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 re-arranged the results and discussion section.

Anonymous Referee #1

General comments

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), $\delta^{15}N$ values of total hydrolyzed amino acid ($\delta^{15}N_{THAA}$), degradation index (DI), and the variance within trophic AAs ($\sum V$). 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. Line 72-76.

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. Line 100-101.

Quartz fiber filters were used and filters were heated at 450℃ 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 "Concentrations and mol% composition profile of HAA in size- segregated aerosol (Section 3.1)". Besides that, the structure of the entire result section has been adjusted. We have put the results and discussion part together as reviewer #2 suggested.

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. Line 325-327 and Line 334-336.

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. In revised manuscript, the meaning of values, threshold of DI values was defined and the DI values of fine and coarse particles were compared with the previous published results.

"Protein as major components in all source organisms are sensitive to all stages of degradation (Cowie and Hedges 1992). Moreover, compared to the alteration of the degradation, the dissimilarity in amino acid composition of protein in the source organisms are minor (Dauwe and Middelburg 1998). Therefore, the degradation index (DI) is developed, which are based on protein amino acid composition and factor coefficients based on the first axis of the PCA analysis (equation 1). Since AAs concentrated in cell walls are preferential accumulated during decomposition, whereas amino acids that are concentrated in cell plasma tend to be depleted during degradation (Dauwe et al., 1999), the compositional changes of amino acids associated with degradation can be traced by the DI value. The higher DI values indicate the protein is relatively "fresh" (Yan et al., 2015) and changes tracked by DI are proposed to be driven in large part by enrichment of AAs concentrated in cell wall (Mccarthy et al., 2007).

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). 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, which were proved to be more degraded materials (Fig. 8). 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 lower DI values observed in coarse particles, implying that AAs in coarse particles may undergo more degradation than fine particles. Our result is also comparable to that observed in precipitation at Uljin and Seoul (Yan et al., 2015). The DI values measured in coarse particles are closer to those observed in Seoul, where is believed to have more advanced bacterial degradation than Uljin, further supporting the degradation degree of amino acids in coarse particles is higher than that in fine particles.

Moreover, the section 3.3.4 in previous manuscript was re-arranged. All content concerning the meaning of DI and degradation state of AAs in size-segregated aerosol have been put into the section 3.4 "Different degradation state of AAs between fine and coarse aerosol particles".

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 $\delta^{15}N$ 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’’ $\delta^{15}N$ pattern of Trophic AA with heterotrophic resynthesis is presumed.

In contrast, the $\delta^{15}N$ 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 $\delta^{15}N$-AA distribution in Trophic-AA group of coarse particles was observed while the difference in $\delta^{15}N$ values of Source-AA group between coarse particles and fine particles were small. This indicate that AAs in coarse particles have stronger bacterial degradation state than those in fine particles.

On the other hands, average $\delta^{15}N$ value for hydrolyzed Gly from the biomass burning, soil, and plant sources was +15.6 ± 4.3‰, +3.0 ± 4.4‰, and −11.9±1.4‰, respectively, and the mean $\delta^{15}N_{THAA}$ value was +15.8 ± 4.5‰, +5.5 ± 2.2‰, and −0.0 ± 1.8‰, respectively. $\delta^{15}N$ value for HAAs from the biomass burning sources are significantly higher than those observed from natural sources (plant and soil sources). Therefore, $\delta^{15}N$ value for hydrolyzed HAAs may be a good tracer to identify sources.

To avoid ambiguity, we defined the main emission sources in the aim.” $\delta^{15}N$ 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” Line 88-90.

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 38-40.

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 38-40.

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 38-48.

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. It was changed to **“**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 46-48.

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 70-72.

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 in Figure S1. "blue" was changed to"green". Thank you.

Analytical characteristics for amino acid derivatives using GC–MS (full scan) method. Correlation coefficients obtained from linear regression analysis of calibration curves. Instrumental limit of detection (LOD) based on a signal-to-noise ratio of 3. Instrumental limit of quantification (LOQ) based on a signal-to-noise ratio of 10. EMDL was the corresponding effective limit in the aerosol samples.

Amino acids	**Retention time**	**FAA % recovery**	**CAA % recovery**	**Correlation coefficient (r^2)**	**LOD (pmol)**	**LOQ (pmol)**	**EMDL (pmol m-3)**
Alanine (Ala)	22.1	103±4	94±3	0.9928	0.1	0.3	0.1
Glycine (Gly)	22.8	**97±5**	**103±25**	0.9948	0.1	0.5	0.1
Valine (Val)	26.4	98±3	97±3	0.9936	0.1	0.3	0.1
Leucine (Leu)	27.8	96±1	95±6	0.9917	0.1	0.3	0.1
Isoleucine (Ile)	28.9	94±1	93±1	0.9930	0.1	0.3	0.1
γ-Aminobutyric acid (Gaba)	29.8	95±3	92±6	0.9955	0.2	0.7	0.2
Proline (Pro)	30.2	101±10	74±2	0.9975	0.7	2.3	0.7
Methionine (Met)	36.5	99±5	91±5	0.9946	0.1	0.3	0.1
Serine (Ser)	37.1	101±5	84±2	0.9883	0.1	0.4	0.1
Threonine (Thr)	37.8	83±11	91±5	0.9891	0.1	0.3	0.1
Phenylalanine (Phe)	39.0	82±1	84±2	0.9921	0.1	0.2	0.1
Aspartic acid (Asp)	40.0	96±2	86±18	0.9914	0.1	0.4	0.1
Glutamic acid (Glu)	41.7	96±1	112±20	0.9868	0.9	3.1	1.0
Asparagine (Asn)	42.1	89±5	NA	0.9978	1.7	5.8	1.8
Lysine (Lys)	43.2	93±7	67±5	0.9865	0.3	1.0	0.3
Glutamine (Gln)	43.8	95±7	NA	0.9959	0.8	2.8	0.9

Arginine (Arg)	44.8	86±9	60±6	0.9969	0.9	2.9	0.9
Histidine (His)	46.6	95±15	92±5	0.9944	2.8	9.2	2.9
Tyrosine (Tyr)	47.4	79±1	52±2	0.9954	0.3	0.8	0.3
Tryptophan (Trp)	48.4	80±4	NA	0.9917	14.4	48.0	15.0

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 revised 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." Line 23-241.

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. S2), 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 δ^{15}N-HAA data for marine aerosols. Pooled $\delta^{15}N_{Gly}$ values from literature data, we found the $\delta^{15}N_{Gly}$ 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. Line 275-289.

2-day (24 h) back trajectories was added in the supporting information (Fig. S2).

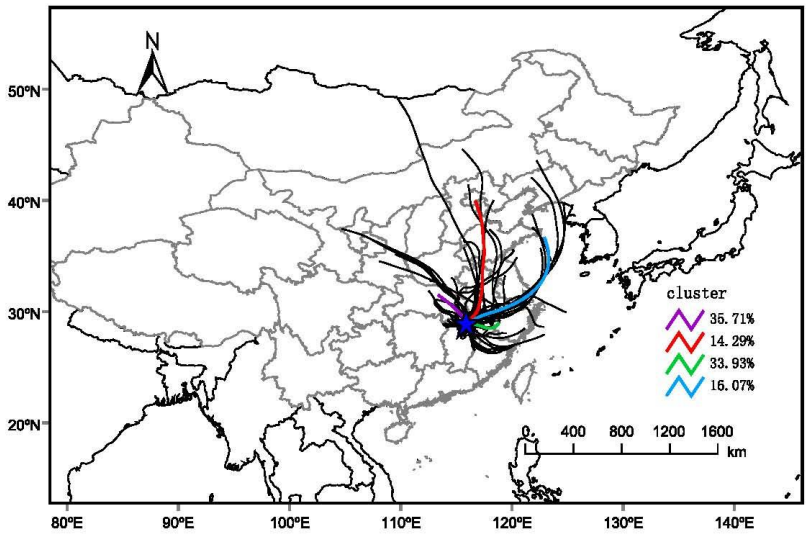


Figure S2. The 2-day (48 h) back trajectories illustrating the typical air mass flows to the sampling site (28.85°N, 115.91°E) during the sampling periods. The map comes from the MeteoInfoMap (version 1.4.9R2) software (Chinese Academy of Meteorological Sciences, China).

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.

Anonymous Referee #2

The title should be revised. Firstly, it is strange to mention "measurement report", isn't it? Is it really necessary? Secondly, "combined amino acids" should be clear. Otherwise, it may refer to free amino acids.

Answer: Thank you for your suggestion. According to the suggestion of the editor, the type of this article was changed to the measurement report rather than research article. Therefore, “measurement report” should be added in the title according to the submission requirements. Furthermore, “Hydrolyzed amino acids” was added in the title in order to differential “free amino acids”.

The application of isotopic ratios of stable nitrogen and degradation index would be very interesting for source investigation. In this work, the author may think about what they would really like to focus on and why they are important. The current manuscript contains data from observation and measurement but I feel it is a bit ambiguous on their conclusions. The Abstract could also be improved in order to present and show the main idea of this manuscript.

Answer: Thank you for your suggestion. The abstract was improved. In this work, we focus on the distribution, sources and possible bacterial degradation state of HAAs in size-segregated aerosol (>2.5μm and PM2.5). This work is important for uncovering the origin, transformation and fate of HAAs in the atmosphere. In revised abstract, we focus on the main idea of this manuscript and the significance of the work.

This size distribution of AAs can help understand its transformation and fate in the atmosphere. However, detailed information on this topic is limited to a few studies and very variable results for the size-segregated concentrations and mole composition of atmospheric combined AAs have been observed in previous studies. The factors controlling this large difference between fine and coarse particle are still unclear. Thus, verification of the different types, concentrations, origin and atmospheric processes of AAs distribution along the different air particle sizes is important and meaningful.

This study presents the first isotopic evidence that the sources of AAs for fine and coarse aerosol particles may be similar, all of which were influenced by biomass burning, soil, and plant sources.

It is still unknown that whether bacterial degradation play a role in the levels and compositions of AAs in different particle sizes. This is the first report of using degradation marker (DI) to investigate the degradation state of aerosol particles. Fine particles had significantly higher DI values than that of coarse particles (p<0.05), suggesting the degradation degree of amino acids in coarse particles is higher than that in fine particles.

Combining new compound-specific nitrogen isotope tool (δ^{15}N-HAA) and effective bacterial heterotrophy indicator ($\sum V$), this study firstly provide evidence that the stronger degradation state the found in coarse particles are coupled with more bacterial heterotrophic resynthesis occurred in coarse particles.

In conclusion, the difference in the THAA concentration and mol% composition distribution between fine and coarse particles may be closely related to the stronger bacterial degradation of AAs occurred in coarse particles than those in fine particles.

By the way, isotopic ratio is a nice and promising tool for understanding the sources of combined amino acids but please note that the influence of atmospheric processes may affect the fractionation.

Answer: Thank you for your suggestion. It is true that atmospheric processes may affect the fractionation. We focus on whether AAs in fine or coarse undergo more atmospheric processes. In order to assess the fractionation of the atmospheric processes (oxidation, nitration and oligomerization of AA), we compared $\delta^{15}N$ values of AA in both fine and coarse particles. If AA in fine or coarse particles undergo particularly more photochemical transformation than the other, nitrogen isotopic fractionation during atmospheric processes could lead to the difference in $\delta^{15}N$ values of AA between fine and coarse particles. We found the difference in $\delta^{15}N$ values of Source-AA (Gly, Ser, Phe and Lys) and total hydrolysable amino acids ($\delta^{15}N_{THAA}$) between coarse particles and fine particles was relatively small (Fig. 3 and Fig. 4c). The average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰ (Fig. 4a). These results appear to contrast with what one might expect for protein AA in either sizes particles undergo particularly more photochemical transformation than the other.

The authors should also explain more of the connection between DI and bacterial degradation (especially in Section 4.2). At least for me, I could not really understand why? If I understood it correctly, amino acids were hydrolyzed and might present the composition of proteins. How could DI be used to estimate the bacterial degradation? The variation of DI may present the degree of aging but how to relate it to bacterial degradation?

Answer: Thank you for your suggestion. The relationship between DI and bacterial degradation were not clearly stated. Amino acids have been used to estimate the relative degradation state of the organic matter. Proteins are ubiquitous components of all source organisms and degradation mixtures (Cowie and Hedges 1992). Although there is some dissimilarity in amino acid composition of the ultimate source organisms (e.g., diatoms, coccolithophorids, and bacteria) (Cowie and Hedges 1992), these differences are minor compared to the alteration of the spectra upon degradation (Dauwe and Middelburg 1998). 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. If only use DI as indicator, the variation of DI may only present the extent of the degradation. The mistake in our previous manuscript has been corrected. Section 3.4.

However, the negative correlation of the DI with the concentration of free γ-aminobutyric acid (GABA) and its mole percentage are depicted in Figure S7. Since bacteria are known to produce free GABA from their protein precursors (Cowie and Hedges 1994; Koolman and Roehme, 2005), the concentrations and mole percentage of free GABA may tend to increase during the biodegradation process. Therefore, negative relationship between the DI values and GABA in aerosol suggested that the degradation of atmospheric protein is probably induced by bacteria. Dauwe et al. (1999) have also reported that the negative correlation of the DI with the mole percentage of the GABA and β-alanine (BALA) in marine particulate matter samples and they attributed the correlation of the DI with the variation of GABA mole percentage to the stimulation of degradation by the activity of microorganism. Furthermore, the ‘‘scattered’’ characteristic of δ^{15}N-AA distribution in Tr-AA group of coarse particles and significant higher values of $\sum V$ were measured in coarse particles compared to fine particles ($p<0.05$). These further supporting the higher degradation degree of amino acids in coarse particles than that in fine particles are closely related to more bacterial heterotrophic resynthesis occurred in coarse particles.

The discussion in 4.1 leads to the conclusion that the sources of amino acids are somehow identical between fine and coarse particles. The question may come to the point of more degradation in coarse particle. If degradation is important for amino acids, some difference of composition profile or source contribution should be found between fine and coarse particles. The other possibility is that the support of _15N may not be sufficient in this case. PCA was used in this study. Why not putting more chemical species and organic tracers in the PCA analysis as many studies did? These amino acids were combined and should how could they contributed from different sources?

Answer: Sorry for our unclear description and thank you for your suggestion. Your assumption is right. In this work, the composition profiles of HAA in fine particles are quite different from those in coarse particles (Fig. 2). Both source contribution and the degradation process may cause the difference of composition profile of AAs. In this work, we measured the nitrogen isotopic compositions of hydrolyzed AAs released from main emission sources in the study areas, including biomass burning, soil and local plants (Fig. 3). The mean $\delta^{15}N_{THAA}$ value from the biomass burning, soil, and plant sources was +15.8 ± 4.5‰, +5.5 ± 2.2‰, and −0.0 ± 1.8‰, respectively. The differences between δ^{15}N value of Gly among biomass burning source and plant sources up to 15.8‰. If either particle is more affected by biomass burning sources, increased particle $\delta^{15}N_{THAA}$ value would be observed and larger offset of $\delta^{15}N_{THAA}$ between fine and coarse would be expected, vice versa. However, the average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5 ± 1.7‰ in each sampling site, demonstrating the sources of AAs for fine and coarse aerosol particles may be similar. It is therefore that degradation processes cause the difference of

composition profile of AAs between fine and coarse particles.

Our purpose of using the PCA analyses is explore the influence of degradation process on the percentage profile of AAs rather than tracing source of AAs. In order to calculate the degradation index (DI), PCA used in this study and 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).

$$\mathrm{DI} = \sum_i \left(\frac{Var_i - Avg_i}{SD_i}\right) \times PC1_i$$

Where $PC1_i$ is the loading of the amino acid *i* obtained from PC1. If we using more chemical species and organic tracers in the PCA analysis as many studies did, we cannot obtain this key parameter (PC1 loading of each amino acids).

Combined amino acids in aerosol also could come from different sources. There are some reports suggested primary biological aerosol particles, fugitive dust, biomass burning, and agricultural or human activities (Kang et al., 2012; Matos et al., 2016). Therefore, we investigated the main emission sources in the study areas, including biomass burning (straw burning), soil (road soil, paddy soil and forest soil) and local plants (needles of pine and leaves of camphor). Line 49-53.

The discussion on the release of coarse "fresh" bioparticles at the onset of rainfall seems arbitrary and could be clarified with the support of precipitation data (how longer and how strong the rain happened). As is known, rainfall may promote the release of bioaerosols but it also depends on the frequency and intensity. In most cases, it occurs mainly in a much shorter time scale. The rainfall then could suppress the concentrations of bioaerosols in the air. The sampling was daily based in this study and it may not be very well to observe this variation in my personal opinion.

Answer: Thank you for your suggestion. We are sorry for our arbitrary. The frequency and intensity of rainfall during the sampling day were added in the supplementary materials. By comparing the data of the daily precipitation amount and the temporal variations of the concentration and mol% composition of HAA for coarse particle. We found the higher concentration of THAA was occurred in April 30, May 5, May 6 and May 13 when daily precipitation amount was higher and duration of rainfall was longer. Simultaneously, the mol% composition of HAA on those days were significantly different from that observed on dry days. These imply that rainfall may promote the release of bioaerosols but it depends on the rainfall amounts and intensity as your suggested. The stronger and longer rainfall events may promote more "fresh" protein matters in coarse aerosol. The discussion and conclusion have been changed in the manuscript. Line 511-527.

Table S4. Daily precipitation amount(mm) and hourly rainfall(mm) of sampling day.

Date	Daily precipitation amount(mm)	Rainfall duration(hour)	Hourly rainfall(mm)
April 30	27.2	15	1.8
May 1	-	-	-
May 2	-	-	-
May 3	-	-	-
May 4	-	-	-
May 5	1	3	0.3
May 6	1	6	0.2
May 7	0.6	9	0.1
May 8	0.2	6	0.03
May 9	-	-	-
May 10	-	-	-
May 11	-	-	-
May 12	0.1	3	0.03
May 13	31.4	12	2.6

-represent no precipitation.

The part of Results contains many short sub-sections which is not very friendly for the readers. These sub-sections only repeat the Table and Figures, making it very hard to follow. Please re-arrange it. Why not put results and discussion together?

Answer: Thank you for your suggestion. We have rearranged the part of results and put the results and discussion together.

