productivity (via remotely sensed chlorophyll-a) influence FAA concentrations in water and air? 3. further exploration of commonalities among and differences between their amino acid data across different sample types. 4. what implications can be drawn from the analyses accomplished and those I suggest? Are there certain ratios of amino acids in seawater that hold constant in seawater samples but not in the aerosol and clouds? What could cause this? 5. better connecting to past work. How do the observations compare not just to the values reported in other work but to the conclusions drawn in other research? How do drivers of amino acid concentrations differ between the ocean and atmosphere? What are the surface activities of the amino acids and can they predict their transfer in sea spray aerosol?

Ultimately I would like the authors to demonstrate that they have done more than make some measurements and that we have gained new insight into the ocean-atmosphere system beyond an inventory of amino acids. The manuscript needs to set up what was done on top of our current understanding of sea spray aerosol formation and the transfer of different compounds/classes into sea spray aerosol. By building on past research the present work is prepared to more clearly communicate its findings and to also contribute new knowledge to the field.

Introduction. page 3. line 22. Barbaro et al. (2015) investigated FAA in size-segregated Antarctic aerosol particles to gain information about FAA as possible tracers of primary biological production in Antarctic aerosol particles line 24. Although there are several studies in different marine regions, there is a lack of ambient measurements of FAA simultaneously in seawater and in size-segregated aerosol particles in the tropical Atlantic Ocean. It would strengthen the justification for the work if it was stated why we

C3

must know this information specifically for the Atlantic Ocean and atmosphere.

There is little effort made to investigate the drivers of amino acids data for the ULW and SML. The data are not plotted against other measurements. We are merely offered (page 9, line 19): "On the basis of previous studies, the transportation and the releasing mechanisms seems to be most likely for the observed enrichment of FAA." At this point, we were not given a strong motivation for the measurements and we haven't learned anything from them. Then it is explained that the data are in agreement with other datasets and then this one dataset is extrapolated to the entire North Atlantic Ocean. I wouldn't extrapolate data from one location to the entire North Atlantic Ocean.

Similar to the seawater measurements, the atmospheric research would be stronger if it explored the drivers of the amino acid data. Particularly lacking from the aerosol work are aerosol sizing measurements. In their absence, we do not know if the variability in amino acid concentrations in the air are driven by changes in particle concentrations. Similarly, amino acid concentrations in the air could be related to wind direction.

Other:

Did particle type vary across the different aerosol sampling periods?

If amino acids have already been measured in remote marine air/aerosol, how does the present manuscript advance our knowledge?

Specific Comments

Abstract. page 1. line 20. "The total concentration (PM₁₀) was between 1.8–6.8 µg m⁻³ and tended to increase during the campaign." Perhaps instead of "during the campaign", give the time period or relate to a potential/suspected driver of the observation.

Introduction.

page 2.

C4

lines ~8-12. The marine nitrogen cycle is alluded to but vaguely. "(T)he bulk DON pool CAN BECOME bioavailable" or "IS bioavailable"? What is remineralized nitrogen? Perhaps get straight to proteinaceous compounds and amino acids as being large members of the DON pool.

line 21. much more work has been done on amino acids as ice nucleating entities (and as antifreeze entities) than just Szyrmer and Zawadzki, 1997 and should be acknowledged because it gives importance to this work.

line 23. "Amino acids are also present and have been described in the marine environment." This has already been established. The first 3 sentences of this paragraph feel like we are going backwards. In the previous paragraph we went from the ocean to the atmosphere and now we are back to describing amino acids in the ocean.

line 28. (Engel et al., 2017) lacking other citations for the microlayer's importance in the ocean and sea spray aerosol.

page 3.

line 7. "However, chl-a concentration solely does not adequately describe the complete spectrum of biological activity (Quinn et al., 2014)" should reference a paper on marine microbiology, like Azam and Malfatti. 2007. Microbial Structuring of Marine Ecosystems. DOI: 10.1038/nrmicro1747

page 4.

line 13. "During this campaign, concerted measurements were performed including sampling of size-segregated aerosol particles at the CVAO and seawater sampling at the ocean site (~16°53'N, ~24°54'W). The location was carefully chosen with minimal influence of the island and located in wind direction to the CVAO" This second sentence is crucial to the rationale of the study and should be demonstrated. I'm surprised to not see a figure referenced here.

line 20. "The seawater samples were taken with a fishing boat, starting from Bahia

C5

das Gatas, São Vicente." A study site map with water and aerosol locations and winds during sampling periods would be good to "connect the dots". Figure S1 does not do this.

page 6.

line 2. "Since no chiral column was used in the UHPLC separation, it is possible that not only L-amino acids, which were used as the standard, were quantified, but that the here presented concentrations were possibly quantified as the sum of the L- and D-amino acids." So why not simply report them as L- and D-amino acids instead of reporting them as L-amino acids but acknowledging that is not accurate?

