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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement report: Amino acids in fine and coarse atmospheric aerosol: concentrations, compositions, sources and possible bacterial degradation state" *by* Ren-guo Zhu et al.

Ren-guo Zhu et al.

xiaohuayun@ecit.cn

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Dear Reviewer:

Thank you for your letter and comments concerning our manuscript acp-2020-534 entitled "Measurement report: Amino acids in fine and coarse atmospheric aerosol: concentrations, compositions, sources and possible bacterial degradation state". Those comments are all valuable and very helpful improving our paper. We accept your suggestions and revise the manuscript according to the points as follows. Particularly, we

have reduced the number of results section.

Abstract. In the abstract the use of acronyms is inappropriate as well as it is dissuaded to insert the references. Answer: Thank you for your suggestion. Since the samples analyzed in this paper were obtained in the same sampling campaign of Zhu et al. (2020), according to editor requirement, we referenced the Zhu et al. 2020 and clearly stated that the samples are the same in both papers but the data used in this manuscript were not analyzed in Zhu et al., (2020). Besides that, we try our best to reduce the use of acronyms in the abstract. Gly, Ser, Phe and Lys have changed to the full name in the abstract. But we still preserved some acronyms, including amino acids (AAs), hydrolyzed amino acid (HAA), δ15N values of total hydrolyzed amino acid (δ15NTHAA), degradation index (DI), and the variance within trophic AAs (). These acronyms occurred several times in the abstract (at least three times) and the full name of these acronyms are long. To reduce the length of the abstract and improve the readability of articles, we use acronyms as a last resort. But we defined these acronyms when they first appeared. We are very sorry about it.

Line 70. I think that you have to better introduce the degradation index to help the reader. I saw its explanation in section 2.3 but some details have to be introduced also in the introduction. Answer: Thank you for your suggestion. We have introduced the explanation of degradation index here.

The degradation index (DI) proposed by Dauwe et al. (1998, 1999) has been wildly used to assess the degradation state of organic materials (OM) in terrestrial, aquatic, and marine environment (Dauwe and Middelburg, 1998; Wang et al., 2018; Dauwe et al., 1999). This value is based on the molar percentage (Mol%) of the amino acid pool and higher DI values denote a more "fresh" state of protein matter.

Section 2.1. I think that you have to add some information about the type of filter used and the cleaning procedure of this filter. You have to add the reference but I think that you have to insert this information in the main manuscript. Answer: Thank you for your

suggestion. We have added more information about the type of filter used and the cleaning procedure of this filter.

Quartz fiber filters were used and filters were heated at 450âĎČ for 10 h to remove any organics before sampling.

Section 3.2.3. This part is too short to be one section and I suggest to add this sentence to another section. Answer: Thank you for your suggestion. This part is incorporated into the section "the composition profiles of HAA in fine and coarse particles (Section 3.2.2)". Besides that, the structure of the entire result section has been adjusted.

Line 295. I don't understand why you use PC1 as coefficient. This principal component clearly distinguishes the fine and the coarse particles. I think that this point should be clarified in the manuscript. Answer: Thank you for your suggestion. The point that PC1 clearly distinguishes the fine and the coarse particles was clarified in the manuscript. For calculation of DI values for fine and coarse particles, the first principal component score from principal component analysis (PCA) was applied to our own data (including Ala, Gly, Val, Leu, Ile, Pro, Ser, Thr, Phe, Asp, Glu, Lys, His and Tyr, except GABA), following the method described by Dauwe et al. (1999). Fine and coarse particles were clearly distinguished by first principal component scores, suggesting that the first principal component score may also be designed as a degradation index of THAA in aerosols.

Section 3.3.4. I think that you have to define the meaning of DI values, also considering previous published results. You have to define the threshold when bacterial degradation occurred. I don't like so much this fragmentation of the section. This is only my opinion, but I think that this fragmentation produces to lose the thread. You have the sections with 4-5 lines. Answer: Thank you for your suggestion. The threshold of DI values was defined in this manuscript and the DI values of fine and coarse particles were compared with the previous published results.

In marine environment, high DI values (>0.5) indicate the better preservation of more

fresh organic matter from marine primary production (Jiang et al., 2014). On the contrary, low DI values (<0.5) indicate the presence of relatively degraded organic matter (Burdige, 2007; Wang et al., 2018). In this study, the DI values of fine particles were close to those of "fresh" material. For instance, source materials (e.g., plankton, bacteria and sediment trap material) and the precipitation in Uljin. On the contrary, the DI values of coarse particles were comparable to those of surface soil, POM in coastal sediments and DOM in coastal area and precipitation in Seoul, which were proved to be more degraded materials (Fig. 8).

In the conclusion, you affirm that "The difference in 15N values of Source-AA and THAA between coarse particles and fine particles were small," but one of the main aim of the manuscript is the follows: "15N values of Gly and THAA in fine and coarse particle were compared with those in main emission sources to identify the potential sources of fine and coarse particles.". So is the conclusion that 15N values are not good tracers to define the sources?