I would suggest the authors to select and keep some nice figures and move some to the supporting file. It may help to make the manuscript clear and concise.

Answer: Thank you for your suggestion. The figures have been streamlined and move some to the supporting file. The total number of figures in revised manuscript is 9.

Fig. 1 and Fig. 3: The information of fine/coarse particles is missing. I was confused by them and had to search which data belong to fine/coarse particles.

Answer: Sorry for our negligence. Fine and coarse particles were added to Fig. 1 and Fig. 3. Thank you.

Minor mistakes/errors: Seems quite many minor mistakes/errors throughout the text. Please check through. For example: L24: "p<0.0.1" should be "p<0.1" L47: "allergy" should be "allergenicity"? L141: "PCi" should be deleted? I suggest to introduce more information of DI. L146: Rstandard should be described here. L159: Please check the formula. It seems

wrong. L291: "Compared our calculating method with other works"? comparing the results or comparing the method?

Answer: Sorry for our mistake.

L24: "p<0.0.1" was changed to "p<0.01".

L47: "allergy" was changed to "allergenicity".

L141: "PCi" was deleted and more information of DI was added. Line 156-159.

L146: Rstandard should be described here.

Rstandard is atmospheric N_2. Moreover, a derivatized mixture of 20 amino acid standards (Ala, Gaba, Arg, Asn, Asp, Gln, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, and Val) and several international amino acid standards (Ala, Gly3, Gly4, Phe, USGS40, USGS41a, and Val) with known $\delta^{15}N$ values (−26.35 to +47.55‰) was prepared to assess the isotope measurement reproducibility and normalize the $\delta^{15}N$ values of the amino acids in the samples (Zhu et al., 2018). Line 165-173.

L159: Please check the formula.

Sorry for our mistake. The formula was changed.

$\delta^{15}N_{THAA} = \sum(\delta^{15}N_{HAA} \cdot \text{mol\%HAA})$

Where mol%HAA is the mole contribution of each HAA and $\delta^{15}N_{HAA}$ is the $\delta^{15}N$ value of individual HAA.

It seems wrong. L291: "Compared our calculating method with other works"? comparing the results or comparing the method?

It is wrong. It is comparing our results with other works. We have modified.

Anonymous Referee #3

Specific comments: 1. The title is misleading. Is the knowledge from this study applicable universally? Actually, it seems only reflect the scenario at the sampling sites, i.e. Nangchang, China. So the information of the study area should be added in the title.

Answer: Thank you for your suggestion. The information of the study area (Nanchang, China) has been added in the title. In this work, 5 sampling sites with different potential emission sources of atmospheric AAs were investigated in this study (See table below for details). The purpose of this work is using compound-specific $\delta^{15}N$ patterns of hydrolyzed amino acid (HAA), $\delta^{15}N$ values of total hydrolyzed amino acid (δ^{15}NTHAA), degradation index (DI), and the variance within trophic AAs (∑V) as markers to examine the sources and processing history of fine and coarse aerosol particles (>2.5μm and PM2.5). Our results demonstrated that the large difference in the concentration and mole percentage between fine and coarse particles might be closely related to the biologically relevant degradation processes. There is no particular situation in our sampling area (Nanchang, China). The results obtained in this work reflect a general law.

Table S1. The Characteristics and potential emission sources of atmospheric amino acids at 5 sampling area.

Sampling sites	Characteristics and potential emission sources of atmospheric amino acids at sampling area
Urban	an area with dense population and human activities, industrial emissions, biomass burning and road dust
Town	local people cook and heat using straw, charcoal and wood, an area is more influenced by biomass burning
Suburban	a convergence area between city and rural, influenced by mixture sources, including biomass burning, agricultural activities and natural sources
Agricultural area	open area, surrounded by paddy fields, affected by agricultural activities
Forest	more affected by natural source, including viruses, algae, fungi, bacteria, protozoa, spores and pollen, fragments of plants and insects

2. In the section 2.1 Sampling collection. What is the consideration to choose urban, town, town, suburban, airport and forest as reprehensive sites for the amino acids study? Especially, why airport was selected as one of the sampling sites? It seems agricultural site is more important than other areas for the amino acids.

Answer: Sorry for our unclear description. The concentration and composition of amino acids in the aerosols vary widely at different environment scenarios (Barbaro et al., 2011; Mace et al., 2003; Matsumoto et al., 2017; Mandalakis et al., 2011; Wang et al., 2019; Samy et al., 2011; Samy et al., 2013), and polar regions (Scalabrin et al., 2012; Barbaro et al., 2015).). This variability is highly dependent on the sources of AAs and meteorological conditions. Generally, atmospheric AAs is from primary biological aerosol particles (e.g., pollen, bacteria, fungi, spores, and fragments of living things), biomass burning, and agricultural activities (Kang et al., 2012; Matos et al., 2016). Therefore, the selection of sampling sites is based on the different emission sources of atmospheric amino acids in different characteristic areas of the city. As described in Table S1, from urban, town, suburban, airport and forest, the main emission sources of atmospheric AAs may change from the biomass burning sources to agricultural and natural sources. The airport is an open area, which is far away from the Nanchang city and surrounded by paddy fields. So, we suppose this sampling site is more affected by agricultural activities and natural sources. The airport is just a name of this sampling site, the real characteristic of this site was ignored. So, in revised manuscript, the name of the airport has been changed to agricultural area. This is also supported by the $\delta^{15}N_{Gly}$ and $\delta^{15}N_{THAA}$

signature. Compared with the town and urban areas, airport area (agricultural area) has relatively low $\delta^{15}N_{Gly}$ and $\delta^{15}N_{THAA}$ value in both fine and coarse particles ($P < 0.05$), which supporting that the atmospheric AA of fine and coarse particles in this site was more affected by agricultural and natural sources.

Thank you for your suggestion. The description of the characteristics and potential emission sources of atmospheric amino acids at 5 sampling area were added in supplement materials (Table S1).

3. Also Section 2.1, How many forest soil, paddy soil, road soil were collected and analyzed?

Answer: Sorry for our unclear description. For each type of soil samples, triplicate representative soil samples (approximately 100 g) were collected. Line 108-109.

4. In the Section 2.2, I did not find the description of the pretreatment and chemical analysis for soil samples. Current contents are only about the analysis of aerosol samples.

Answer: Sorry for our mistake. The description of the pretreatment and chemical analysis for soil and plant samples has been added in section 2.2. For plant and soil samples, approximately 30-40mg of plant or 500-600mg of soil powder were ground separately in liquid nitrogen into fine powders using a mortar and pestle. Then, well ground and homogenized soil and plant power were hydrolyzed in the same way as the aerosol samples. Line128-130.

5. In the results, Section 3.1.2, Line 191, It was found that the concentration level of THAA at airport is highest among the five different sites. But the reason was not appropriately explained later.

Answer: Sorry for our mistake. Indeed, the concentration level of THAA at airport is highest among the five different sites. The presence of amino acids in the atmosphere has been assessed in different environmental scenarios, e.g., urban (Barbaro et al., 2011; Wang et al., 2019), suburban (Samy et al., 2013), rural (Mace et al., 2003; Samy et al., 2011), marine (Mace et al., 2003; Matsumoto et al., 2017; Mandalakis et al., 2011), and polar regions (Scalabrin et al., 2012; Barbaro et al., 2015). The concentration of atmospheric amino acids in different environmental scenarios vary widely. This variability is highly dependent on the emission sources of AAs to the atmosphere and meteorological conditions. Since the distance between 5 sampling sites is less than 30 kilometers, it is therefore unlikely that meteorological conditions exert a major influence on the variability between sampling sites. So, the difference between the concentration level of THAA among the five different sites could be attributed to the emission sources of atmospheric AAs. The airport is an open area, which is far away from the city center and surrounded by paddy fields. Thus, it would be reasonable to deduce that in spring, enhanced agricultural activities and natural source emission (e.g., pollen grain) may lead to an increase in the concentration level of atmospheric AAs at the airport location. Line 222-225.

6. Line 198-204, here I understand that precipitation is an important factor to affect the amino acids in air, not only the concentration level, but also the composition pattern. However, actually there are many meteorological factors could change the amino acid in air. Why did you only consider the impact of precipitation? If you want to reveal the influence of precipitation on AA, actually the precipitation samples should also collected and analyzed simultaneously, along the aerosol sampling. The AA in precipitation samples could offer more information.

Answer: Thank you for your suggestion. We did not consider other meteorological conditions because except for precipitation, other meteorological conditions are not the main factors determining the concentration and percentage of amino acids in the atmosphere. The complexity of the results obtained for the potential influence of the meteorological conditions on the atmospheric levels of HAA at different environment scenarios (Mandalakis et al., 2011; Barbaro et al., 2015; Samy et al., 2013). With limited availability of such data, previous studies do not provide any definitive conclusion regarding the influence of other meteorological conditions on the atmospheric levels of HAA.

On the contrary, a tight relationship between atmospheric bioaerosols and precipitation has been found by previous studies (Huffman et al., 2013; Yue et al., 2016). Since amino acids predominantly exist as zwitterions (i.e., with protonated amine groups and deprotonated carboxylic acid groups) in aerosol, they will be found exclusively in condensed phases and their gas phase reactions do not need to be considered (Anastasio and McGregor, 2000). It is expected that the concentrations of individual AAs in aerosol are control by 2 mechanisms: the first one is the precipitation scavenging (Gorzelska and Galloway, 1990). This mechanism is supported by our recently work (Xu et al., 2020). We found that particulate AAs in precipitation are closely associated with aerosol particles and cloud condensation nuclei as a result of rainout and wash out effects (Xu et al., 2020). The second mechanism is that droplets splashing on the porous medium can deliver fresh biological aerosols in porous medium to the aerosol (Joung and Buie, 2015; Huffman et al., 2013; Yue et al., 2016). The first mechanism would certainly decrease the concentration of AAs in the aerosol, whereas the second mechanism may enhance the concentration of AAs. It is interesting to note that the average concentrations of THAA in coarse particles displayed no significant changes during rain events ($p>0.05$). For coarse particles, the average concentrations of THAA on rainy and dry days was 660.3±947.4 pmol m-3 and 212.2± 266.8 pmol m-3, respectively (Fig. 1 and Fig. S1). Owing to the high scavenging ratio of AAs in aerosol, the concentrations of individual AAs in aerosol were assumed to decrease during rainfall events. On the contrary, the concentrations of THAA in coarse particles displayed no significant changes during rain events, indicating particle emission mechanism (the second mechanism) were stronger than the precipitation scavenging mechanism (the first mechanism).

Moreover, the sources of AAs in coarse particles released by the particle emission mechanism are derived from porous medium rather than rainfall. These sources are primarily biological origin, including bacteria or fungal spores released from surrounding vegetation surfaces through mechanical agitation, spores ejected by fungi, lichens and other cryptogamic covers growing on soil, rock and vegetation (Elbert et al., 2007, 2012; Huffman et al., 2013). The principle of particle emission mechanism is mechanical agitation on porous medium and not closely related to the chemical composition of rainfall. Section 3.6.

7. Line 208, here you mentioned the results of pine and straw in Figure2. Which kind of straw? Actually I did not find the relevant information in the sample collection section.

Answer: Sorry for our mistake. The information of the pine and camphor have been added in the section 2.1. Masson pine (*Pinus massoniana* (Lamb.)) and camphor (*Cinnamomum Camphora*) tree as a common vegetation in the study area (115.8°E, 28.8°N) were collected during May 2019. Approximately 4-6 g of pine needles or camphor leaves were collected from the outer branches in the east, south, north, and west directions (about 10 m above the ground). We collected 5-6 representative samples for each kind of leaves.

All fresh samples were placed in plastic bags, labeled and stored in a chilled box immediately. In the laboratory, all plant and soil samples were freeze-dried. Then, freeze-dried samples were stored at -80℃ until further use. Line 106-116.

8. For the PCA analysis, there are different influencing factors (sources and degradation process) for AA in the five sites. Is it appropriate to include the all data from different sites to conduct the PCA analysis? If the sample amount is enough, it seems more reasonable to just use the data for specific site, respectively, the reveal the difference between fine and coarse particles.

Answer: Thank you for your suggestion. Proteins as major components in all source organisms are sensitive to all stages of degradation (Cowie and Hedges 1992). Moreover, Dauwe and Middelburg (1998) proved that the dissimilarity in amino acid composition of protein in the source organisms are minor, compared to the alteration of the degradation. It is therefore that the dissimilarity in the composition of protein between fine and coarse particles is caused by the degradation processes of protein rather than emission sources. So, in order to compare the changes of AAs percentage caused by degradation processes between fine and coarse particles, we use the all data to perform PCA analysis.

In this study, although the emission sources of atmospheric HAA were different among 5 sampling sites, the differences in DI values were not significant among 5 sampling sites for both fine and coarse particles ($p>0.05$) (Fig. S6). For fine particles, the average DI values in airport, urban, forest, town and suburban location was 0.6±0.4, 0.5±0.5, 0.7±0.3, 0.6±0.3 and 0.7±0.2, respectively. For

coarse particles, the mean DI values in airport, urban, forest, town and suburban location was -0.5±0.9, -1.0±1.1, -0.8±1.1, -0.3±1.1 and -0.5±1.1, respectively. This result suggested that the degradation process of amino acids in the atmosphere is less affected by their emission sources. We are sorry for the lack of introduction to the DI concept in the previous manuscript.

9. Line416-420, those sentences seem should be moved to Introduction part.

Answer: Thank you for your suggestion. These sentences have been moved to the introduction part. Line 49-53. Furthermore, the part of the result and discussion sections were re-arranged.

10. Generally, in the results and discussion, more description on the novelty of this study is needed. What are the new findings from this study compared to what already known, and what the significance and implication of the new findings for others?

Answer: Thank you for your suggestion. In revised manuscript, we put results and discussion together. Moreover, more description on the novelty and implication of this study have been added in conclusion. Line 550-554.

This size distribution of AAs can help understand its transformation and fate in the atmosphere. However, detailed information on this topic is limited to a few studies and very variable results for the size-segregated concentrations and mole composition of atmospheric combined AAs have been observed in previous studies (Filippo et al. 2014; Scalabrin et al., 2012; Matsumoto and Uematsu, 2005; Barbaro et al., 2015). The factors controlling this large difference between fine and coarse particle are still unclear. Thus, verification of the different types, concentrations, origin and atmospheric processes of AAs distribution along the different air particle sizes is important and meaningful.

This study presents the first isotopic evidence that the sources of AAs for fine and coarse aerosol particles may be similar, all of which were influenced by biomass burning, soil, and plant sources. It is therefore that the huge difference in the concentrations and mol% compositions of THAAs between fine and coarse particles observed in this study is closely relevant to the degradation processes of AAs in aerosols.

Although the oxidation, nitrification and oligomerization processes of protein substances in the atmosphere have been widely reported in previous studies (Liu et al., 2017; Wang et al., 2019; Song et al., 2017; Haan et al., 2009), but these abiotic photochemical aging processes that occur between fine particles and coarse particles have not been compared. In this study, the difference in $\delta^{15}N$ values of Source-AA (Gly, Ser, Phe and Lys) and total hydrolysable amino acids ($\delta^{15}N_{THAA}$) between coarse particles and fine particles was relatively small (Fig. 10). The average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰ (Fig. 11a). These results appear to contrast with what one might expect for AAs in either sizes particles undergo particularly more photochemical transformation than the other.

On the contrary, the degradation of atmospheric AAs in aerosols is rarely investigated, except for one study on marine aerosols by Wedyan and Preston (2008). It is still unknown that whether bacterial degradation play a role in the levels and compositions of AAs in different particle sizes. This is the first report of using degradation marker (DI) to investigate the degradation state of aerosol particles. Both composition profiles of HAA and concentrations of THAAs in aerosols are showed to be closely related to DI. And fine particles had significantly higher DI values than that of coarse particles (p<0.05) (Fig. 7a), suggesting the degradation degree of amino acids in coarse particles is higher than that in fine particles.

Combining new compound-specific nitrogen isotope tool (δ^{15}N-HAA) and effective bacterial heterotrophy indicator ($\sum V$) , "scattered" characteristic of δ^{15}N distribution in Tr-AA and higher $\sum V$ values were observed in coarse particles in this study, which firstly provide evidence that the stronger degradation state the found in coarse particles are coupled with more bacterial heterotrophic resynthesis occurred in coarse particles. In conclusion, the difference in the THAA concentration and mol% composition distribution between fine and coarse particles may be related to AAs in coarse particles have stronger bacterial degradation state than those in fine particles.

Moreover, DI values in coarse aerosol particles were significant increased ($p<0.05$) but the $\sum V$ value was significantly decreased ($p < 0.05$) during rain events, suggesting more fresh AAs in coarse particles were released by droplets and it highly depends on the amounts and intensity of the rainfall.

This study firstly suggests the potentially significant role of bacterial degradation processes in concentration and composition of protein distribution in size-segregated aerosol particles. Since the degradation state of airborne protein distribution along size-segregated particles is closely linked to its biological availability, ecological processes and plant nutrition after deposition, further studies of quantitative assessment of this biological related process in aerosols should be conducted.

All changes can be tracked in the revised manuscript. Thank you very much again.

Yours sincerely,

Ren-guo Zhu, Hua-Yun Xiao, Li Luo, Hongwei Xiao, Zequn Wen, Yuwen Zhu, Xiaozheng Fang, Yuanyuan Pan, Zhenping Chen

Measurement report: Hydrolyzed Amino acids in fine and coarse atmospheric aerosol in Nanchang, China: concentrations, compositions, sources and possible bacterial degradation state

Ren-guo Zhu[1], Hua-Yun Xiao[2,~~1~~*], Li Luo[1], Hongwei Xiao[1], Zequn Wen[3], Yuwen Zhu[1,4], Xiaozheng Fang[1], Yuanyuan Pan[1], Zhenping Chen[1]

[1]Jiangxi Province Key Laboratory of the Causes and Control of Atmospheric Pollution, East China University of Technology, Nanchang 330013, China.

