Review of revised manuscript: acp-2019-976-manuscript-version4.pdf

General comments

I read in the response to reviews language along the lines of "this amino acid can be ejected by the ocean and end up in sea spray aerosol" and this implies a misunderstanding of sea spray aerosol basics, or even aerosol basics. Compounds are emitted from the ocean either in sea spray aerosol or in gases. Gases can condense onto aerosols. Otherwise, a compound found in sea spray aerosol was ejected from the ocean in a sea spray aerosol. It (the compound) didn't get ejected from the ocean in some ambiguous, undefined phase and then somehow "end up" in (a) sea spray aerosol.

What I also consider a misunderstanding of sea spray aerosol basics is that the presence in sea spray aerosol of a substance produced by microorganisms does not mean a microorganism was present in the aerosol. The substance can be produced in the seawater and then transfer in sea spray aerosol without the microorganism present.

While implying the presence of microorganisms in submicron aerosol, the authors may want to consider and mention that a 1 um (or, here, 1.2 um) size cutoff excludes, by size, many microorganisms, even many marine bacteria. Perhaps they should state which marine microorganisms they think might be in their submicron aerosol and what are the size ranges of those microorganisms. For example, viruses are small enough, are abundant in the ocean, and are well documented in sea spray aerosol. And since the aerosol isn't exclusively sea spray aerosol, are there non-marine microorganisms that may be present?

I commend the authors on making it clear in the Introduction that amino acids in aerosols can come from diverse sources. As such, I think the paper needs to clearly explain how amino acids in aerosols can be attributed to sea spray aerosol.

Please make sure all tables clearly state the sample type to which the data correspond. There is at least one table in the supplemental material that does not do this.

Specific comments

Introduction

p. 3 line 13.
GABA (γ-aminobutyric acid) was referred to as an indicator for the microbiological

decomposition of OM (Dauwe et al., 1999;Engel et al., 2018) and is probably used as a microbiological proxy in aerosol particles.

I am guessing you want to remove "probably", cite the studies that have used GABA in this capacity, and then perhaps make it a little more clear on how GABA was used.

p. 3 line 14.
free and combined amino acids are introduced but not defined. Perhaps don't specify "free" or "combined" until you want to also define them and just refer to "amino acids" (no free or combined) here.

p. 3 line 16.
There is a disconnect in this sentence at "...what Pommie..."

2.1.2

p. 5 line 4
"By heating the sampled air, the high relative humidity of the ambient air before collecting the aerosol particles was reduced to 75-80%."
Was reduced to 75-80% from what? Plunging tanks have RH about 85%. How high was the ambient RH?

p. 5 line 12
A minor note on: "the Berner impactors ran continuously, thus the impactor on the MV sampled aerosol particles also during cloud events. However, due to the pre-conditioning unit, the cloud droplets were efficiently removed before the aerosol particles were collected on the aluminium foils."
If functioning as intended, the pre-conditioning unit (dryer) would only remove water and any species more volatile than water, and should leave a dried aerosol. These samples could be analyzed and compared against the cloud water samples collected at the same time.

2.2 Analyses

Could you please more clearly define & describe the filtration steps involved in the FAA process? For example, the DOC/TDN seawater samples start with a 0.45 um syringe tip filtration. Was this also done for the subsamples analysed for FAA? For both seawater and aerosol samples?
I don't think FAA vs CAA is ever clearly defined in the manuscript. Does FAA strictly include singular, individual amino acids, not linked to other amino acids in a protein? If not, then what is the upper size range of proteins and proteinaceous particles that this method includes in the analysis of FAA?

3.2.1 Size-segregated aerosol particles at the CVAO

p. 11 line 28

"According to physical and chemical specifications such as the air mass origins, particulate MSA concentrations and MSA/sulfate ratios as well as particulate mass concentrations of dust tracers, aerosol particles predominantly of marine origin with low to medium dust influences were observed."