Answer: Sorry for our unclear description. "The difference in δ15N values of Source-AA and THAA between coarse particles and fine particles." In this sentence, Source-AA is not the AAs released from potential emission sources. Here, Source-AA is defined as Gly, Val, Ser, Thr, Phe, Lys, His and Tyr, which is compared with Trophic-AA including Ala, Leu, Ile, Pro, Asp and Glu. This concept is proposed by McCarthy et al., 2007. They group individual AA based on the extensive metabolic diversity of microbes, coupled with their ability to salvage, resynthesize, or even alter synthetic pathways. The Trophic-AA group consists of aliphatic and acidic side chain AAs (Asp, Glu, Ala, Ile, Leu, and Val) as well as Pro, which has one N (excepting the associated forms Gln and Asn), which is obtained directly from Glu via transamination. The "scatting" δ15N pattern of Trophic AA with total heterotrophic resynthesis is presumed. In contrast, the δ15N pattern of Source-AA group remain relatively constant with total heterotrophic resynthesis includes Gly as well as most of the more chemically complex side chain AA (Ser, Thr, Phe, Tyr, and Lys). In this study, this "scattered" characteristic of δ15N-AA

distribution in Trophic-AA group of coarse particles was observed while the difference in δ15N values of Source-AA group between coarse particles and fine particles were small.

On the other hands, average δ15N value for hydrolyzed Gly from the biomass burning, soil, and plant sources was +15.6 $\pm$ 4.3‰ +3.0 $\pm$ 4.4‰ and $-$11.9$\pm$1.4‰ respectively, and the mean δ15NTHAA value was +15.8 $\pm$ 4.5‰ +5.5 $\pm$ 2.2‰ and $-$0.0 $\pm$ 1.8‰ respectively. δ15N value for HAAs from the biomass burning sources are significantly higher than those observed from natural sources (plant and soil sources). Therefore, δ15N value for hydrolyzed HAAs may be a good tracer to identify sources.

To avoid ambiguity, we specific the main emission sources in the aim." δ15N values of Gly and THAA in fine and coarse particle were compared with those in main emission sources (biomass burning, soil and plant sources) to identify the potential sources of fine and coarse particles"

Specific comments Lines 42-43. I suggest rephrasing this part because I think that English form is not correct. For example you repeated "compound". Answer: This sentence was rephrased. Recently, an increasing number of researchers highlight the importance of amino acids (AAs) in the atmosphere because AA is considered to be one of the most important organic nitrogen compounds in atmosphere (Zhang et al., 2002; Matos et al., 2016).

Line 43. I suggest to insert this reference because it summarized very well the state of knowledge in the 2016: "Matos, João TV, Regina MBO Duarte, and Armando C. Duarte. "Challenges in the identification and characterization of free amino acids and proteinaceous compounds in atmospheric aerosols: a critical review." TrAC Trends in Analytical Chemistry 75 (2016): 97-107." Answer: Thank you for your suggestion. This reference was added. "Recently, an increasing number of researchers highlight the importance of amino acids (AAs) in the atmosphere because AA is considered to be one of the most important organic nitrogen compounds in atmosphere (Zhang et al.,

2002; Matos et al., 2016)."

Line 45. Here a reference is needed. Answer: Thank you for your suggestion. The reference was added. "Recently, an increasing number of researchers highlight the importance of amino acids (AAs) in the atmosphere because AA is considered to be one of the most important organic nitrogen compounds in atmosphere (Zhang et al., 2002; Matos et al., 2016). Moreover, AAs are bioavailable and can be directly utilized by plant and soil communities (Wedyan and Preston, 2008; Song et al., 2017). Its key role in atmosphere-biosphere nutrient cycling and global nitrogen cycle has aroused greatly concern (Samy et al., 2013; Zhang and Anastasio, 2003). Besides that, AAs and proteins are important constituents of allergenic bioaerosol (Miguel et al., 2009; Huffman et al., 2013). The distribution of AAs and proteins in different particle sizes will determine whether these compounds can reach the pulmonary alveoli and the allergy of aerosols (Di Filippo et al., 2014)."

Line 50. I suggest you this paper where the particle size distribution of free amino acids is investigated until nano dimension: "Barbaro, et al. "Characterization of the water soluble fraction in ultrafine, fine, and coarse atmospheric aerosol." Science of The Total Environment 658 (2019): 1423-1439.". Answer: Thank you for your suggestion. This reference was added and this sentence "However, detail information on the concentrations and mole composition profiles of AA distributed in different size particle is still limited." was deleted. "And the distribution of AAs associated with different particle sizes can help to trace the sources and transformation of atmospheric aerosols (Barbaro et al., 2019; Feltracco et al., 2019; Di Filippo et al., 2014)."