[2]School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[3]Department of Earth Sciences, Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650021, China

[4]School of Earth Sciences, East China University of Technology, Nanchang 330013, China;

Corresponding author: Hua-Yun Xiao (xiaohuayun@ecut.edu.cn)

Abstracts. ~~The size distribution of amino~~ Amino acids (AAs) are relevant for nitrogen cycles, climate change and public health. Their size distribution may help to uncover the source, transformation and fate of protein in the atmosphere~~. in atmospheric particles determines the atmospheric allergenicity, which may have deleterious effects on human health.~~ This paper explores the use of compound-specific $\delta^{15}N$ patterns of hydrolyzed amino acid (HAA), $\delta^{15}N$ values of total hydrolyzed amino acid ($\delta^{15}N_{THAA}$), degradation index (DI), and the variance within trophic AAs ($\sum V$) as markers to examine the sources and processing history of different sizes particle in the atmosphere. 2-weeks of daily aerosol samples from five sampling sites in the Nanchang area (Jiangxi Province, China) and samples of main emission sources of AAs in aerosols (biomass burning, soil and plants) were collected (Zhu et al., 2020). Here, we measured the concentrations and $\delta^{15}N$ values of each HAA~~HAA~~ in two size segregated aerosol particles (>2.5μm and PM2.5). Our results showed that the average concentrations of THAA in fine particles was nearly 6 times higher than that in coarse particles ($p<0.0$~~.~~1) and composition profiles of fine and coarse particles were quite different from each other. The $\delta^{15}N$ values of hydrolyzed glycine ~~(Gly) in both fine (−1.0‰ to +20.3‰) and coarse particles (−0.8‰ to +15.7‰) exhibited wide ranges, but both fall within the ranges of Gly from biomass burning, soil and plant sources. Similarly, $\delta^{15}N$ values of~~ and THAA in both fine ~~(+0.7‰ to +13.3‰)~~ and coarse particles ~~(−2.3‰ to +10.0‰)~~ were typically in the range of ~~THAA~~ those from ~~these three emission~~ biomass burning, soil and plant sources. Moreover, the average difference in the $\delta^{15}N_{THAA}$ value between fine and coarse particles was smaller than 1.5‰. These results suggested that the sources of atmospheric HAAs for fine and coarse particles might be similar~~, which are dominated by AAs from biomass burning, soil, and plant sources~~. Meanwhile, compared to fine particles, significantly lower DI values ($p<0.05$), "scattered" $\delta^{15}N$ distribution in Trophic-AA and higher $\sum V$ values ($p<0.05$) were observed in coarse particles. But the difference in $\delta^{15}N$ values of Source-AA (glycine~~Gly~~, ~~Ser~~serine, ~~Phe~~ phenylalanine and ~~Lys~~lysine) and THAA ~~($\delta^{15}N_{THAA}$)~~ between coarse particles

and fine particles was relatively small. It is likely that AAs in coarse particles have advanced bacterial degradation state compared to fine particles. Besides that, the significant increase in DI values and a decrease in $\sum V$ values for coarse particles were observed during ~~at the onset of~~ the rainfall events (p<0.05). This implies that "fresh" AAs in coarse particles were mainly released ~~at the onset of the~~following the precipitation ~~and decayed swiftly~~.

1 Introduction

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 ~~compound classes of~~ organic nitrogen compounds in atmosphere (~~Samy et al., 2013;Wedyan and Preston, 2008;Song et al., 2017;~~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 allergenicity ~~allergy~~ of aerosols (Di Filippo et al., 2014). 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). ~~However, detail information on the concentrations and mole composition profiles of AA distributed in different size particle is still limited.~~ The sources of atmospheric proteinaceous matter are very complex. Primary biological aerosol particles (e.g, plants, soil, pollen, bacteria, fungi, spores and deris of living things), biomass burning, and agricultural activities are generally suggested to be the main contributing sources of atmospheric AAs (Matos et al., 2016;Mace et al., 2003). It is still unclear whether AAs fine and coarse particles influenced by different sources.

Compound-specific nitrogen isotope analysis of individual amino acids provide an opportunity to offer the key information on widely varied photochemical processes and origins of proteinaceous matter in the atmosphere. Nitrogen sources information and any possible nitrogen isotopic fractionation caused by transformation processes could be hold by the δ^{15}N-AA pattern (Mccarthy et al., 2007;Bol et al., 2002). At the same time, the δ^{15}N value of total hydrolysable AA ($\delta^{15}N_{Avg\text{-}THAA}$), calculated as the average molar-weighted δ^{15}N value of individual AA, has been used as a proxy for total protein δ^{15}N value (Mccarthy et al., 2013). However, to our knowledge, no study has used the δ^{15}N-AA pattern and $\delta^{15}N_{Avg\text{-}THAA}$ values to identify the sources of AAs distributed in different particle sizes.

It is generally accepted that AAs in aerosols are mainly controlled by abiotic photochemical aging processes. On the contrary, the biological degradation of AAs in aerosols are neglected. This can be attributed to two factors. First, the sources and transformation pathways of protein matter and AAs in aerosols are highly complex (Wang et al., 2019;Zhu et al., 2020). Second, and the residence time of protein matter in aerosols is relatively short (Papastefanou, 2006). Admittedly, bacteria and fungi are

ubiquitous and can be observed in all PM samples where people look for them, and this has been done routinely for many decades (Bauer et al., 2002; Bowers et al., 2013; Huffman et al., 2013; Wei et al., 2016; Wei et al., 2019). *In-situ* bacterial degradation processes occurred in the aerosols and the cloud water was also observed (Amato et al., 2007; Husárová et al., 2011).Unfortunately, bacterial degradation of atmospheric AAs is ~~limited~~~~rarely investigated.~~, ~~except for~~ For example, two~~one study~~ studies on marine aerosols by Wedyan and Preston (2008) ~~and~~ and Kuznetsova et al. (2005), and one study on precipitation by Yan et al. (2015). ~~It is still unknown that whether bacterial degradation play a role in the levels and compositions of AAs in different particle sizes.~~ 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. ~~It is still unknown that~~ However, DI values of AAs in aerosol particles and whether bacterial degradation plays a role in the levels and compositions of AAs in different particle sizes are still unknown.

~~In terrestrial, aquatic, and marine environment~~, ~~the degradation state of organic materials (OM)~~ is ~~frequently characterized by DI based on the molar composition of amino acids (Dauwe and Middelburg, 1998;Wang et al., 2018;Dauwe et al., 1999). The higher DI values denote more "fresh" state of protein matter.~~ ~~Besides, a~~A consensus has recently been reached on selective use of the ^{15}N depleted or enriched trophic AAs during bacterial heterotrophy processes can lead to large nitrogen isotopic fractionation in trophic AAs (McCarthy et al., 2004). Thus, substantial $\delta^{15}N$ pattern shifts of trophic AAs can index bacterial heterotrophy processes. $\sum V$, defined as the average deviation in the $\delta^{15}N$ values of the Tr-AA, has therefore been established to track the degree of bacterial degradation of AAs in marine and terrestrial environment (Mccarthy et al., 2007;Philben et al., 2018;Yamaguchi et al., 2017).

In the present work, we sought to improve our understanding of AAs distributed in different ~~sizes~~ particle sizes. We measured the concentrations and $\delta^{15}N$ values of each hydrolyzed amino acid in two size segregated aerosol particles (>2.5 μm and PM2.5) ~~and main emission sources of AAs~~ in aerosols collected in the Nanchang area (southeastern China). Furthermore, $\delta^{15}N$ 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. In addition, the DI, $\sum V$ values and $\delta^{15}N$ values pattern of hydrolyzed AA in fine and coarse particles were analyzed to explore the possible bacterial degradation of HAAs in fine and coarse particles.

2 Experimental section

2.1 Sample collection

Aerosol samples were ~~was~~ collected at 5 locations included urban, town, suburban, ~~airport~~agricultural area and forest in Nanchang area (South China) from April 30, 2019 to May 13, 2019, using a high-volume air sampler (KC-1000, Qingdao Laoshan Electronic Instrument company, China) at a flow rate of 1.05 ± 0.03 m^3 min^{-1}. The Characteristics of 5 sampling area were defined in Table S1. The sampler

allows to separate particles of different aerodynamic diameters in two stages with diameter (D) above 2.5 μm (coarse particles) and D≤2.5 μm (fine particles). Quartz fiber filters were used and filters were heated at 450℃ for 10 h to remove any organics before sampling. Aerosol sampling was conducted at the rooftop of the building in each site, about 10 meters above the ground except for the ~~airport~~agricultural area where the sampler was placed in a clear spot about 1000 meters away from the runway. The sampling time for each sample was from 5 p.m. to 4:30 p.m. of next day. More details on the sample collection are provided in Zhu et al. (2020).

Forest soil samples were collected at the top 10-cm of the evergreen broad-leaved forest soil in Nanchang area (115.8°E, 28.8°N). Paddy soil samples were collected from the topmost 10-cm layer of rice cultivation soil (115.1°E, 28.2°N). Road soil was collected from highway topsoil (115.8°E, 28.7°N). For each type of soil samples, triplicate representative soil samples (approximately 100 g) were collected. Masson pine (*Pinus massoniana* (Lamb.)) and camphor (*Cinnamomum Camphora*) tree as a common vegetation in the study area (115.8°E, 28.8°N) were collected during May 2019. Approximately 4-6 g of pine needles or camphor leaves were collected from the outer branches in the east, south, north, and west directions (about 10 m above the ground). We collected 5-6 representative samples for each kind of leaves. All fresh samples were placed in plastic bags, labeled and stored in a chilled box immediately. In the laboratory, all plant and soil samples were freeze-dried. Then, freeze-dried samples were stored at -80℃ until further use.

Aerosols from straw burning were sampled by pumping into a high-volume air sampler (KC-1000, Qingdao Laoshan Electronic Instrument Company, China) from the funnel on the combustion furnace during July 2017. The combustion furnace is a domestic furnace widely used by local residents.

2.2 Analyses of the concentration and $\delta^{15}N$ value of individual hydrolyzed amino acid (HAA)

For hydrolyzed AA analysis, samples were prepared using a modified version of Wang et al. (2019) and Ren et al. (2018). One-sixteenth of each fine aerosol filter (~80 m^3 of air) or Two-seventh of each coarse aerosol filter (~366 m^3 of air) was broken into small pieces and placed in a glass hydrolysis tube. Prior to the hydrolysis, 25 μL of ascorbic acid at a concentration of 20 μg μL^{-1} (500 μg absolute) was added to each filter sample. Then, 10mL and 6M Hydrochloric acid (HCl) was used to convert all of the combined AAs to free AAs. To avoid oxidation of AAs, the hydrolysis tube was flushed with nitrogen and tightly sealed before hydrolysis. The mixture was later placed in an oven at 110 °C for 24 h.

For plant and soil samples, approximately 30-40mg of plant or 500-600mg of soil were ground separately in liquid nitrogen into fine powders using a mortar and pestle. Then, well ground and homogenized soil and plant power were hydrolyzed in the same way as the aerosol samples.

After cooling to room temperature, the hydrolyzed solution was dried with a stream of nitrogen and HCl was removed. The dried solution was then redissolved in 0.1 M HCl and purified by a cation exchange column (Dowex 50W X $8H^+$, 200-400 mesh; Sigma-Aldrich, St Louis, MO, USA). Later, tert-Butyldimethylsilyl (tBDMS) derivatives of HAAs were prepared following the method described by our previous study Zhu et al. (2018).

The concentrations of HAAs were analyzed using a gas chromatograph-mass spectrometer (GC-MS).

The GC-MS instrument was composed of a Thermo Trace GC (Thermo Scientific, Bremen, Germany) connected into a Thermo ISQ QD single quadrupole MS. The single quadrupole MS was operated in electron impact ionization (70 eV electron energy) and full scan mode. The temperatures of the transfer line and ion source were 250°C and 200°C, respectively. More details on quality assurance and control (recoveries, linearity, detection limits, quantitation limits, and corresponding effective limits in the aerosol samples of AAs), are provided in Zhu et al. (2020)

$\delta^{15}N$ values of AA-tert-butyl dimethylsilyl (tBDMS) derivatives were analyzed using a Thermo Trace GC (Thermo Scientific, Bremen, Germany) and a conflo IV interface (Thermo Scientific, Bremen, Germany) interfaced with a Thermo Delta V IRMS (Thermo Scientific, Bremen, Germany). The analytical precision (SD, n=3) of $\delta^{15}N$ was better than ±1.4‰. Moreover, AABA with known $\delta^{15}N$ value (-8.17‰±0.03‰) was added in each sample to check the accuracy of the isotope measurements. The analytical run was accepted when the differences of $\delta^{15}N$ values of AABA between GC- IRMS and EA-IRMS values were at most ±1.5‰. Each reported value is a mean of at least three $\delta^{15}N$ determinations. For more details of the analyses of HAA $\delta^{15}N$ values refer to our previous publication (Zhu et al., 2018). The concentrations and $\delta^{15}N$ value of Cys, Trp, Asn and Gln in HAAs could not be determined using this method because, under strong acidic condition, Cys and Trp is destroyed, and Asn and Gln are converted to Asp and Glu, respectively. The concentration and $\delta^{15}N$ value of hydrolysable Asp represents the sum of Asp and Asn; the concentration and $\delta^{15}N$ value of hydrolysable Glu represents the sum of Glu and Gln.

2.3 DI index

Degradation process could significantly modify the mole composition of protein amino acids (Dauwe et al., 1999). Accordingly, a quantitative degradation index (DI) has been developed based on the mole composition of hydrolyzed amino acids pool. The degradation index (DI) was calculated using the formula Eq. (1) originally proposed by Dauwe et al. (1999):

$$\mathrm{DI} = \sum_i \left(\frac{Var_i - Avg_i}{SD_i}\right) \times PC1_i \quad (1)$$

where DI is the degradation index, Var is the mole% of the each individual HAA, Avgi, and SDi ~~and PCi~~ are the average mole% and standard deviation of each HAA in our data set, respectively, and PC1 is the loading of the amino acid *i* obtained from principal component analysis (~~Table S1~~Table S2).

2.4 $\delta^{15}N$ values

The natural abundance of ^{15}N was calculated as $\delta^{15}N$ values in per mil (‰), using atmospheric N_2 as the international standard:~~:~~

$$\delta^{15}N(‰ \text{ vs air}) = \left(\frac{R_{sample}}{R_{standard}-1}\right) \times 1000 \quad (2)$$

where R is the ratio of mass 29/mass 28.

A derivatized mixture of 20 amino acid standards (Ala, Gaba, Arg, Asn, Asp, Gln, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, and Val) and several international amino acid standards (Ala, Gly3, Gly4, Phe, USGS40, USGS41a, and Val) with known $\delta^{15}N$ values (−26.35 to +47.55‰) was prepared to assess the isotope measurement reproducibility and normalize the $\delta^{15}N$ values of the amino acids in the

samples (Zhu et al., 2018).

2.5 $\sum V$ parameter

The $\sum V$ parameter is defined as the average absolute deviation in the $\delta^{15}N$ values of the Trophic AA (including: Ala, Asp, Glu, Ile, Leu, and Pro) (Mccarthy et al., 2007). This parameter has been used as a proxy for the degree of heterotrophic resynthesis and calculated by Eq. (3):

$$\sum V = \frac{1}{n} \times \sum Abs(\chi_{AA}) \quad (3)$$

where χ_{AA} is defined as the deviation of the $\delta^{15}N$ of each trophic amino acid from the $\delta^{15}N$ of the mean of trophic amino acids ($\delta^{15}N$ AA- average $\delta^{15}N$ of Ala, Asp, Glu, Ile, Leu, and Pro), and n is the total number of trophic amino acids used in the calculation.

2.6 $\delta^{15}N_{THAA}$ values

The $\delta^{15}N$ values of total hydrolysable amino acids ($\delta^{15}N_{THAA}$) is calculated as the mole percent weighted sum of the $\delta^{15}N$ values of each individual HAA, following Eq. (4):

$$\delta^{15}N_{THAA} = \sum(\delta^{15}N_{HAA} \cdot \text{mol\%HAA}) \quad (4)$$

Where mol%HAA is the mole contribution of each HAA and $\delta^{15}N_{THAA}$ is the $\delta^{15}N$ value of individual HAA.

2.7 Statistics

All statistical analyses were performed using SPSS 16.0 (SPSS Science, USA). Graphs were generated using OriginPro 2018 (OriginLab Corporation, USA) and Sigmaplot 12.5 software (SPSS Science, USA). We performed a Two-way ANOVA for the concentration of THAA, the DI index, $\delta^{15}N_{THAA}$ values and $\sum V$ values, testing the effect of aerosol sizes, location, and their interaction. Tukey's Honestly Significant Differences (Tukey-HSD) test was used to evaluate which combinations of location and aerosol size were significantly different. Two-way ANOVA was also conducted for DI values, examining the effect of aerosol sizes, coefficients (obtained by using first principal component score or previous reported coefficients) and their interaction. The differences in $\delta^{15}N_{Gly}$ values for fine particles between 5 sampling locations were examined using the one-way analysis of variance (ANOVA) procedure, and compared using the Tukey-HSD test.

The exponential regression was analyzed to evaluate changes in DI index as a function of the concentration of THAA.

To test for changes in the concentration of THAA, DI index and $\sum V$ values following the rain events, a two-way ANOVA was performed, testing for effects of precipitation, aerosol sizes and their interactions. Tukey-HSD test was conducted to compare the significant difference. Changes in mol% of each HAAs concentrations following precipitation were tested for significance by using ANOVA procedure followed by a Tukey-HSD test to compare significant differences. For all tests, statistically significant differences were considered at $p<0.05$.

3 Results and discussion

3.1 Concentrations and mol% composition profile of HAA in size- segregated aerosol~~of THAA~~

~~3.1.1 Difference in the concentrations of THAA for fine and coarse particles~~

Fourteen hydrolyzed amino acids (Ala, Val, Leu, Ile, Pro, Gly, Ser, Thr, Phe, Asp, Glu, Lys, His and Tyr) were found in fine and coarse aerosol samples collected in Nanchang areas during spring 2019 (Fig. 1). The average concentrations of THAA in fine and coarse particles were 2542~~.9~~±1820~~.1~~ pmol m^{-3} and 434~~.0~~±722~~.6~~ pmol m^{-3}, respectively. The mean concentration of THAA for fine particles was nearly 6 times higher than that for coarse particles ($p<0.01$) (Fig. S1).