2.2.4 Enrichment Factors

For calculating enrichment factors (EFs) between aerosol and the SML, I wonder if it would be more appropriate to first calculate the aerosol-ULW EF using equation 2 and then apply the SML-ULW EF (EF_{SML}) from equation 1 for that analyte. So there would be EFs for aerosol relative to the underlying water and relative to the SML and they would differ by the EF_{SML} (Eq.1). Ideally this would resolve the current inconsistency in invoking the Na⁺ concentration of the SML when comparing to aerosol to SML (Eq. 2) but not when comparing SML to ULW. The way it stands now, if you calculate aerosol EFs relative to the ULW and the SML they won't differ by the EF_{SML} and instead will differ by an EF_{SML} calculated using equation 2.

page 10.

line 1. This sentence is confusing: "In the study of Reinthaler et al. (2008) DFAA contributed with ~12 % to DOC and with ~ 30 % to dissolved organic nitrogen (DON) in the SML of the Atlantic ocean and the western Mediterranean Sea." Is it DFAA in seawater accounting for ~12% of DOC (in seawater), and DFAA in SML accounting for ~30% of DON in the SML?

line 28. The characterization of FAA into the hydrophilic, hydrophobic, and neutral

C6

classes is nice. What might be the drivers and implications?

page 11

line 11. "However, the presence of Glu, Asp and GABA as part of the hydrophilic species in the submicron aerosol particles (on 22/09/2017, 4/10/2017, 6/10/2017, 7/10/2017) strongly indicated a local oceanic origin." If amino acids can indicate aerosol type or source, this should be central to this work, explained in the introduction, and examined for each sample. Also, how did the amino acid profiles of the different sample types (and individual samples) compare? Were the same relative abundances consistent across the ULW, SML, and different aerosol size classes? Are all the amino acids measured commonly found in the ocean and are they exclusive to the ocean?

page 12

line 2. "Considering the amino acid classifications from Barbaro et al. (2015)), it can be concluded that the submicron aerosol particles with low averaged percentage of hydrophobic species (5 %) and higher percentages of hydrophilic species (4-55 %, mean of 15 %) could have local oceanic origin." Similar to previous comment. The different amino acid characterizations: hydropathy index of Kyte & Doolittle 1982; Pommie et al. 2004; and Barbaro et al. 2005 should be explained early on and would add value to the present work.

line 5. "This is supported by a predominant marine origin of the aerosol particles according to the air masses history, particulate MSA concentrations and MSA/sulfate ratios and particulate concentrations of dust tracers (Table S8)." It would be nice to lay this out because we make it this far into the manuscript wondering about the presence of aerosols from land in these samples. I would characterize the air masses early on. Do the back trajectories differ for the samples collected at 2 different elevations? And which back trajectories were used? Hysplit or Flexpart? Is this mentioned in the Experimental section?

C7

line 7. "The higher complexity in the FAA composition on the submicron aerosol particles could only be determined because the analytical method applied here is able to quantify the individual molecular FAA species." Yes, that is good, and I would encourage the authors to leverage this resolution in their data. See previous comments regarding the comparison of amino acid "profiles" for different sample types and what do the presence of each amino acid tell us.

line 10. "The composition of FAA on the size-segregated aerosol particle samples with focus on the comparison of the submicron with the supermicron aerosol particles as well as the comparison of aerosol composition with the seawater composition will be discussed more detailed in section 3.4." Please simplify this sentence.

3.2.2 Size-segregated aerosol particles at the mountain station (MV) This section reports particulate matter (PM) masses for both the MV and CVAO stations. The Experimental section only reports particle volume measured for cloud water sampling at Mount Verde, and not at CVAO, with liquid water content (LWC) somehow derived. I am in favor of reporting what is measured directly. Here, is particle mass derived from the particle volume measurements or from the mass of filter samples (at CVAO) and cloud water (at MV) recovered? I assume there was a particle volume monitor at both CVAO and MV. I encourage plotting all particle volume data against other particle measurements like FAA. Does FAA abundance track particle volume?

page 13

line 24. "In cloud water samples with $\Sigma\text{FAA} < 65 \text{ ng m}^{-3}$, usually Gly was dominant followed by Ser. Cloud water samples with $\Sigma\text{FAA} > 290 \text{ ng m}^{-3}$ showed a higher complexity in the FAA composition, especially towards the end of the campaign, including the appearance of Asp." Did the relative abundances of the FAA vary, indicating different FAA profiles, or were they similar, indicating a consistent FAA profile? What was the profile of hydrophobic, hydrophilic, and neutral amino acids and how did that compare to the aerosol samples?