I think this work adds a lot of strength to the manuscript. But I also think the authors should spend just a few more sentences on this, stating what are the values of the different indicators that imply sea spray aerosol or desert dust. Without doing that, the authors seem to say "We have the data. Trust us on our interpretation." which I don't think is the best approach, especially with the study site being located in a part of the atmosphere that can contain high dust levels, being just offshore and downwind, at times, from the Sahara Desert (and at times downwind of other deserts and large dust sources). Plotting the data along with nominal desert dust levels and sea spray aerosol levels from the literature would be an improvement on tabulated data in the supplemental information.

p. 11 line 30
"It has to be noted 30 that dust generally influences the supermicron particles to a larger extent than the submicron particles (Fomba et al., 2013)."
Perhaps state why this has to be noted (I assume it comes up later on).

Free amino acids in size-segregated aerosol particles: Composition

p. 14 line 26.
"According to the conclusions by Barbaro et al. (2015), the relatively high content of hydrophilic FAA found here points at least at some influence of local oceanic sources."
If "Barbaro et al. (2015) reported that hydrophilic components were predominant (60 %) in locally produced marine Antarctic aerosol particles" and here hydrophilic FAA in submicron = 15% and supermicron = 0%, then I would clarify that only the periods of hydrophilic FAA much higher than the mean values would be deemed by Barbaro el al. (2015) as indicative of sea spray aerosol.

3.2.2 Size-segregated aerosol particles at the MV

p. 15
The following statements do not agree:
"The submicron aerosol particles at the MV had an averaged ΣFAA concentration of 1.5 ng m-3 (0.8-1.9 ng m-3) and were about three times lower compared to the ΣFAA concentration at the CVAO." (line 13)
"the aerosol particles measured at ground level represented the aerosol particles at cloud level" (line 18)
I am guessing that the implication being made here is that it is the same particle population sampled at CVAO and MV but that aerosol ageing or processing is happening between the two sites and causing the significant change in FAA concentration. This is a guess because it is not stated. What are the wind speeds and transport times between the two sites?

p. 15 line 18
"the aerosol particles measured at ground level represented the aerosol particles at cloud level, i.e. the aerosol particles within the marine boundary layer were well mixed."
There was no aerosol sampling at ground level, correct? CVAO sampling ocurred at 30 m and MV at 744 m, right?
The argument made in the methods section is vague but I think it is that 30 m (CVAO) and 744 m (MV) are in the same layer of the atmoshpere. Its not clear if this is within the internal boundary layer, or above it, within the marine boundary layer, or otherwise. Please clarify, including marine boundary layer vs. internal boundary layer.

p. 15 line 20
"The concentration and composition of the aerosol particles can therefore be affected by the clouds that formed and disappeared consistently during the sampling period of the aerosol particles at the Mt. Monte Verde"
I like that analytes detected in cloud water are reported as a concentration per volume of air, instead of per volume of cloud water (LWC), thus providing the aerosol content of the air mass, and being unaffected by varying levels of liquid water content.

p. 15 line ~25

I wonder if it would be better to not discuss cloud processing until after the data from the cloud water have been presented.

3.3 Cloud water samples

p. 16 line 3.
"The individual atmospheric concentration of FAA in cloud water was calculated based on the measured liquid water content (LWC)"
OK. Very good. [concentration in cloud water] x [cloud water volume] / [air volume sampled]

p. 17 line 13
"The reason for the high concentrations of FAA in cloud water (compared to the oceanic and aerosol particle concentrations) remain speculative to date and will be subject of further studies."
Probably the most significant finding of this study is not pursued.

p. 17 line 14
"Altogether, the in-situ formation of FAA in cloud water by chemical processes in the cloud or by atmospheric biogenic formation or enzymatic degradation of proteins, as proposed by Malfatti et al. (2019), as well as by selective enrichment processes and pH dependent chemical reactions might be potential sources."