~~3.1.2 Concentrations of THAA at different locations~~

For fine particles, the average concentration of THAA in 5 sampling sites were significantly different ($p<0.05$), with the highest mean concentration of THAA in ~~airport~~aA~~A~~gricultural area (3455~~.4~~±2203~~.7~~ pmol m^{-3}), followed by those in urban (2941~~.0~~±2443~~.5~~ pmol m^{-3}), forest (2730~~.2~~±1435~~.5~~ pmol m^{-3}) and town (2314~~.5~~±1211~~.7~~ pmol m^{-3}). The lowest THAA concentration occurred at suburban (1633~~.5~~±1087~~.2~~ pmol m^{-3}) (Fig. S1).

However, for coarse particles, the difference in THAA concentrations between 5 sampling sites were not significant ($p>0.05$) (Fig. S1). The mean concentration of THAA in ~~airport~~agricultural area, urban, forest, town and suburban location was 540±-821~~.4~~ pmol m^{-3}, 230~~.9~~±300~~.8~~ pmol m^{-3}, 654~~.4~~±1152~~.4~~ pmol m^{-3}, 437~~.7~~±583~~.7~~ pmol m^{-3} and 291~~.0~~±426~~.2~~ pmol m^{-3}, respectively. The highest concentration of atmospheric AAs at the agricultural area would be ascribed to the enhanced agricultural activities and natural source emission (e.g., pollen grain) in spring (Xu et al., 2019).

The composition profiles of HAA in fine and coarse particles during the whole campaign are shown in Fig. 2. The composition profiles of HAA in fine particles are quite different from those in coarse particles (Fig. 2). For fine particles, Gly, Pro, Leu and Glu were the four most abundant compounds, accounting for an average of 25 ± 12%, 17 ± 8%, 12± 3% and 11 ± 6%, respectively, of the THAA pool.

For coarse particles, Pro were the most abundant THAA specie, with an average contribution of 63± 31% to the THAA pool. Leu, Ala and Val were the next most abundant species, each accounting for 7-9% of the THAA pool, while other individual HAA was only minor component in coarse particles (Fig. 2 and Fig. 2). The HAA distribution among the different sampling locations for both fine and coarse particles appeared similar (Fig. 2).

~~3.1.3 Influence of precipitation on concentrations of THAA~~

~~Precipitation was observed to exert remarkable impacts on the concentrations of the THAA in fine particles. The average concentration of THAA in fine particles on rainfall days (1948.3±1546.8 pmol m^{-3}) was significantly lower than that measured on dry days (3137.5±1898.1 pmol m^{-3}) ($p < 0.05$), whereas the average concentrations of THAA in coarse particles displayed no significant changes during rain events ($p>0.05$) (Fig. 1 and Fig. S1). For coarse particles, the average concentrations of THAA on rainy and dry days was 660.3±947.4 pmol m^{-3} and 212.2± 266.8 pmol m^{-3}, respectively.~~

3.2– Similar contribution sources of fine and coarse particles

~~## 3.2 Amino acid mol% composition~~

~~### 3.2.1 mol% composition profile of HAA in potential sources~~

The detailed size-resolved investigation for the sources of atmospheric AAs is limited. Filippo et al. (2014) obtained very variable results for the size-segregated concentrations of atmospheric combined amino acids in the city Rome. In the warm season, highest concentration of CAAs distributed in the fine fraction, whereas, in the colder season, the increase distribution of CAAs in the coarse fractions was observed. 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. These results could not provide conclusive evidence to define the origin of atmospheric AAs in the different particle sizes.

With the development of stable N isotope technology, $\delta^{15}N$ values and $\delta^{15}N$ pattern has become effective tools to trace the sources of nitrogen compounds. Our previous study found that the $\delta^{15}N$ value of Gly in PM2.5 can be used to trace the potential emission sources for aerosol AAs because the N isotope fractionation associated with Gly transformation in aerosol is relatively small (Zhu et al., 2020). To trace the sources of fine and coarse particles, we measured the nitrogen isotopic compositions of hydrolyzed Gly and THAA sampled from main emission sources in the study areas, including biomass burning, soil and local plants (~~Fig. 10~~Fig. 3). The average $\delta^{15}N$ value for hydrolyzed Gly from the biomass burning, soil, and plant sources was +15.6 ± 4.3‰, +3.0 ± 4.4‰, and −11.9±1.4‰, respectively, and the mean $\delta^{15}N_{THAA}$ value was +15.8 ± 4.5‰, +5.5 ± 2.2‰, and −0.0 ± 1.8‰, respectively.

In this study, t~~T~~he $\delta^{15}N$ values of hydrolyzed Gly in fine and coarse particles exhibited wide ranges: −1.0‰ to +20.3‰ and −0.8‰ to +15.7‰, which fall within the ranges of biomass burning, soil, and plants sources (Fig. 3). The $\delta^{15}N$ of protein AA ($\delta^{15}N_{THAA}$) has been also served as a proxy for indicating the nutrient N in marine sediments (Batista et al., 2014). To test $\delta^{15}N_{THAA}$ values of aerosol particles could also be used to trace the sources of aerosol particles, $\delta^{15}N_{THAA}$ values were compared with the $\delta^{15}N_{Gly}$ values. Since the concentration of hydrolyzed Gly is very low in coarse particles, a few the $\delta^{15}N_{Gly}$ values could be measured in coarse aerosol samples. Thus, only the $\delta^{15}N_{THAA}$ values of fine particles were compared with the $\delta^{15}N_{Gly}$ values of fine particles in the same sampling sites.

A remarkably consistent spatial-related trend was observed in $\delta^{15}N_{THAA}$ values and the $\delta^{15}N$ values of hydrolyzed Gly (Fig. 4b and 4c). Both $\delta^{15}N_{Gly}$ values and the $\delta^{15}N_{THAA}$ values of fine particles in the urban and town locations showed more positive than those in suburban, ~~airportA~~agricultural area and forest locations ($p<0.05$). Furthermore, the mean $\delta^{15}N_{THAA}$ value was not significantly different from the average $\delta^{15}N$ value of hydrolyzed Gly in the 5 sampling locations ($p>0.05$), supporting $\delta^{15}N_{THAA}$ values of aerosols may also imprint the sources of atmospheric AAs. Similarly, according to the $\delta^{15}N$ inventories of THAA in potential emission sources of atmospheric protein AA, both fine (+0.7‰ to +13.3‰) and coarse particles (−2.3‰ to +10.0‰) had the $\delta^{15}N_{THAA}$ value also typically in the range of these three main emission sources (Fig. 3). Therefore, it is likely that the main sources of atmospheric AAs for both fine and coarse particles were mainly biomass burning, soil, and plants.

~~Moreover~~However, ~~the $\delta^{15}N$-HAA pattern of fine and coarse particles was remarkably consistent (Fig. 9 and 10). t~~There is no significant difference in the $\delta^{15}N_{THAA}$ value between fine and coarse particles in each sampling sites (p>0.05) (~~Fig. 11~~Fig. 4c) and the average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5 ± 1.7‰ at 5 sampling sites~~1.5‰ (Fig. 11~~Fig. 4a).Thus, it is suggested that the main sources of AAs in fine and coarse particles might be similar, all of which were influenced by biomass burning, soil, and plant sources.

In addition, as one of the main components of primary biological aerosol particles (PBAP), AAs are proved to be ejected from ocean water by bursting bubbles (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. S2), 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, PBAP may be removed by dry and wet deposition (Després 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 $\delta^{15}N$-HAA data for marine aerosols. Pooled $\delta^{15}N_{Gly}$ values from literature data, we found the $\delta^{15}N_{Gly}$ 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; Calleja et al., 2013), which was close to the 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 include a very small amount of marine contribution.

3.3 Sources of HAA in aerosol at different locations

The $\delta^{15}N_{Gly}$ values of fine particles was significantly different at 5 sampling sites (p<0.05). The average $\delta^{15}N_{Gly}$ value of fine particles in urban (average=14.3 ± 8.5‰) and town (average=9.4 ± 4.2‰) were more positive than that in suburban (average=6.7 ± 4.3‰), ~~airport~~Aagricultural area (average= 6.9 ± 5.3‰) and forest site (average=6.5 ± 5.0‰) (~~Fig. 11~~Fig. 4b). The significantly higher $\delta^{15}N_{Gly}$ values observed in the urban and town locations suggested an increased contribution from biomass burning sources to Gly in fine particles at these two locations.

Similar spatial variation trend in $\delta^{15}N_{THAA}$ values of fine and coarse particles among 5 sampling sites was found. For fine particles, the highest $\delta^{15}N_{THAA}$ value of fine particles were observed in urban (average=9.4 ± 2.5‰), town (average=8.4 ± 1.5‰), then in the suburban (average=5.4 ± 1.1‰), ~~airport~~Aagricultural area (average=5.9 ± 2.8‰) and forest (average=5.7 ± 1.9‰) sites. For coarse particles, the most positive $\delta^{15}N_{THAA}$ value were also occurred in urban (average=8.6 ± 0.9‰), town (average=7.0 ± 1.6‰), then in the suburban (average=4.3 ± 3.4‰), ~~airport~~Aagricultural area (average=6.0 ± 3.1‰) and forest (average=5.4 ± 2.6‰) sites (~~Fig. 11~~Fig. 4c). The more positive $\delta^{15}N_{THAA}$ values occurred in urban and town compared to other sampling sites for both fine and coarse particles (p<0.05), indicating that atmospheric AAs for both fine and coarse particles in urban and town were more influenced by biomass burning.

3.4 Different degradation state of AAs between fine and coarse aerosol particles

In this study, a huge difference was observed in the concentrations and mol% compositions of THAAs between fine and coarse particles (Fig. 1 and 3). As we discussed above, the sources of AAs in fine and coarse particles are similar, therefore this lager difference may be attributed to protein matter in fine and coarse undergoing different degrees of oxidation, nitration and oligomerization in the atmosphere (Liu et al., 2017;Wang et al., 2019;Song et al., 2017;Haan et al., 2009). Another possibility is that, biologically relevant degradation of AAs may contribute to this variation observed between fine and coarse particles. To investigate whether AAs in fine and coarse particles may be degraded by bacteria to different degrees, degradation marker (DI) and bacterial heterotrophy indicators (δ^{15}N-AA distribution and $\sum V$) were used. Protein as major components in all source organisms are sensitive to all stages of degradation (Cowie and Hedges 1992). Moreover, compared to the alteration of the degradation, the dissimilarity in amino acid composition of protein in the source organisms are minor (Dauwe and Middelburg 1998). Therefore, the degradation index (DI) is developed, which are based on protein amino acid composition and factor coefficients based on the first axis of the PCA analysis (equation 1). Since AAs concentrated in cell walls are preferential accumulated during decomposition, whereas amino acids that are concentrated in cell plasma tend to be depleted during degradation (Dauwe et al., 1999), the compositional changes of amino acids associated with degradation can be traced by the DI value. The higher DI values indicate the protein is relatively "fresh" (Yan et al., 2015) and changes tracked by DI are proposed to be driven in large part by enrichment of AAs concentrated in cell wall (Mccarthy et al., 2007).

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), following the method described by Dauwe et al. (1999). The first principal component explained 38% of the variability, and the second principal component explained 21% (Table S2). Fig. 5a shows plots of the scores of the first and second principal components of fine and coarse particles in 5 sites. Components of fine and coarse particles could be roughly separated. The plots of the fine particles tended to cluster in the upper middle and right areas (approximately -1.7 to +2.0, and -0.4 to 1.4 at first and second principal component scores, respectively). In contrast, the plots of the coarse particles tended to locate in the lower and left areas (approximately -1.9 to 1.4, and -2.8 to +0.5 at first and second principal component scores, respectively). 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.

This is the first report of the DI values for aerosol particles. We compared DI values obtained by our calculating method with those calculated by using the coefficients given in previous references (Dauwe et al., 1999;Yamashita and Tanoue, 2003). There is no significant difference between the DI values calculated using the first principal component score and the DI values calculated using the coefficients given in the previous reference (Dauwe et al., 1999;Yamashita and Tanoue, 2003) ($p>0.05$) (Fig. S3), confirming our calculation method is reliable.

A plot of factor coefficients of each individual amino acid in the first and second principal components was examined to clarify the reasons for variation of the scores of fine and coarse particles (Fig. 5b).

Based on this cross plot, 14 HAA species were divided into four groups. In Fig. 5b, Group 1 located in the lower right portion of the plot, included Val, Leu, Ile and Ala. Group 2, in the upper right of the plot, included Lys, Glu, Asp, Phe, Thr, Ser and Gly. Group 3, in the middle direction, included Tyr and His. Group 4, in the left of the plot, included Pro. The principal component scores of atmospheric particles were affected by the relative abundance and the factor coefficient of each individual amino acid. The relative high principal component scores of fine particles in PC1 and PC2 were more affected by the high relative abundances of amino acids which has high factor coefficient (Group 1 and Group 2). In contrast, the relative low principal component scores of coarse particles in PC1 and PC2 were more affected by the low relative abundances of amino acids which has low factor coefficient (Group 1 and Group 4).

Furthermore, DI values for fine particles showed positive correlation with percentage of HAA species in Group1 (e.g., Lys, Glu, Asp, Phe, Thr, Ser), but DI values for coarse particles were positively correlated to percentage of HAA species in Group 2 (e.g., Ala, Val, Leu and Ile) (Fig. S4), indicating the difference in composition profiles of HAA between fine and coarse particles may affected by the degradation process. Plots of DI as a function of THAA concentration in both fine and coarse particles showed an exponential relationship ($y=1067.4e^{-1.0x}$; $r=0.6$, $p<0.01$); that was, that at higher values of DI, concentrations of THAA were higher, and vice versa (~~Fig. 6~~Fig. S5). The coarse particles had significantly lower THAA concentrations compared to fine particles (Fig. S1). Clearly, both composition profiles of HAA and concentrations of THAAs in aerosols may be related to degradation processes.

DI values from literature data, where possible and DI values for fine and coarse aerosol particles are shown in Fig. 6a and Fig. 7. Fine particles had significantly higher DI values than that of coarse particles ($p<0.05$) (Fig. 6a). The DI values for fine and coarse particles ranged from -0.3 to 1.4 (average=0.6±0.4) and -1.8 to 1.4 (average=-0.6±1.0), respectively (Fig. 7). 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). 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-, which were proved to be more degraded materials (Fig. 7). 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 lower DI values observed in coarse particles, implying that AAs in coarse particles may undergo more degradation than fine particles. Our result is also comparable to that observed in precipitation at Uljin and Seoul (Yan et al., 2015). The DI values measured in coarse particles are closer to those observed in Seoul, where is believed to have more advanced ~~bacterial~~ degradation than Uljin, further supporting the degradation degree of amino acids in coarse particles is higher than that in fine particles.

However, the differences in DI values were not significant among 5 sampling sites for both fine and coarse particles ($p>0.05$) (~~Fig. S4~~Fig. S6). For fine particles, the average DI values in ~~airport~~~~A~~agricultural area, urban, forest, town and suburban location was 0.6±0.4, 0.5±0.5, 0.7±0.3, 0.6±0.3 and 0.7±0.2, respectively. For coarse particles, the mean DI values in ~~airport~~~~A~~agricultural area, urban, forest, town and suburban location was -0.5±0.9, -1.0±1.1, -0.8±1.1, -0.3±1.1 and -0.5±1.1, respectively. As we

discussed above, the sources of atmospheric HAA were different among 5 sampling sites. This result suggested that the degradation process of amino acids in the atmosphere is less affected by their emission sources.

3.5 Bacterial signature in aerosol AAs

The existence of microorganisms in aerosol particles has been documented. However, whether bacterial degradation processes play a role in atmospheric protein degradation is not well understood. The negative correlation of the DI with the concentration of free γ-aminobutyric acid (GABA) and its mole percentage are depicted in Figure S7. Since bacteria are known to produce free GABA from their protein precursors (Cowie and Hedges 1994; Koolman and Roehme, 2005), the concentrations and mole percentage of free GABA may tend to increase during the biodegradation process. Therefore, negative relationship between the DI values and GABA in aerosol suggested that the degradation of atmospheric protein is probably induced by bacteria. Dauwe et al. (1999) have also reported that the negative correlation of the DI with the mole percentage of the GABA and β-alanine (BALA) in marine particulate matter samples and they attributed the correlation of the DI with the variation of GABA mole percentage to the stimulation of degradation by the activity of microorganism.

Moreover, it is interesting to note that a substantial δ^{15}N-AA shifts in trophic AA group was observed between fine and coarse particles among 5 sampling sites. Ala, Leu, Ile and Asp was ^{15}N-enriched in coarse particles compared to fine particles, whereas Pro in coarse particles was ^{15}N-depleted than those in fine particles (~~Fig. 10~~Fig. 8). Clearly, there is no uni-directional ^{15}N depletion or enrichment of Trophic-AA was observed between fine and coarse particle samples. The δ^{15}N -AA distribution in the Trophic-AA group is more "scattered" in coarse particles than that in fine particles (~~Fig. 10~~Fig. 8). However, the difference in δ^{15}N values of Source-AA between coarse particles and fine particles was relatively small except for Val. δ^{15}N values of Gly, Ser, Phe and Lys measured in coarse particles are close to those measured in fine particles. Recent work on δ^{15}N signatures of individual AA has suggested that bacterial heterotrophy often results in strong fractionation in some specific AA, which are tied directly to specific microbial biochemical pathways. Among those specific AA, both Ala and Leu are commonly observed to show strong δ^{15}N shifts with the processes of bacterial heterotrophy (McCarthy et al., 2004). Hence, ^{15}N-enriched Ala and Ile founded in coarse particles compared to fine particles suggested more bacterial heterotrophy have taken place in coarse particle.

Heterotrophic reworking of protein encompasses a series of processes including hydrolysis, uptake and de novo synthesis, salvage AA incorporation into new protein. Therefore, new protein reworked by heterotrophically processes represent a mixture of resynthesized AAs and AAs that has never been hydrolyzed (salvaged AAs). McCarthy et al. (2007) hypothesized that the process of incorporating the salvage AAs into new protein should not alter original δ^{15}N values of salvage AAs. The substantial δ^{15}N -AA shifts in only selected AA indicates the N of an assimilated AA has been replaced through a de novo *heterotrophic* AA resynthesis pathway with N isotope fractionation. Therefore, the substantial δ^{15}N-AA shifts in trophic AA group could be observed when bacterial heterotrophy has occurred and those new resynthesized protein has become an important part of protein material measured (Mccarthy et al., 2007).