C8

Were the sodium, sulfate, and MSA measurements made on cloud water also made on the aerosol samples? Other than FAA (in section 3.4) which other data are common to the two sample types - aerosol and cloud water - that would allow us to compare them?

page 15

line 10. "the reactivity/ mean life time τ of the amino acids" Please explain.

line 22. "The mean lifetime τ of Glu (remote aerosol case: 0.02 d" Thats 29 minutes. Is that considered long?

line 30. "The presence of GABA on the submicron aerosol particles pointed out that (marine) microorganisms were present on the aerosol particles and produced GABA via microbiological decarboxylation of Glu." Until the authors demonstrate that GABA cannot exist outside of a (marine) microorganism, this statement is unfounded. The opposite is a safe assumption: that any compound produced by marine microorganisms will also be found in the wastewater, either by active release by the living microorganism or via release of the dead microorganism (residence times will vary).

page 17

line 2. "the presence of bacteria in cloud waters has been reported in the literature (Jiaxian et al., 2019)." Microorganisms have been documented in the air since at least Darwin's HMS Beagle voyages so a few more citations here would be appropriate. A few of note:

Jardine, B. Between the Beagle and the barnacle: Darwin's microscopy, 1837-1854. *Stud. Hist. Philos. Sci. Part A* 40, 382–395 (2009).

Salisbury, J. H. On the Cause of Intermittent and Remittent Fevers. *Am. J. Med. Sci.* 51–75 (1866).

M. Vařtilingom et al., Potential impact of microbial activity on the oxidant capacity and organic carbon budget in clouds. *Proceedings of the National Academy of Sciences of*

C9

the United States of America. 110, 559–564 (2013).

3.4.2 Neutral and hydrophobic amino acids How do the surface activities vary across the different amino acids? Does abundance in aerosol correlate to surface activity? Or a combination of surface activity and reactivity/lifetime?

page 18.

line 13. "a possible transport from other than marine sources is included in this parameter." The language is (not on purpose) vague and should clearly state that the waters measured and used for the enrichment factors have not been demonstrated to be the source of the aerosols measured.

line 16. "Regarding the transfer of OM from the ocean into ambient aerosol particles, solely organic carbon as a sum parameter has been regarded to date and no distinction of single organic matter classes for ambient measurements has been performed."

Although not written altogether clearly, this statement seems to state that compound classes nor compounds have been resolved from ambient aerosol. This is false as there is a number of studies that have accomplished this. See:

Molecular diversity of sea spray aerosol particles: Impact of ocean biology on particle composition and hygroscopicity RE Cochran, O Laskina, JV Trueblood, AD Estillore, HS Morris, ... *Chem* 2 (5), 655-667

Quinn, P. K., Collins, D. B., Grassian, V. H., Prather, K. A., & Bates, T. S. (2015). Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol. *Chemical Reviews*. American Chemical Society. <https://doi.org/10.1021/cr500713g>

Figure 5. Please include in the figure the size range for each Berner stage.

page 19.

line 7. "Previous studies showed that organic material ejected into the atmosphere during bubble bursting, resulting in sea spray aerosol particles containing similar organic

C10

material to that of the SML (Russell et al. (2010);Cunliffe et al. (2013) and references therein)." This - the basics of sea spray aerosol formation - need to be brought up later and the investigation of hydrophilic/-phobic amino acids in different particle types needs to be established in this context.

line 29. "In situ-formation of FAA in cloud water, maybe due to biogenic formation or enzymatic degradation of proteins, selective enrichment processes as well as pH dependent chemical reactions might be potential sources." site Malfatti, F., Lee, C., Tinta, T., Pendergraft, M. A., Celussi, M., Zhou, Y., ... Prather, K. A. (2019). Detection of Active Microbial Enzymes in Nascent Sea Spray Aerosol: Implications for Atmospheric Chemistry and Climate. *Environmental Science and Technology Letters*, 6(3), 171–177. <https://doi.org/10.1021/acs.estlett.8b00699>

Technical Corrections

Introduction.

page 2. line 8. "surface global ocean" to "global surface ocean" line 16. "utilizable sources of nitrogen" to "utilizable FORMS of nitrogen"

page 3. line 31. "underline seawater" to "underlying seawater"

page 4. line 4. "as proxies or tracer" to "as proxies or tracerS"

In the Experimental section perhaps change "analytics" to "analyses"

2.2.1 Seawater sample analytics Was the standard addition method applied to samples to assess for recovery efficiency of the entire process?

page 6. line 23. "All here presented values" to "All values presented here" line 29. "The cloud water samples were operated the same as seawater samples". change "operated" to "handled" or "processed". line 31. "syringe filters filters" to "syringe filters" or "syringe tip filters"

page 10. line 12. Remove "It is obvious that" as it is confusing language. line 14-15.

C11

Reword. Use "neither" instead of "both".

page 12 line 32. "aerosol particles" is redundant. aerosols are particles. say just "aerosol" or "particle", here and elsewhere.

page 17. line 7. "Neutral amino acids" to "acids" line 10. "A further explanation approach" remove "approach"

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2019-976>, 2020.