I am very surprised by the term "in-stu formation of FAA in cloud water" here. Are you (suddenly) claiming that any or all of the amino acids detected in cloud water were created in the atmosphere? None of them existed in the particles when the particles were produced?
I fear a misundertanding of aerosol basics here, unless this is just a language issue. Sea spray aerosol contains subsamples of seawater constituents that are small enough to become aerosolized; this includes amino acids. Enzymes do not create amino acids; they consist of amino acids and aminopeptidase enzymes cleave (or catalyse the hydrolysis) amino acids from larger molecules. All cloud droplets form on aerosols, thus, from the time they are formed, cloud droplets contain more than just water. If the water from the cloud droplets evaporate, the cloud nuclei remain. Rain will remove the cloud nuclei and other particles below. Was there any rain in the area during or just prior to the sampling periods?
To consider atmospheric processing or ageing, I wanted to know the transport time between CVAO and MV. The downwind distance between them is about 2 km. Wind speed on average was about 5.5 m/s. So the average transport time would be about 6 minutes.

3.4.1. Hydrophilic amino acids

p. 18 line 15
"The hydrophilic amino acids (Asp, Glu, GABA) comprised a significant fraction in the ULW and the SML, as well as in the (submicron) aerosol particles and in cloud water (Fig. 4a-d). They were not detected in the supermicron aerosol particles."
This is relevant to a major theme in sea spray aerosol research: the organic fraction of SSA across SSA sizes. The research would be more valuable if this were discussed.

p. 18 line 22
"The abundance of GABA on the submicron aerosol particles suggests that (marine) microorganisms were present on the aerosol particles and likely produced GABA via microbiological decarboxylation of Glu."
So it is impossible for GABA to transfer from the ocean into the atmosphere in a nascent sea spray aerosol?
Which microorganisms would be small enough to be found in submicron aerosol? Small marine bacteria? These sizes are of the dried particles, so the particle sizes in the atmosphere were larger, and perhaps the aerosol population that were submicron after drying contained supermicron aerosols before drying and were big enough to contain marine bacteria.

p. 18 line 24
The connection to Malfatti et al. (2019) here is confusingly redundant.

p. 19 Figure 4
Thank you for plotting the data together in this figure. It appears the cloud water and seawater have similar profiles. Are there others?

3.4.2 Neutral and hydrophobic amino acids

p. 20
Some very low lifetimes are reported for amino acids in the atmosphere: ~0.5-1 hour. Relate this to the sampling period lengths and the duration of time between sampling and analyses. Did the samples/analytes need to be isolated from air/atmosphere between collection and analyses? Should we question the amino acid residence times? Or are they accurate and is it possible that the amino acids detected are largely from intact microorganisms collected in the aerosol?

3.4.4 Transfer of amino acids from the ocean into the atmosphere

p. 21 line 7
"The high similarity concerning the main FAA species within the different compartments, together with the high concentration of ocean-derived compounds (Na+, MSA) in the aerosol particles and cloud waters, suggest a coupling between the FAA in the ocean and the atmosphere."
I don't think this "high similarity" was established. The GABA in submicron CVAO is a high dissimilarity with SML and ULW.
It would be useful to have FAA profiles of dust (or other aerosol types) for comparison. If those profiles are very different, then perhaps the profiles presented in this work would appear more similar.

p. 23 line 8
"FAAs were present in the size range for aerosol particles associated with CCN activity and cloud water, and might be connected to CCN activity due to their hygroscopicity and soluble character, but this effect was not investigated here."
It is disappointing to read this. The authors found something very interesting: very high atmospheric concentrations of amino acids in cloud water, relative to the ambient aerosol population. But that finding is ignored.

Supplemental Information: acp-2019-976-supplement-version3.pdf

p. 16 Back Trajectory
It is great that you ran back trajectories for all your sampling periods. Having done so, please share them all. Why not share them all when they support the science?