Fogel and Tuross (1999) first observed that δ^{15}N-AA patterns of degraded material was highly "scattered" and the N isotope fracionation between degraded material and fresh protein were up to 15‰. Moreover, obviously changes for the δ^{15}N values of several AA were founded in high molecular weight dissolved organic carbon after bacterial reworking (Calleja et al., 2013). Similarly, the "scattered" characteristic of δ^{15}N-AA distribution in Tr-AA group of coarse particles may be due to the nitrogen fractionation occurred in microbial consumers selectively using Trophic-AA.

$\sum V$ is defined as the average deviation in six Trophic-AA and has been proposed to reflect the extent of protein resynthesis during microbial degradation processes (Mccarthy et al., 2007). Fig. 9 shows the $\sum V$ values measured in fine particles, coarse particles, and local natural sources, as well as $\sum V$ values reported in previous references. $\sum V$ values for main natural sources collected around the sampling sites were calculated. $\sum V$ values for local plants (needles of *Pinus massoniana* (Lamb.) and leaves of *Camphora officinarum*) ranged from 1.0‰ to 2.1‰, with a mean of 1.7±0.4‰ (Fig. 9). $\sum V$ values in local soil (paddy soil, road soil and forest soil) ranged from 1.4‰ to 2.1‰, with a mean of 1.7±0.3‰. Overall, coarse particles had higher $\sum V$ value (average = 3.6±1.5‰) than that of fine particles ($p<0.05$) (Fig. 9). The mean $\sum V$ value of fine particles in 5 sampling sites (average=2.4±1.1‰) was similar to or slightly higher than that of plants and soil collected around sampling sites, phytoplankton (1.0‰) and zooplankton (1.5‰) in marine (Mccarthy et al., 2007), needle (average=1.5±0.1‰), mosses (average=1.1±0.02‰) and soil (average=1.4±0.1‰) measured in balsam fir forest (Philben et al., 2018), and marine POM (average=2.3±0.7‰) (Batista et al., 2014;Mccarthy et al., 2007). In contrast, $\sum V$ values of coarse particles were equal to or even higher than those of more degraded materials, such as marine dissolved organic matter (DOM) reworked by bacterial heterotrophy (average =3.0±0.5‰) (Batista et al., 2014).

∑V could reflect the increasing trend of "scatting" δ^{15}N-Trophic AA pattern related to more intensive bacterial resynthesis (Batista et al., 2014; Calleja et al., 2013;Yamaguchi et al., 2017). In this study, the significant higher values of $\sum V$ were measured in coarse particles than those in fine particles ($p<0.05$) (Fig. 6). Moreover, the mean $\sum V$ value of fine particles was similar to or slightly higher than that measured in "fresh" materials (Mccarthy et al., 2007;Philben et al., 2018;Batista et al., 2014), while $\sum V$ values of coarse particles were equal to or even higher than those of more degraded materials (Fig. 9). These corroborate that more bacterial heterotrophic resynthesis occurred in coarse particles compared to fine particles.

Despite the uncertainties surrounding oxidation, nitration and oligomerization of AAs in the atmosphere, main observations remain that the difference in δ^{15}N values of Source-AA (Gly, Ser, Phe and Lys) and total hydrolysable amino acids ($\delta^{15}N_{THAA}$) between coarse particles and fine particles was relatively small (Fig. 3). The average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰ (Fig. 4a). These results appear to contrast with what one might expect for AAs in either sizes particles undergo particularly more photochemical transformation than the other. Therefore, significantly lower DI values, "scattered" characteristic of δ^{15}N distribution in Tr-AA and higher $\sum V$ values observed in coarse particles in this study provide evidence that the difference in the THAA concentration and mol% composition distribution between fine and coarse particles may be related to AAs in coarse particles have

stronger bacterial degradation state than those in fine particles.

3.6 Release of coarse "Fresh" bioparticles during the rainfall

A tight relationship between atmospheric bioaerosols and precipitation has been found by previous studies (Huffman et al., 2013;Yue et al., 2016). Since biological sources contain a large abundance of AAs (Ren et al., 2018), HAAs in aerosols can be used as tracer compounds to indicate the release of biological sources during precipitation. However, detailed size-resolved and time-resolved observation for the release of bioparticles initiated by precipitation are spare and the degradation state of different sizes bioparticles has never been examined.

In this study, precipitation was observed to exert different impacts on the concentrations of the THAA in fine and coarse particles. The average concentration of THAA in fine particles on rainfall days (1948±1546 pmol m^{-3}) was significantly lower than that measured on dry days (3137±1898 pmol m^{-3}) ($p < 0.05$), whereas the average concentrations of THAA in coarse particles displayed no significant changes during rain events ($p>0.05$) (Fig. 1 and Fig. S1). For coarse particles, the average concentrations of THAA on rainy and dry days was 660±947 pmol m^{-3} and 212± 266 pmol m^{-3}, respectively. It is expected that the concentrations of individual AAs in aerosol were assumed to decrease during rainfall events because of the high scavenging ratio of AAs in aerosol (Gorzelska and Galloway, 1990). In this study, form rain to dry periods, the concentrations of THAA for fine particles decreased ($p<0.05$) (Fig. S1), but the concentration of THAAs for coarse particles displayed not significant change ($p>0.05$) (Fig. S1). Similar variation trends of different size particles following the precipitation were also observed by (Huffman et al., 2013). They also found the steep increase of coarse particles while low concentrations of fluorescent bioparticles and total aerosol particles were found in fine particles during the precipitation, suggesting the new released AAs during the precipitation are mainly distributed in coarse particles.

It is worth noting that the influence of precipitation on the mole composition profile of HAA is different for the coarse and fine particles (Fig. 2). For fine particles, only the percentage of Pro significantly increased from 14±6% on dry days to 20±9% on rainfall days ($p<0.05$). There was no apparent trend in the percentage of other individual HAAs for fine particles following the precipitation.

For coarse aerosol, the percentage composition of HAA in dry periods is quite different from that in rainy periods for coarse particles (Fig. 2). From dry periods to rainfall periods, the percentage of Pro in coarse particles significantly decreased from 74±25% to 53±34% ($p<0.05$), meanwhile the percentage of Ala, Val, Leu, Ile and Glu in coarse particles significantly increased ($p<0.05$). These HAA species together accounted for 39% of the total THAA pool during dry periods, while during rainfall events this proportion was only 20%. Besides that, compared to fine particles, the large variation in mole composition of THAA for coarse particles was observed following rain events (Fig. 2). From dry periods to rainfall periods, the percentage changes of Pro for coarse particles (21%) was roughly 4 times greater than that for fine particles (6%). Similarly, from dry periods to rain periods, the increase in the percentage of Ala, Val, Leu, Ile and Glu in coarse particles is significantly greater than that in fine particles. For example, following the precipitation, Val in coarse particles increased by 4%, whereas Val in fine particles only increased by 0.3%. These large variations in the percentage of some HAA species (e.g., Pro, Ala, Val, Leu, Ile and Glu)

were observed in coarse particles following the rainfall events, which imply the states of coarse particles measured during rain periods were different from the ones measured during dry periods (Fig. 2).

This conclusion also supported by the variation of DI and ∑V values for coarse particles following rain events. As exhibited in Fig. 6a, DI values of coarse aerosol particles were influenced by precipitation. For coarse aerosol particles, a significant increase was found from dry (average=-1.0±0.8) to rain periods (average=-0.3±1.1) (p<0.05), whereas the DI values of fine particles during dry (average=0.7±0.3) and rain periods (average=0.6±0.4) were not significantly different (p>0.05). Fig. 6b shows the $\sum V$ values of fine and coarse particles during dry and rainy days. The $\sum V$ values of coarse aerosol particles were significantly affected by precipitation. From dry to rainy days, $\sum V$ values of coarse aerosol particles decreased from 4.5±1.5‰ to 3.0±1.3‰ (p<0.05). In contrast, the average $\sum V$ value of fine particles on dry and rainy days was identical (2.4±1.1‰). From dry to rain periods, DI values in coarse aerosol particles were significant increased (p<0.05) but the ∑V value was significantly decreased (p<0.05), suggesting more fresh AAs in coarse particles were released during rain events, whereas, on dry days AAs in coarse particles were more degraded.

Furthermore, we observed an obviously temporal variations of the concentration and mol% composition of HAA for coarse particles during the precipitation. The higher concentration of THAAs in coarse particles occurred in April 30, May 5, May 6 and May 13 when daily precipitation amount was higher and duration of rainfall was longer (Fig. 1 and Table S4). Previous studies demonstrated that droplets splashing on porous medium can deliver fresh biological aerosols in porous medium to the aerosol and this mechanism is closely related to the amounts and intensity of the rainfall events (Joung and Buie, 2015;Huffman et al., 2013;Yue et al., 2016). Thus, the temporal variation trend of HAA concentration for coarse particles in this study can attributed to the active release of biological aerosols caused by droplets and it highly depends on the amounts and intensity of the rainfall. Moreover, the mol% composition of HAA in coarse particles measured in the stronger rainfall events were significantly different from that observed in rainfall events with lower precipitation amount amount and shorter rainfall duration (weak rainfall events). Specifically, a steep decrease in the percentage of Pro and increase of other HAAs in coarse particles mainly occurred in the stronger rainfall events, whereas the mol% composition of HAA in the weak rainfall events were similar to that observed on dry days (Fig. 2). As we discussed above, AAs in coarse particles on dry days were more degraded. Therefore, we can conclude that those "fresh" protein matters in coarse particle are prone to release by droplets and amounts and intensity of the rainfall are the key factors controlling this mechnism.

~~The mol% composition of HAA were distinct in the biomass burning aerosols (straw burning), soil (road, paddy and forest soil), and plant sources (pine and straw) (Fig. 2). For straw burning, 11 hydrolyzed amino acids were detected in straw burning samples, including Ala, Val, Leu, Ile, Pro, Gly, Ser, Thr, Phe, Asp and Glu. Gly was the predominant HAA species from straw burning sources, contributed 45.8% of THAA pool. For soil sources, 12 hydrolyzed amino acids were detected, including Ala, Val, Leu, Ile, Pro, Gly, Ser, Thr, Phe, Glu, Lys and Tyr. Hydrophobic species (Ala, Val, Leu, and Ile) and neutral (Pro) were the most aboundant HAA components in soil sources, together accounting for 81.8% of THAA pool in soil sources. For plant sources, 15 hydrolyzed amino acids were measured, including Ala, Val, Leu, Ile,~~

Pro, Gly, Ser, Thr, Phe, Asp, Glu, Lys, His, Tyr and Met. Hydrophilic species (Lys and Asp), Hydrophobic species (Ala, Val, Leu, and Ile) and neutral (Pro) were the major HAA components, together accounting for 66.9% of THAA pool.

3.2.2 Difference in composition profiles of HAA between fine and coarse particles

The composition profiles of HAA in fine and coarse particles during the whole campaign are shown in Fig. 3Fig. 2Fig. 2Fig. 2. The composition profiles of HAA in fine particles are quite different from those in coarse particles (Fig. 2 and Fig. 3Fig. 2Fig. 2Fig. 2). For fine particles, Gly, Pro, Leu and Glu were the four most abundant compounds, accounting for an average of 25.0 ± 11.6%, 16.9 ± 8.0%, 11.8 ± 3.3% and 10.8 ± 5.7%, respectively, of the THAA pool.

For coarse particles, Pro were the most abundant THAA specie, with an average contribution of 63.3± 31.1% to the THAA pool. Leu, Ala and Val were the next most abundant species, each accounting for 6.6 -9.2% of the THAA pool, while other individual HAA was only minor component in coarse particles (Fig. 2 and Fig. 3Fig. 2Fig. 2Fig. 2).

3.2.3 Difference in composition profiles of HAA among different sampling locations

The HAA distribution among the different sampling locations for both fine and coarse particles appeared similar (Fig. 3Fig. 2Fig. 2Fig. 2).

3.2.4 Influence of precipitation on the composition profiles of HAA

It is worth noting that the influence of precipitation on the mole composition profile of HAA is different for the coarse and fine particles (Fig. 3Fig. 2Fig. 2Fig. 2). According to our previous study (Zhu et al., 2020) and the mol% composition of HAA observed in this study, hydrophobic (Ala, Val, Leu, and Ile), neutral (Pro) and hydrophilic (Glu, Lys, and Asp) species are the major HAA components in natural sources (plant and soil sources). For fine particles, the contributions of HAAs species with high abundance in natural sources (including: Ala, Val, Leu, Ile, Pro, Glu, Lys, and Asp), increased from dry periods (65%) to rainfall periods (69%) (Fig. S2). Among these AAs, the percentage of Pro significantly increased from 14.1±6.2% on dry days to 19.7±8.8% on rainfall days (p<0.05). There was no apparent trend in the percentage of other individual HAAs for fine particles following the precipitation.

For coarse aerosol, the percentage of HAAs with high abundance in natural sources exhibited little changes from dry periods (averaged 94%) to rainfall periods (averaged 93%) (Fig. S2). However, the percentage composition of HAA in dry periods is quite different from that in rainy periods for coarse particles (Fig. 3Fig. 2Fig. 2Fig. 2). From dry periods to rainfall periods, the percentage of Pro in coarse particles significantly decreased from 73.6±24.7% to 52.7±33.6% (p<0.05), meanwhile the percentage of Ala, Val, Leu, Ile and Glu in coarse particles significantly increased (p<0.05). These HAA species together accounted for 38.5% of the total THAA pool during dry periods, while during rainfall events this proportion was only 19.8%.

Besides that, compared to fine particles, the large variation in mole composition of THAA for coarse particles was observed following rain events (Fig. 3Fig. 2Fig. 2Fig. 2). From dry periods to rainfall

periods, the percentage changes of Pro for coarse particles (20.9%) was roughly 4 times greater than that for fine particles (5.6%). Similarly, from dry periods to rain periods, the increase in the percentage of Ala, Val, Leu, Ile and Glu in coarse particles is significantly greater than that in fine particles. For example, following the precipitation, Val in coarse particles increased by 3.5%, whereas Val in fine particles only increased by 0.3%.

Particularly, this steep decrease in the percentage of Pro and increase of other HAAs in coarse particles mainly occurred in the first day of rainfall events (Fig. 3Fig. 2Fig. 2Fig. 2).

3.3 DI values

Microbial degradation process could significantly modify the mole composition of protein amino acids (Dauwe et al., 1999). Accordingly, a quantitative degradation index (DI) has been developed based on the mole composition of hydrolyzed amino acids pool (Yan et al., 2015).

3.3.1 PCA of HAA in fine and coarse aerosol particles

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).

The first principal component explained 38.3% of the variability, and the second principal component explained 20.9% (Table S1Table S2). Fig. 4a shows plots of the scores of the first and second principal components of fine and coarse particles in 5 sites. Components of fine and coarse particles could be roughly separated. The plots of the fine particles tended to cluster in the upper middle and right areas (approximately -1.7 to +2.0, and -0.4 to 1.4 at first and second principal component scores, respectively). In contrast, the plots of the coarse particles tended to locate in the lower and left areas (approximately -1.9 to 1.4, and -2.8 to +0.5 at first and second principal component scores, respectively). Fine and coarse particles were roughly distinguished by first and second principal component scores, suggesting that the first principal component score may also be designed as a degradation index of THAA in aerosols.

A plot of factor coefficients of each individual amino acid in the first and second principal components was examined to clarify the reasons for variation of the scores of fine and coarse particles (Fig. 4b). Based on this cross plot, 14 HAA species were divided into four groups. In Fig. 4b, Group 1 located in the lower right portion of the plot, included Val, Leu, Ile and Ala. Group 2, in the upper right of the plot, included Lys, Glu, Asp, Phe, Thr, Ser and Gly. Group 3, in the middle direction, included Tyr and His. Group 4, in the left of the plot, included Pro. The principal component scores of atmospheric particles were affected by the relative abundance and the factor coefficient of each individual amino acid. The relative high principal component scores of fine particles in PC1 and PC2 were more affected by the high relative abundances of amino acids which has high factor coefficient (Group 1 and Group 2). In contrast, the relative low principal component scores of coarse particles in PC1 and PC2 were more affected by the low relative abundances of amino acids which has low factor coefficient (Group 1 and Group 4).

Furthermore, DI values for fine particles showed positive correlation with percentage of HAA species in

Group1 (e.g., Lys, Glu, Asp, Phe, Thr, Ser), but DI values for coarse particles were positively correlated to percentage of HAA species in Group 2 (e.g., Ala, Val, Leu and Ile) (Fig. 5Fig. S6Fig. S6Fig. S6), indicating the difference in composition profiles of HAA between fine and coarse particles may affected by the degradation process.

3.3.2 Compared our calculating method with other works

This is the first report of the DI values for aerosol particles. We compared DI values obtained by our calculating method with those calculated by using the coefficients given in previous references (Dauwe et al., 1999;Yamashita and Tanoue, 2003). There is no significant difference between the DI values calculated using the first principal component score and the DI values calculated using the coefficients given in the previous reference (Dauwe et al., 1999;Yamashita and Tanoue, 2003) ($p>0.05$) (Fig. S3), confirming our calculation method is reliable.

3.3.3 Correlation between DI and THAA

Plots of DI as a function of THAA concentration in both fine and coarse particles showed an exponential relationship ($y=1067.4e^{-1.0x}$; $r=0.6$, $p<0.01$); that was, that at higher values of DI, concentrations of THAA were higher, and vice versa (Fig. 6), indicating THAA for both fine and coarse aerosols probably undergone bacterial degradation.

3.3.4 DI values of fine and coarse aerosol particles

DI values from literature data, where possible and DI values for fine and coarse aerosol particles are shown in Fig. 7Fig. S7Fig. S7Fig. S7a and Fig. 8Fig. 7Fig. 7Fig. 7Fig. 7. Fine particles had significantly higher DI values than that of coarse particles ($p<0.05$) (Fig. 7Fig. S7Fig. S7Fig. S7a). The DI values for fine and coarse particles ranged from -0.3 to 1.4 (average=0.6±0.4) and -1.8 to 1.4 (average=-0.6±1.0), respectively (Fig. 8Fig. 7Fig. 7Fig. 7Fig. 7). 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. 8Fig. 7Fig. 7Fig. 7Fig. 7).