Line 67-69. I think that you should also add the investigation of Kuznetsova et al. "Kuznetsova, M., Lee, C., Aller, J., 2005. Characterization of the proteinaceous matter in marine aerosols. Mar. Chem. 96, 359e377. https://doi.org/10.1016/j.marchem.2005.03.007 Answer: Thank you for your suggestion. This reference was added. Unfortunately, bacterial degradation of atmospheric AAs is limited. For example, two studies on marine aerosols by Wedyan and Preston

(2008) and Kuznetsova et al. (2005), and one study on precipitation by Yan et al. (2015).

Line 114. Have you verified the recovery of amino acids from the cationic cation exchange column? Figure S1. Please add (F) and (C) in the caption after fine and coarse. Change “blue” with “green” because I saw green the coarse particles Answer: Yes, we verified the recovery of amino acids from the cationic cation exchange column. It has been published in our previous study. “Zhu, R.-g., et al. (2020). "Nitrogen isotopic composition of free Gly in aerosols at a forest site." Atmospheric Environment 222: 117179.” See the table below. (F) and (C) in the caption after fine and coarse were added. “blue” was changed to“green”. Thank you.

Lines 186-187 and in other sections of manuscript. Please consider to significant figures. For example, “2542.9±1820.1 pmol m-3” should be 2542±1820 or the best way is 3±2 nmol m-3. I found the same mistake in the % values. Answer: Sorry for our mistake. Significant figures of the concentration of HAA and % values were corrected in this manuscript.

Lines 421. Please consider that the combined amino acids were investigated also in the Arctic region, considering also the particle size distribution. Feltracco, et al. "Free and combined L-and D-amino acids in Arctic aerosol." Chemosphere 220 (2019): 412- Answer: Thank you for your suggestion. This reference was added. “Feltracco et al. (2019) demonstrated that free and combined amino acids in Arctic aerosol were mainly distributed in fine fraction, which could be affect by several sources, including biological primary production and biomass burning.”

Lines 430-432. You have completely skipped the marine contribution. Several studies conducted by prof. Leck (Leck and Bigg, 2005a, 2005b; Bigg, 2007; Bigg and Leck, 2008) demonstrated the sea emission of PBAP. Combined amino acids is surely one of the main component of PBAP.

Answer: Sorry for our mistake. Indeed, as one of the main components of PBAP, AAs

are proved to be released by ocean (Leck and Bigg, 2005a, 2005b; Bigg, 2007; Bigg and Leck, 2008). Marine source may also contribute to atmospheric AAs for both fine and coarse particles observed here. However, the sampling sites are located in an inland city. Considering the 2-day back trajectory of during sampling periods (Fig. S5), we can observe that the aerosol collected flowed principally from the mainland and air mass from marine only accounted for 16%. Moreover, during the long transport, PABP may be removed by dry and wet deposition (Bespres et al., 2012). Therefore, in this study, compared to land origin, the contribution of marine source to aerosol AAs observed here may be relatively small. Unfortunately, we do not have δ15N-HAA data for marine aerosols. Pooled δ15NGly values from literature data, we found the δ15NGly values in ocean high molecular weight dissolved organic matter, cyanobacteria and plankton ranged from -16.6‰ to +7.7‰ (McCarthy et al.,2007; Mcclelland and Montoya,2002; Chikaraishi et al., 2009; McClelland et al. 2003; Calleja et al., 2013), which were close to range of the natural source including plant (range: -13.2‰ to -9.7‰ and soil (range: -1.6‰ to +7.4‰ sources. Conclusively, the contribution from soil and plant sources mentioned in this study may possibly including a small amount of marine contribution.

Technical correction Line 23. Please remove one point from (p<0.0.1). Line 80. Please change as “particle sizes” Line 90. Change “was” with “were” Line 105. Please introduce the acronym HAA. Answer: Sorry for our mistake. All these technical mistakes were changed in this manuscript and acronym HAA was defined.

Please also note the supplement to this comment:
https://acp.copernicus.org/preprints/acp-2020-534/acp-2020-534-AC1-supplement.pdf

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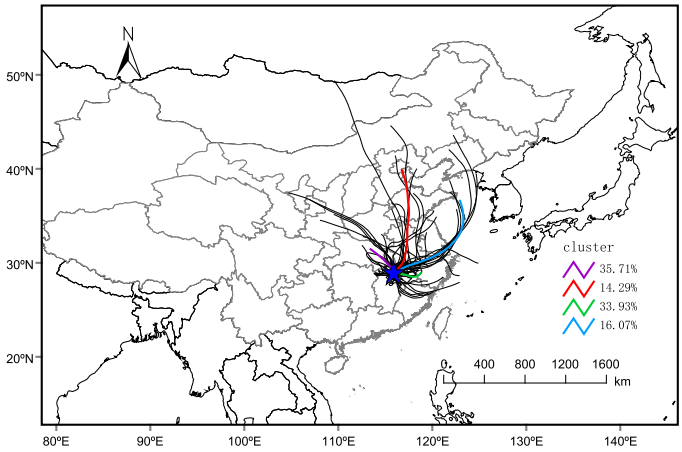

Fig. 1. 2-day (48 h) back trajectories illustrating the typical air mass flows to the sampling site