3.3.5 DI values of aerosol particles at different locations

However, the differences in DI values were not significant among 5 sampling sites for both fine and coarse particles ($p>0.05$) (Fig. S4Fig. S6Fig. S6Fig. S6). For fine particles, the average DI values in airport urban, forest, town and suburban location was 0.6±0.4, 0.5±0.5, 0.7±0.3, 0.6±0.3 and 0.7±0.2, respectively. For coarse particles, the mean DI values in airport, urban, forest, town and suburban location was -0.5±0.9, -1.0±1.1, -0.8±1.1, -0.3±1.1 and -0.5±1.1, respectively.

3.3.6 Influence of precipitation on the DI values of aerosol particles

As exhibited in Fig. 7Fig. S7Fig. S7Fig. S7a, DI values of coarse aerosol particles were influenced by

precipitation. For coarse aerosol particles, a significant increase was found from dry (average= 1.0±0.8) to rain periods (average= 0.3±1.1) (p<0.05), whereas the DI values of fine particles during dry (average=0.7±0.3) and rain periods (average=0.6±0.4) were not significantly different (p>0.05).

3.4 δ^{15}N-AA patterns

3.4.1 δ^{15}N-AA patterns of fine and coarse particles

The δ^{15}N value for each individual AA measured and average amino acids in 5 sites were provided in Fig. 9Fig. 8Fig. 8Fig. 8. The δ^{15}N-AA pattern for most AA was similar between fine and coarse aerosol particles. Generally, of the individual amino acids, Ala and Leu were enriched relative to $\delta^{15}N_{THAA}$, while Pro, Thr and Lys exhibited depleted δ^{15}N values to the $\delta^{15}N_{THAA}$ for both fine and coarse particles in 5 sites.

3.4.2 $\delta^{15}N_{Gly}$ and $\delta^{15}N_{THAA}$ values of local natural sources

Our previous study found that the δ^{15}N value of Gly in PM2.5 can be used to trace the potential emission sources for aerosol AAs because the N isotope fractionation associated with Gly transformation in aerosol is relatively small (Zhu et al., 2020). The δ^{15}N of protein AA ($\delta^{15}N_{THAA}$) has been served as a proxy for indicating the nutrient N in marine sediments (Batista et al., 2014). To trace the sources of fine and coarse particles, we measured the nitrogen isotopic compositions of hydrolyzed Gly and THAA sampled from main emission sources in the study areas, including biomass burning, soil and local plants (Fig. 10Fig. 3Fig. 3Fig. 3). The average δ^{15}N value for hydrolyzed Gly from the biomass burning, soil, and plant sources was +15.6 ± 4.3‰, +3.0 ± 4.4‰, and −11.9±1.4‰, respectively, and the mean $\delta^{15}N_{THAA}$ value was +15.8 ± 4.5‰, +5.5 ± 2.2‰, and −0.0 ± 1.8‰, respectively.

3.4.3 $\delta^{15}N_{Gly}$ and $\delta^{15}N_{THAA}$ values in different size particles

In this study, to test $\delta^{15}N_{THAA}$ values of aerosol particles could also be used to trace the sources of aerosol particles, $\delta^{15}N_{THAA}$ values were compared with the $\delta^{15}N_{Gly}$ values. Since the concentration of hydrolyzed Gly is very low in coarse particles, a few the $\delta^{15}N_{Gly}$ values could be measured in coarse aerosol samples. Thus, only the $\delta^{15}N_{THAA}$ values of fine particles were compared with the $\delta^{15}N_{Gly}$ values of fine particles in the same sampling sites.

A remarkably consistent spatial-related trend was observed in $\delta^{15}N_{THAA}$ values and the δ^{15}N values of hydrolyzed Gly (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4b and 11c). Both $\delta^{15}N_{Gly}$ values and the $\delta^{15}N_{THAA}$ values of fine particles in the urban and town locations showed more positive than those in suburban, airport and forest locations (p<0.05). Furthermore, the mean $\delta^{15}N_{THAA}$ value was not significantly different from the average δ^{15}N value of hydrolyzed Gly in the 5 sampling locations (p>0.05), supporting $\delta^{15}N_{THAA}$ values of aerosols may also imprint the sources of atmospheric AAs.

The δ^{15}N values of hydrolyzed Gly in fine and coarse particles exhibited wide ranges: −1.0‰ to +20.3‰ and −0.8‰ to +15.7‰, which fall within the ranges of biomass burning, soil, and plants sources. Similarly, both fine (+0.7‰ to +13.3‰) and coarse particles (−2.3‰ to +10.0‰) had the $\delta^{15}N_{THAA}$ value also typically in the range of these three main emission sources (Fig. 10Fig. 3Fig. 3Fig. 3). Therefore, it

is likely that the main sources of atmospheric AAs for both fine and coarse particles were mainly biomass burning, soil, and plants.

In addition, the difference in $\delta^{15}N_{THAA}$ values were not significant for fine and coarse particles ($p>0.05$) (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4c) and the average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5 ± 1.7‰ in 5 sampling sites (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4a), further supporting the sources of AAs for fine and coarse aerosol particles may be similar.

3.4.4 $\delta^{15}N_{Gly}$ and $\delta^{15}N_{THAA}$ values of particles at different locations

The $\delta^{15}N_{Gly}$ values of fine particles was significantly different at 5 sampling sites ($p<0.05$). The average $\delta^{15}N_{Gly}$ value of fine particles in urban (average=14.3 ± 8.5‰) and town (average=9.4 ± 4.2‰) were more positive than that in suburban (average=6.7 ± 4.3‰), airport (average= 6.9 ± 5.3‰) and forest site (average=6.5 ± 5.0‰) (Fig. 11b). The significantly higher $\delta^{15}N_{Gly}$ values observed in the urban and town locations suggested an increased contribution from biomass burning sources to Gly in fine particles at these two locations.

Similar spatial variation trend in $\delta^{15}N_{THAA}$ values of fine and coarse particles among 5 sampling sites was found. For fine particles, the highest $\delta^{15}N_{THAA}$ value of fine particles were observed in urban (average=9.4 ± 2.5‰), town (average=8.4 ± 1.5‰), then in the suburban (average=5.4 ± 1.1‰), airport (average=5.9 ± 2.8‰) and forest (average=5.7 ± 1.9‰) sites. For coarse particles, the most positive $\delta^{15}N_{THAA}$ value were also occurred in urban (average=8.6 ± 0.9‰), town (average=7.0 ± 1.6‰), then in the suburban (average=4.3 ± 3.4‰), airport (average=6.0 ± 3.1‰) and forest (average=5.4 ± 2.6‰) sites (Fig. 11c). The more positive $\delta^{15}N_{THAA}$ values occurred in urban and town compared to other sampling sites for both fine and coarse particles ($p<0.05$), indicating that atmospheric AAs for both fine and coarse particles in urban and town were more influenced by biomass burning.

3.5 ∑V

∑V is defined as the average deviation in six Trophic AA and has been proposed to reflect protein resynthesis during microbial degradation processes (Mccarthy et al., 2007). Fig. 12Fig. 9Fig. 9Fig. 9 shows the *∑V* values measured in fine particles, coarse particles, and local natural sources, as well as *∑V* values reported in previous references.

3.5.1 *∑V* values in natural sources

∑V values for main natural sources collected around the sampling sites were calculated. *∑V* values for local plants (needles of *Pinus massoniana* (Lamb.) and leaves of *Camphora officinarum*) ranged from 1.0‰ to 2.1‰, with a mean of 1.7±0.4‰ (Fig. 12Fig. 9Fig. 9Fig. 9). *∑V* values in local soil (paddy soil, road soil and forest soil) ranged from 1.4‰ to 2.1‰, with a mean of 1.7±0.3‰.

3.5.2 Difference in *∑V* between fine and coarse particles

Overall, coarse particles had higher *∑V* value (average = 3.6±1.5‰) than that of fine particles ($p<0.05$) (Fig. 12Fig. 9Fig. 9Fig. 9). The mean *∑V* value of fine particles in 5 sampling sites (average=2.4±1.1‰)

was similar to or slightly higher than that of plants and soil collected around sampling sites, phytoplankton (1.0‰) and zooplankton (1.5‰) in marine (Mccarthy et al., 2007), needle (average=1.5±0.1‰), mosses (average=1.1±0.02‰) and soil (average=1.4±0.1‰) measured in balsam fir forest (Philben et al., 2018), and marine POM (average=2.3±0.7‰) (Batista et al., 2014;Mccarthy et al., 2007). In contrast, $\sum V$ values of coarse particles were equal to or even higher than those of more degraded materials, such as marine dissolved organic matter reworked by bacterial heterotrophy (average =3.0±0.5‰) (Batista et al., 2014).

3.5.3 $\sum V$ value in aerosol particles at different locations

The $\sum V$ values of both fine and coarse particles were not significantly different among the 5 sampling sites ($p>0.05$). The $\sum V$ values of fine particles in the urban, town, suburban, airport, and forest sites averaged 2.8±1.3‰, 2.3±0.7‰, 2.7±1.2‰, 2.4±1.0‰, and 1.9±1.0‰, respectively, and the $\sum V$ values of coarse particles averaged 2.5±1.0‰, 3.9±0.8‰, 3.3±1.1‰, 3.8±2.3‰, and 4.0±1.3‰ (Fig. 12Fig. 9Fig. 9Fig. 9).

3.5.4 Variations in $\sum V$ value of aerosol particles following rain events

Fig.7b shows the $\sum V$ values of fine and coarse particles during dry and rainy days. The $\sum V$ values of coarse aerosol particles were significantly affected by precipitation. From dry to rainy days, $\sum V$ values of coarse aerosol particles decreased from 4.5±1.5‰ to 3.0±1.3‰ ($p<0.05$). In contrast, the average $\sum V$ value of fine particles on dry and rainy days was identical (2.4±1.1‰).

4 Discussion

4.1 Similar contribution sources of fine and coarse particles

The sources of atmospheric proteinaceous matter are very complex. Primary biological aerosol particles (e.g., plants, soil, pollen, bacteria, fungi, spores and deris of living things), biomass burning, and agricultural activities are generally suggested to be the main contributing sources of atmospheric AAs (Matos et al., 2016;Mace et al., 2003). It is still unclear whether AAs fine and coarse particles influenced by different sources. The detailed size resolved investigation for the sources of atmospheric AAs is limited. Only Filippo et al. (2014) obtained very variable results for the size segregated concentrations of atmospheric combined amino acids in the city Rome. In the warm season, highest concentration of CAAs distributed in the fine fraction, whereas, in the colder season, the increase distribution of CAAs in the coarse fractions was observed. This result could not provide conclusive evidence to define the origin of atmospheric AAs in the different particle sizes.

With the development of stable N isotope technology, $\delta^{15}N$ values and $\delta^{15}N$ pattern has become effective tools to trace the sources of nitrogen compounds. Our previous study found that the $\delta^{15}N_{Gly}$ value in aerosol particles can be used to identify the potential emission sources for aerosol AAs. In this study, the $\delta^{15}N$ values of hydrolyzed Gly for both fine and coarse particles exhibited wide ranges but were typically in the ranges of hydrolyzed Gly from biomass burning, soil and plant sources (Fig. 10Fig. 3Fig. 3Fig. 3).

Therefore, it is likely that the main sources of atmospheric AAs for both fine and coarse particles were mainly biomass burning, soil, and plants.

Similarly, according to the $\delta^{15}N$ inventories of THAA in potential emission sources of atmospheric protein AA, $\delta^{15}N_{THAA}$ values for fine and coarse particles were also in the range of $\delta^{15}N_{THAA}$ values from the three main contributing sources, which further demonstrated that AAs in both fine and coarse particle were affected by biomass burning, soil, and plants sources.

Moreover, the $\delta^{15}N$ HAA pattern of fine and coarse particles was remarkably consistent (Fig. 9Fig. 8Fig. 8Fig. 8 and 10). There is no significant difference in the $\delta^{15}N_{THAA}$ value between fine and coarse particles in each sampling sites (p>0.05) (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4c) and the average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰ (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4a).Thus, it is suggested that the main sources of AAs in fine and coarse particles might be similar, all of which were influenced by biomass burning, soil, and plant sources.

4.2 Difference in degradation state of protein AA between fine and coarse aerosol particles

In this study, a huge difference was observed in the concentrations and mol% compositions of THAAs between fine and coarse particles (Fig. 1 and 3). As we discussed above, the sources of AAs in fine and coarse particles are similar, therefore this lager difference may be attributed to protein matter in fine and coarse undergoing different degrees of oxidation, nitration and oligomerization in the atmosphere (Liu et al., 2017;Wang et al., 2019;Song et al., 2017;Haan et al., 2009). Another possibility is that, bacterial degradation of AAs may contribute to this variation observed between fine and coarse particles. Interestingly, by using bacterial markers (DI, $\delta^{15}N$ AA distribution and $\sum V$), we found that AAs in fine and coarse particles may be degraded by bacteria to different degrees.

The degradation index (DI) value has been developed to assess degradation state of atmospheric matter solely derived from amino acids (e.g., protein materials) (Yan et al., 2015). Relatively high DI values denote a relatively "fresh" matter. In this study, the positive correlation between the concentrations of THAA and DI values for both fine and coarse particles in the atmosphere is established in this study (Fig. 6Fig. S7Fig. S7Fig. S7). Furthermore, for fine particles, DI exhibited positive correlation with the percentage of Lys, Glu, Asp, Phe, Thr, Ser, but for coarse particles, DI showed positive correlation with the percentage of different HAA species (e.g., Ala, Val, Leu and Ile) (Fig. 5Fig. S6Fig. S6Fig. S6). Clearly, concentrations of THAAs and composition profiles of HAA in aerosols may be related to microorganism-induced degradation processes. In compared to fine particles, the coarse particles had significantly lower THAA concentrations (Fig. S1) and DI values (Fig. 7Fig. S7Fig. S7Fig. S7). Moreover, compared with the DI values reported by previous studies, the DI values of coarse particles were comparable to those of more degraded materials (e.g., soil and POM in hemi-pelagic sediments), while the DI values of fine particles were close to those of "fresh" material (e.g., plankton, bacteria and sediment trap material) (Fig. 8Fig. 7Fig. 7Fig. 7Fig. 7), implying that AAs in coarse particles may undergo more bacterial degradation than fine particles. Our result is also comparable to that observed in precipitation at Uljin and Seoul (Yan et al., 2015). The DI values measured in coarse particles are closer to those observed in Seoul, where is believed to have more advanced bacterial degradation than Uljin.

In this study, Ala and Ile were ^{15}N enriched in coarse particles compared to fine particles. Similarly, recent study also observed the strong $\delta^{15}N$ shift of Ala and Ile is accompanied by the processes of bacterial heterotrophy (Calleja et al., 2013;Mccarthy et al., 2007). Moreover, there is no uni-directional depletion or enrichment of $\delta^{15}N$-AA distribution in the Trophic-AA group between fine and coarse particle samples. The $\delta^{15}N$-AA distribution in the Trophic-AA group is more "scattered" in coarse particles than that in fine particles. Specifically, in coarse particles, Ala and Leu were ^{15}N enriched and Pro was ^{15}N depleted than those in fine particles (Fig. 10Fig. 3Fig. 3Fig. 3). This "scattered" characteristic of $\delta^{15}N$-AA distribution in Tr-AA group of coarse particles may be due to the nitrogen fractionation occurred in microbial consumers selectively using Trophic-AA.

$\sum V$ could reflect the increasing trend of "scatting" $\delta^{15}N$ Trophic-AA pattern related to bacterial resynthesis (Calleja et al., 2013;Yamaguchi et al., 2017). Significantly increasing $\sum V$ values indicate organic material are more degraded by heterotrophic bacteria (Batista et al., 2014). In this study, the mean $\sum V$ value of fine particles was similar to or slightly higher than that measured in "fresh" materials (Mccarthy et al., 2007;Philben et al., 2018;Batista et al., 2014), while $\sum V$ values of coarse particles were equal to or even higher than those of more degraded materials (Fig. 12Fig. 9Fig. 9Fig. 9). Accordingly, the significant higher values of $\sum V$ measured in coarse particles than that in fine particles ($p<0.05$) (Fig. 5Fig. S6Fig. S6Fig. S6) may also imply more bacterial heterotrophic resynthesis occurred in coarse particles.

Despite the uncertainties surrounding oxidation, nitration and oligomerization of AAs in the atmosphere, main observations remain that the difference in $\delta^{15}N$ values of Source-AA (Gly, Ser, Phe and Lys) and total hydrolysable amino acids ($\delta^{15}N_{THAA}$) between coarse particles and fine particles was relatively small (Fig. 10Fig. 3Fig. 3Fig. 3). The average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰ (Fig. 11Fig. 4Fig. 4Fig. 4Fig. 4a). These results appear to contrast with what one might expect for AAs in either sizes particles undergo particularly more photochemical transformation than the other. Therefore, significantly lower DI values, "scattered" characteristic of $\delta^{15}N$ distribution in Tr-AA and higher $\sum V$ values observed in coarse particles in this study provide evidence that the difference in the THAA concentration and mol% composition distribution between fine and coarse particles may be related to AAs in coarse particles have stronger bacterial degradation state than those in fine particles.

4.3 Release of coarse "Fresh" bioparticles at the onset of the rainfall

A tight relationship between atmospheric bioaerosols and precipitation has been found by previous studies (Huffman et al., 2013;Yue et al., 2016). Since biological sources contain a large abundance of AAs (Ren et al., 2018), HAAs in aerosols can be used as tracer compounds to indicate the release of biological sources during precipitation. However, detailed size-resolved and time-resolved observation for the release of bioparticles initiated by precipitation are spare and the degradation state of different sizes bioparticles has never been examined.

It is expected that the concentrations of individual AAs in aerosol were assumed to decrease during rainfall events because of the high scavenging ratio of AAs in aerosol (Gorzelska and Galloway, 1990). In this study, form rain to dry periods, the concentrations of THAA for fine particles decreased ($p<0.05$)

(Fig. S1), but the concentration of THAAs for coarse particles displayed not significant change (p>0.05) (Fig. S1). Similar variation trends of different size particles following the precipitation were also observed by (Huffman et al., 2013). They also found the steep increase of coarse particles while low concentrations of fluorescent bioparticles and total aerosol particles were found in fine particles during the precipitation, suggesting the new released AAs during the precipitation are mainly distributed in coarse particles.

In addition, the large variations in the percentage of some HAA species (e.g., Pro, Ala, Val, Leu, Ile and Glu) were observed in coarse particles following the rainfall events, which imply the states of coarse particles measured during rain periods were different from the ones measured during dry periods (Fig. 3Fig. 2Fig. 2Fig. 2). This conclusion also supported by the variation of DI and ∑V values for coarse particles following rain events. From dry to rain periods, DI values in coarse aerosol particles were significant increased (p<0.05) but the ∑V value was significantly decreased (p < 0.05) (Fig. 7Fig. S7Fig. S7Fig. S7), suggesting more fresh AAs in coarse particles were released during rain events, whereas, on dry days AAs in coarse particles were more degraded.

Furthermore, we observed an obviously temporal variations of the concentration and mol% composition of HAA for coarse particles during the precipitation. At the onset of every rainfall events, the highest concentration of THAAs in coarse particles was observed. However, as the rainfall continued, the concentration of THAAs decreased rapidly. This temporal variation trend can attributed to the active release of these fresh biological aerosols caused by droplets splashing on porous medium are much stronger at the onset of rainfall events but with the rainfall continued, bioparticles in coarse particles were suppressed by rain scavenging (Joung and Buie, 2015;Huffman et al., 2013;Yue et al., 2016). Moreover, the mol% composition of HAA in coarse particles measured at the onset of every rainfall events were significantly different from that observed in the continued stage of rainfall events. The mol% composition of HAA in the continued stage of rainfall events were similar to that observed on dry days (Fig. 2). As we discussed above, AAs in coarse particles on dry days were more degraded. Therefore, we can conclude that those "fresh" protein matters are prone to release at the onset of the rainfall events and decayed swiftly with the precipitation continued.

54 Conclusions

2 weeks of daily aerosol samples in two size (>2.5μm and PM2.5) were measured. The significant difference was observed in the characteristics and distributions of AAs between fine and coarse particles. The concentrations of THAA in fine particles were significantly higher than that in coarse particles. A huge difference was also observed in the mol% compositions of THAAs between fine and coarse particle. For fine particles, Gly, Pro, Leu and Glu were the four most abundant compounds of the THAA pool, whereas for coarse particles, Pro were the most abundant THAA specie and Leu, Ala and Val were the next most abundant species.

Similar δ^{15}N-HAA pattern, closer $\delta^{15}N_{THAA}$ values and small offset of $\delta^{15}N_{THAA}$ value observed between fine and coarse particles indicates that AAs in fine and coarse particles might have the same sources. Moreover, the δ^{15}N values of hydrolyzed Gly and THAA for both fine and coarse fall within the ranges

~~of those measured in biomass burning, soil and plant sources suggested that atmospheric AAs for both fine and coarse particles were affected by these three emission sources.~~

~~The difference in $\delta^{15}N$ values of Source-AA and THAA between coarse particles and fine particles were small, implying AAs in fine and coarse particles may undergo the same degree of photochemical transformation. Using bacterial marker, we found that AAs in coarse particles may undergo more bacterial degradation than fine particles, which is supported by lower DI values, "scattered" $\delta^{15}N$ distribution in the Trophic-AA group and higher $\sum V$ values observed in coarse particles compared to fine particles.~~

~~By comparing the variation of DI and ∑V values for coarse particles following the precipitation, we propose that "fresh" protein matters distributed in coarse fraction are prone to release at the onset of the rainfall events.~~This size distribution of AAs can help understand its transformation and fate in the atmosphere. Therefore, verification of the different types, concentrations, origin and atmospheric processes of AAs distribution along the different air particle sizes is important and meaningful.

This study presents the first isotopic evidence that the sources of AAs for fine and coarse aerosol particles may be similar, all of which were influenced by biomass burning, soil, and plant sources. It is therefore that the huge difference in the concentrations and mol% compositions of THAAs between fine and coarse particles observed in this study is closely relevant to the degradation processes of AAs in aerosols.

Although the oxidation, nitrification and oligomerization processes of protein substances in the atmosphere have been widely reported, these abiotic photochemical aging processes that occur between fine particles and coarse particles have not been compared. In this study, the difference in $\delta^{15}N$ values of Source-AA (Gly, Ser, Phe and Lys) and total hydrolysable amino acids ($\delta^{15}N_{THAA}$) between coarse particles and fine particles was relatively small. The average offset of $\delta^{15}N_{THAA}$ value between fine and coarse particles was lower than 1.5‰. These results appear to contrast with what one might expect for AAs in either sizes particles undergo particularly more photochemical transformation than the other.

On the contrary, the degradation of atmospheric AAs in aerosols is rarely investigated. This is the first report of using degradation marker (DI) to investigate the degradation state of aerosol particles. Both composition profiles of HAA and concentrations of THAAs in aerosols are showed to be closely related to DI. And fine particles had significantly higher DI values than that of coarse particles ($p<0.05$), suggesting the degradation degree of amino acids in coarse particles is higher than that in fine particles. Combining new compound-specific nitrogen isotope tool ($\delta^{15}N$-HAA) and effective bacterial heterotrophy indicator ($\sum V$), "scattered" characteristic of $\delta^{15}N$ distribution in Tr-AA and higher $\sum V$ values were observed in coarse particles in this study, which firstly provide evidence that the stronger degradation state the found in coarse particles are coupled with more bacterial heterotrophic resynthesis occurred in coarse particles.

This study suggests the potentially significant role of bacterial degradation processes in concentration and composition of protein distribution in size-segregated aerosol particles. Since the degradation state of airborne protein distribution along size-segregated particles is closely linked to its biological availability, ecological processes and plant nutrition after deposition, further studies of quantitative assessment of this biological related process in aerosols should be conducted.

Author contributions. Ren-guo, Zhu., Zequn Wen and Yuwen Zhu designed the experiments, performed analyses, and analyzed the data. Hua-Yun Xiao were the principal investigators of the project that supported this work. All the authors have helped in the discussion of the results and collaborated in writing this article.

Acknowledgements. This work was supported by the National Natural Science Foundation of China (Grant No.41425014 and 41463007), Key Laboratory Project of Jiangxi Province (20171BCD40010) and Two 1000 Talents Plan Project of Jiangxi Province (S2018CQKJ0755). We are thankful to Global Weather and Climate Information Network (http://www.weatherandclimate.info/) for providing meteorological parameters include temperature (T) and relative humidity (RH), during the sampling period.

References

Amato, P., Demeer, F., Melaouhi, A., Fontanella, S., Martin-Biesse, A.-S., Sancelme, M., Laj, P., and Delort, A.: A fate for organic acids, formaldehyde and methanol in cloud water: their biotransformation by micro-organisms, Atmos. Chem. Phys. D., 7, 5253-5276, 2007.

Barbaro, E., Feltracco, M., Cesari, D., Padoan, S., Zangrando, R., Contini, D., Barbante, C., and Gambaro, A.: Characterization of the water soluble fraction in ultrafine, fine, and coarse atmospheric aerosol, Sci. Total Environ., 658, 1423-1439, https://doi.org/10.1016/j.scitotenv.2018.12.298, 2019.

Batista, F. C., Ravelo, A. C., Crusius, J., Casso, M. A., and McCarthy, M. D.: Compound specific amino acid δ15N in marine sediments: A new approach for studies of the marine nitrogen cycle, Geochim. Cosmochim. Acta, 142, 553-569, doi:10.1016/j.gca.2014.08.002, 2014.

Bauer, H., Kasper-Giebl, A., Löflund, M., Giebl, H., Hitzenberger, R., Zibuschka, F., and Puxbaum, H.: The contribution of bacteria and fungal spores to the organic carbon content of cloud water, precipitation and aerosols, AtmRe, 64, 109-119, doi:10.1016/S0169-8095(02)00084-4, 2002.

Bigg, E. K.: Sources, nature and influence on climate of marine airborne particles, Environ. Chem., 4, 155-161, doi:10.1071/EN07001, 2007.

Bol, R., Ostle, N. J., and Petzke, K. J.: Compound specific plant amino acid δ15N values differ with functional plant strategies in temperate grassland, J. Plant Nutr. Soil Sci., 165, 661-667, doi:10.1002/jpln.200290000, 2002.

Bowers, R. M., Clements, N., Emerson, J. B., Wiedinmyer, C., Hannigan, M. P., and Fierer, N.: Seasonal Variability in Bacterial and Fungal Diversity of the Near-Surface Atmosphere, Environ. Sci. Technol., 47, 12097-12106, doi:10.1021/es402970s, 2013.

Burdige, D. J.: Preservation of Organic Matter in Marine Sediments: Controls, Mechanisms, and an Imbalance in Sediment Organic Carbon Budgets?, Chem. Rev., 107, 467-485, doi: 10.1021/cr050347q, 2007.

Calleja, M. L., Batista, F., Peacock, M., Kudela, R., and McCarthy, M. D.: Changes in compound specific $\delta^{15}N$ amino acid signatures and d / l ratios in marine dissolved organic matter induced by heterotrophic bacterial reworking, Mar. Chem., 149, 32-44, doi:10.1016/j.marchem.2012.12.001, 2013.

Chikaraishi, Y., Ogawa, N. O., Kashiyama, Y., Takano, Y., Suga, H., Tomitani, A., Miyashita, H., Kitazato, H., and Ohkouchi, N.: Determination of aquatic food-web structure based on compound-specific nitrogen isotopic composition of amino acids, Limnol Oceanogr Methods, 7, 740–750, doi: 10.4319/lom.2009.7.740, 2009.

Dauwe, B., and Middelburg, J. J.: Amino Acids and Hexosamines as Indicators of Organic Matter Degradation State in North Sea Sediments, Limnol. Oceanogr., 43, 782-798, doi:10.4319/lo.1998.43.5.0782, 1998.

Dauwe, B., Middelburg, J. J. J. L., and Oceanography: Linking Diagenetic Alteration of Amino Acids and Bulk Organic Matter Reactivity, Limnol. Oceanogr., 44, 1809-1814, doi:10.4319/lo.1999.44.7.1809, 1999.

Després, V., Huffman, J. A., Burrows, S. M., Hoose, C., Safatov, A., Buryak, G., Fröhlich-Nowoisky, J., Elbert, W., Andreae, M., Pöschl, U., and Jaenicke, R.: Primary biological aerosol particles in the atmosphere: a review, Tellus B Chem Phys Meteorol, 64, 15598, 10.3402/tellusb.v64i0.15598, 2012.

Feltracco, M., Barbaro, E., Kirchgeorg, T., Spolaor, A., Turetta, C., Zangrando, R., Barbante, C., and

Gambaro, A., Free and combined L-and D-amino acids in Arctic aerosol, Chemosphere, 220, 412-421, doi:10.1016/j.chemosphere.2018.12.147, 2019.
Filippo, P. D., Pomata, D., Riccardi, C., Buiarelli, F., Gallo, V., and Quaranta, A.: Free and combined amino acids in size-segregated atmospheric aerosol samples, Atmos. Environ., 98, 179-189, doi:10.1016/j.atmosenv.2014.08.069, 2014.
Gorzelska, K., and Galloway, J. N.: Amine nitrogen in the atmospheric environment over the North Atlantic Ocean, Global Biogeochem. Cycles, 4, 309-333, doi:10.1029/GB004i003p00309, 1990.
Haan, D. O. D., Corrigan, A. L., Smith, K. W., Stroik, D. R., Turley, J. J., Lee, F. E., Tolbert, M. A., Jimenez, J. L., Cordova, K. E., and Ferrell, G. R.: Secondary Organic Aerosol-Forming Reactions of Glyoxal with Amino Acids, Environ. Sci. Technol., 43, 2818-2824, doi:10.1021/es803534f, 2009.
Huffman, J. A., Prenni, A. J., DeMott, P. J., Pöhlker, C., Mason, R. H., Robinson, N. H., Fröhlich-Nowoisky, J., Tobo, Y., Després, V. R., Garcia, E., Gochis, D. J., Harris, E., Müller-Germann, I., Ruzene, C., Schmer, B., Sinha, B., Day, D. A., Andreae, M. O., Jimenez, J. L., Gallagher, M., Kreidenweis, S. M., Bertram, A. K., and Pöschl, U.: High concentrations of biological aerosol particles and ice nuclei during and after rain, Atmos. Chem. Phys., 13, 6151-6164, doi:10.5194/acp-13-6151-2013, 2013.
Husárová, S., Vaïtilingom, M., Deguillaume, L., Traikia, M., Vinatier, V., Sancelme, M., Amato, P., Matulová, M., and Delort, A.-M.: Biotransformation of methanol and formaldehyde by bacteria isolated from clouds. Comparison with radical chemistry, Atmos. Environ., 45, 6093-6102, doi:10.1016/j.atmosenv.2011.06.035, 2011.
Jiang, Z., Liu, J., Chen, J., Chen, Q., Yan, X., Xuan, J., and Zeng, J.: Responses of summer phytoplankton community to drastic environmental changes in the Changjiang (Yangtze River) estuary during the past 50 years, Water Res., 54, 1-11, https://doi.org/10.1016/j.watres.2014.01.032, 2014.
Joung, Y. S., and Buie, C. R.: Aerosol generation by raindrop impact on soil, Nat. Commun., 6, 6083-6083, doi:10.1038/ncomms7083, 2015.
Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine aerosols, Mar. Chem., 96, 359-377, https://doi.org/10.1016/j.marchem.2005.03.007, 2005.
Leck, C., and Bigg, E. K.: Source and evolution of the marine aerosol—A new perspective, Geophys. Res. Lett., 32, doi: 10.1029/2005gl023651, 2005.
Leck, C., and Bigg, E. K.: Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer, Tellus B Chem Phys Meteorol, 57, 305-316, doi: 10.3402/tellusb.v57i4.16546, 2005.
Leck, C., and Keith Bigg, E.: Comparison of sources and nature of the tropical aerosol with the summer high Arctic aerosol, Tellus B Chem Phys Meteorol, 60, 118-126, doi: 10.1111/j.1600-0889.2007.00315.x, 2008.
Liu, F., Lai, S., Tong, H., Lakey, P. S. J., Shiraiwa, M., Weller, M. G., Pöschl, U., and Kampf, C. J.: Release of free amino acids upon oxidation of peptides and proteins by hydroxyl radicals, Anal. Bioanal. Chem., 409, 2411-2420, doi:10.1007/s00216-017-0188-y, 2017.
Mace, K. A., Artaxo, P., and Duce, R. A.: Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons, J. Geophys. Res.-Atmos, 108, doi:10.1029/2003JD003557, 2003.
Matos, J. T. V., Duarte, R. M. B. O., and Duarte, A. C.: Challenges in the identification and characterization of free amino acids and proteinaceous compounds in atmospheric aerosols: A critical review, Trends Analyt Chem, 75, 97-107, doi:10.1016/j.trac.2015.08.004, 2016.
Mcclelland, J. W., and Montoya, J. P.: Trophic relationships and the nitrogen isotopic composition of amino acids in plankton, Ecol., 83, 2173-2180, doi: 10.2307/3072049, 2002.
McCarthy, M. D., Benner, R., Lee, C., Hedges, J. I., and Fogel, M. L.: Amino acid carbon isotopic fractionation patterns in oceanic dissolved organic matter: an unaltered photoautotrophic source for dissolved organic nitrogen in the ocean?, Mar. Chem., 92, 123-134, doi:10.1016/j.marchem.2004.06.021, 2004.
Mccarthy, M. D., Benner, R., Lee, C., and Fogel, M. L.: Amino acid nitrogen isotopic fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved organic matter, Geochim. Cosmochim. Acta, 71, 4727-4744, doi:10.1016/j.gca.2007.06.061, 2007.
Mccarthy, M. D., Lehman, J., and Kudela, R.: Compound-specific amino acid δ 15 N patterns in marine algae: Tracer potential for cyanobacterial vs. eukaryotic organic nitrogen sources in the ocean, Geochim. Cosmochim. Acta, 103, 104-120, doi:10.1016/j.gca.2012.10.037 2013.
Papastefanou, C.: Residence time of tropospheric aerosols in association with radioactive nuclides, Appl. Radiat. Isot., 64, 93-100, doi:10.1016/j.apradiso.2005.07.006, 2006.
Philben, M., Billings, S. A., Edwards, K. A., Podrebarac, F. A., van Biesen, G., and Ziegler, S. E.: Amino acid δ 15 N indicates lack of N isotope fractionation during soil organic nitrogen decomposition,

Biogeochemistry, 138, 69-83, doi:10.1007/s10533-018-0429-y, 2018.
Ren, L., Bai, H., Yu, X., Wu, F., Yue, S., Ren, H., Li, L., Lai, S., Sun, Y., and Wang, Z.: Molecular composition and seasonal variation of amino acids in urban aerosols from Beijing, China, AtmRe, 203, 28-35, doi:10.1016/j.atmosres.2017.11.032, 2018.
Samy, S., Robinson, J., Rumsey, I. C., Walker, J. T., Hays, M. D., Robinson, J., Rumsey, I. C., and Hays, M. D.: Speciation and trends of organic nitrogen in southeastern U.S. fine particulate matter (PM2.5), J. Geophys. Res.-Atmos, 118, 1996-2006, doi:10.1029/2012JD017868, 2013.
Song, T., Wang, S., Zhang, Y., Song, J., Liu, F., Fu, P., Shiraiwa, M., Xie, Z., Yue, D., Zhong, L., Zheng, J., and Lai, S.: Proteins and Amino Acids in Fine Particulate Matter in Rural Guangzhou, Southern China: Seasonal Cycles, Sources, and Atmospheric Processes, Environ. Sci. Technol., 51, 6773-6781, doi:10.1021/acs.est.7b00987, 2017.
Wang, K., Chen, J. F., Jin, H. Y., Li, H. L., and Zhang, W. Y.: Organic matter degradation in surface sediments of the Changjiang estuary: Evidence from amino acids, Sci. Total Environ., 637, 1004-1013, doi:10.1016/j.scitotenv.2018.04.242, 2018.
Wang, S., Song, T., Shiraiwa, M., Song, J., Ren, H., Ren, L., Wei, L., Sun, Y., Zhang, Y., Fu, P., and Lai, S.: Occurrence of Aerosol Proteinaceous Matter in Urban Beijing: An Investigation on Composition, Sources, and Atmospheric Processes During the "APEC Blue" Period, Environ. Sci. Technol., 53, 7380-7390, doi:10.1021/acs.est.9b00726, 2019.
Wedyan, M. A., and Preston, M. R.: The coupling of surface seawater organic nitrogen and the marine aerosol as inferred from enantiomer-specific amino acid analysis, Atmos. Environ., 42, 8698-8705, doi:10.1016/j.atmosenv.2008.04.038, 2008.
Wei, K., Zou, Z., Zheng, Y., Li, J., Shen, F., Wu, C.-y., Wu, Y., Hu, M., and Yao, M.: Ambient bioaerosol particle dynamics observed during haze and sunny days in Beijing, Sci. Total Environ., 550, 751-759, doi:10.1016/j.scitotenv.2016.01.137, 2016.
Wei, M., Xu, C., Xu, X., Zhu, C., Li, J., and Lv, G.: Characteristics of atmospheric bacterial and fungal communities in PM2.5 following biomass burning disturbance in a rural area of North China Plain, Sci. Total Environ., 651, 2727-2739, doi:10.1016/j.scitotenv.2018.09.399, 2019.
Xu, Y., Wu, D., Xiao, H., and Zhou, J.: Dissolved hydrolyzed amino acids in precipitation in suburban Guiyang, southwestern China: Seasonal variations and potential atmospheric processes, Atmos. Environ., 2019.
Yamaguchi, Y. T., Chikaraishi, Y., Takano, Y., Ogawa, N. O., Imachi, H., Yokoyama, Y., and Ohkouchi, N.: Fractionation of nitrogen isotopes during amino acid metabolism in heterotrophic and chemolithoautotrophic microbes across Eukarya, Bacteria, and Archaea: Effects of nitrogen sources and metabolic pathways, Org. Geochem., 111, 101-112, doi:10.1016/j.orggeochem.2017.04.004, 2017.
Yamashita, Y., and Tanoue, E.: Distribution and alteration of amino acids in bulk DOM along a transect from bay to oceanic waters, Mar. Chem., 82, 145-160, doi:10.1016/S0304-4203(03)00049-5, 2003.
Yan, G., Kim, G., Kim, J., Jeong, Y.-S., and Kim, Y. I.: Dissolved total hydrolyzable enantiomeric amino acids in precipitation: Implications on bacterial contributions to atmospheric organic matter, Geochim. Cosmochim. Acta, 153, 1-14, doi:10.1016/j.gca.2015.01.005, 2015.
Yue, S., Ren, H., Fan, S., Sun, Y., Wang, Z., and Fu, P.: Springtime precipitation effects on the abundance of fluorescent biological aerosol particles and HULIS in Beijing, J. Sci. Res., 6, 29618, doi:10.1038/srep29618, 2016.
Zhang, Q., Anastasio, C., and Jimenez-Cruz, M.: Water-soluble organic nitrogen in atmospheric fine particles (PM2.5) from northern California, J. Geophys. Res.-Atmos, 107, AAC 3-1-AAC 3-9, doi:10.1029/2001JD000870, 2002.
Zhang, Q., Anastasio, C., Free and combined amino compounds in atmospheric fine particles (PM2.5) and fog waters from Northern California, Atmos. Environ., 37, 2247-2258, doi: 10.1016/S1352-2310(03)00127-4, 2003.
Zhu, R.-g., Xiao, H.-Y., Zhang, Z., and Lai, Y.: Compound-specific δ15N composition of free amino acids in moss as indicators of atmospheric nitrogen sources, J. Sci. Res., 8, 14347, doi:10.1038/s41598-018-32531-x, 2018.
Zhu, R.-g., Xiao, H.-Y., Zhu, Y., Wen, Z., Fang, X., and Pan, Y.: Sources and Transformation Processes of Proteinaceous Matter and Free Amino Acids in PM2.5, J. Geophys. Res.-Atmos, 125, e2020JD032375, doi:10.1029/2020jd032375, 2020.

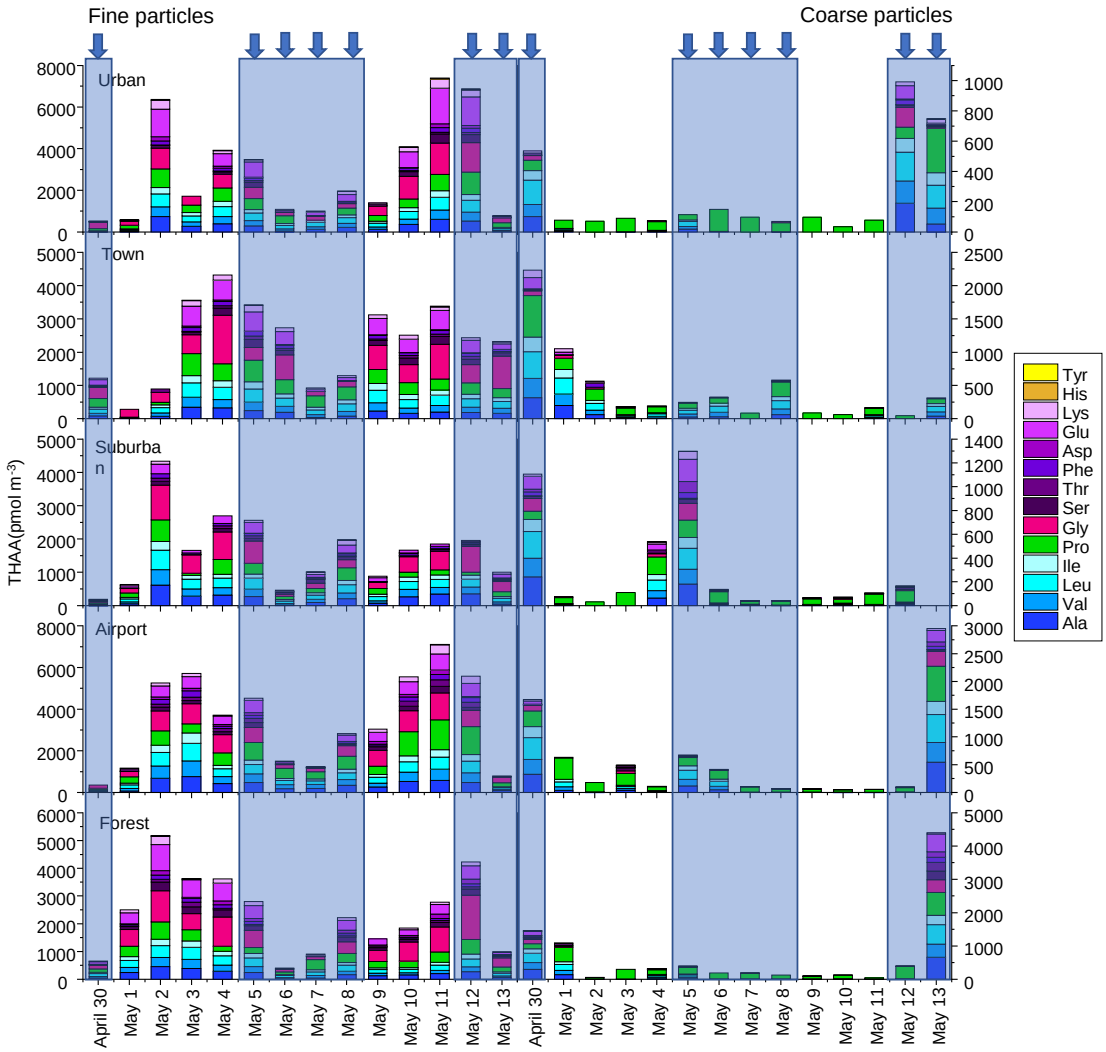


Figure1. Concentrations of hydrolyzed amino acids for fine and coarse particles in urban, town, suburban, airport and forest sites during 14 consecutive sampling days. The concentrations of HAAs for each sample were normalized for the total volume of air sampled. The blue arrow and shallow represent precipitation.

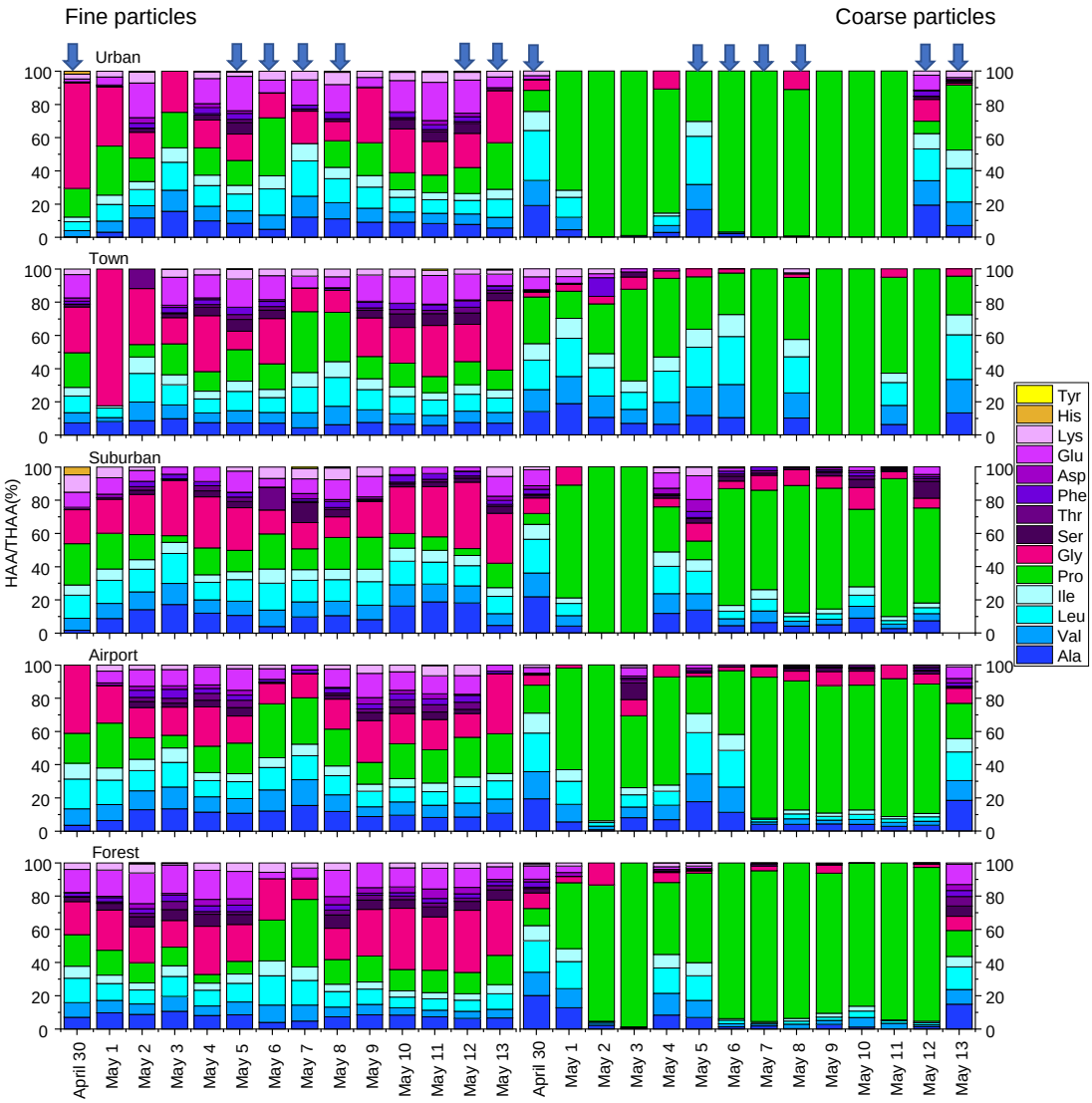


Figure 2. Percentage composition of each hydrolyzed amino acids (% of THAA) for fine and coarse aerosol particles in urban, town, suburban, airport and forest sites during 14 consecutive sampling days. The blue arrow represent precipitation.

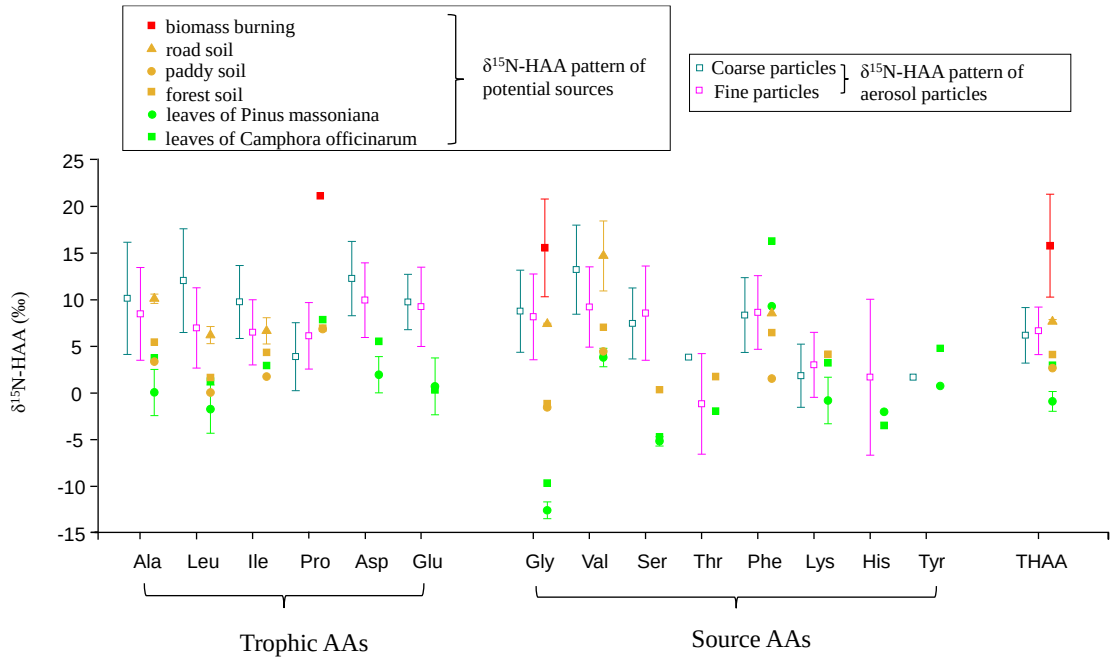


Figure 3. Comparison of δ^{15}N-HAA patterns of fine and coarse aerosol particles with that of potential local sources.

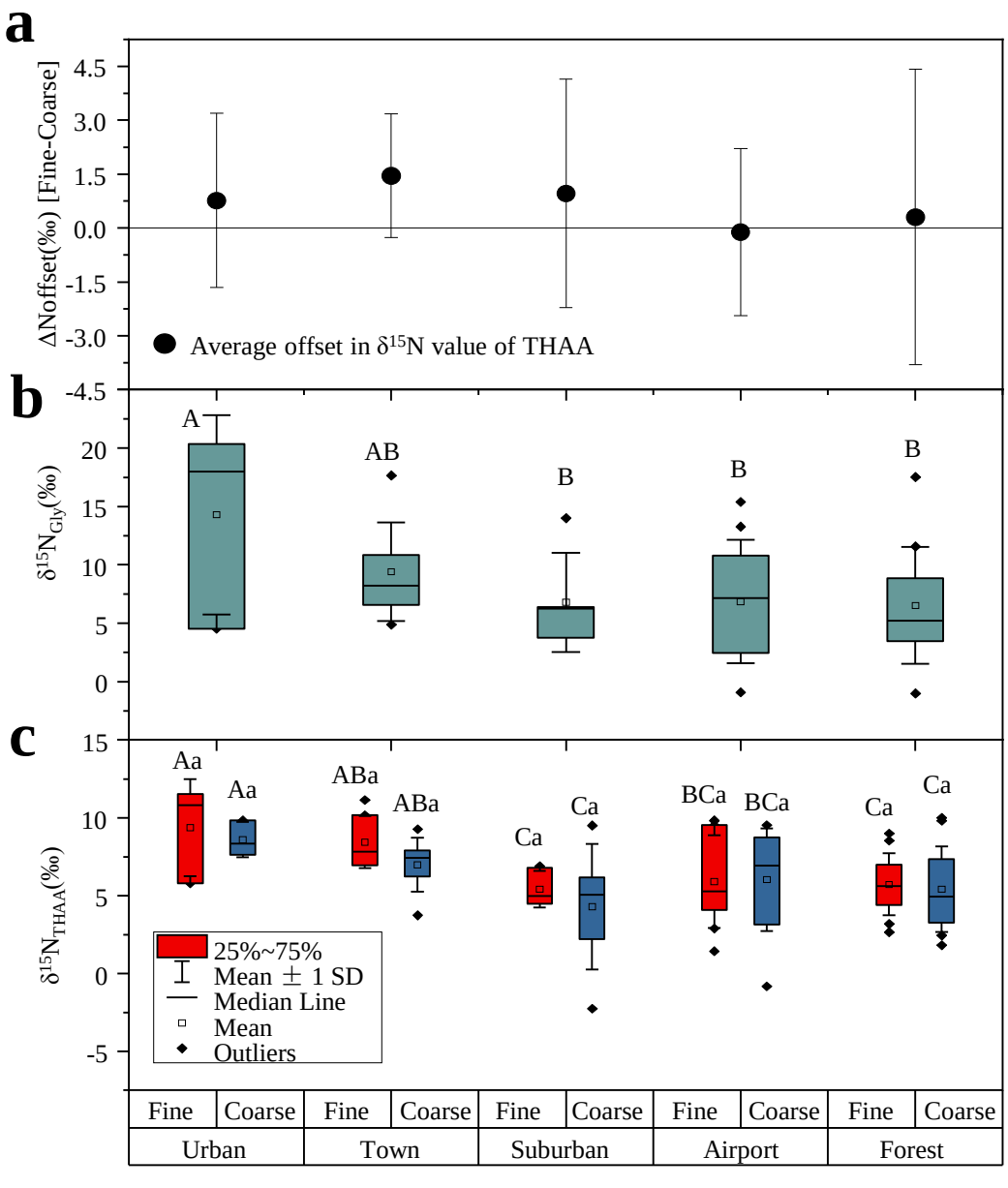


Figure 4. (a) The Offset of $\delta^{15}N_{THAA}$ values between fine and coarse particles; (b) The $\delta^{15}N_{Gly}$ values of fine particles; (c) The $\delta^{15}N_{THAA}$ values of fine and coarse particles in urban, town, suburban, airport and forest sites. Different uppercase letters denote means found to be statistically different (Tukey-HSD test) between sites. Different lower case letters denote a significant difference between fine and coarse particles. The error bars in (a) indicate the standard deviation.

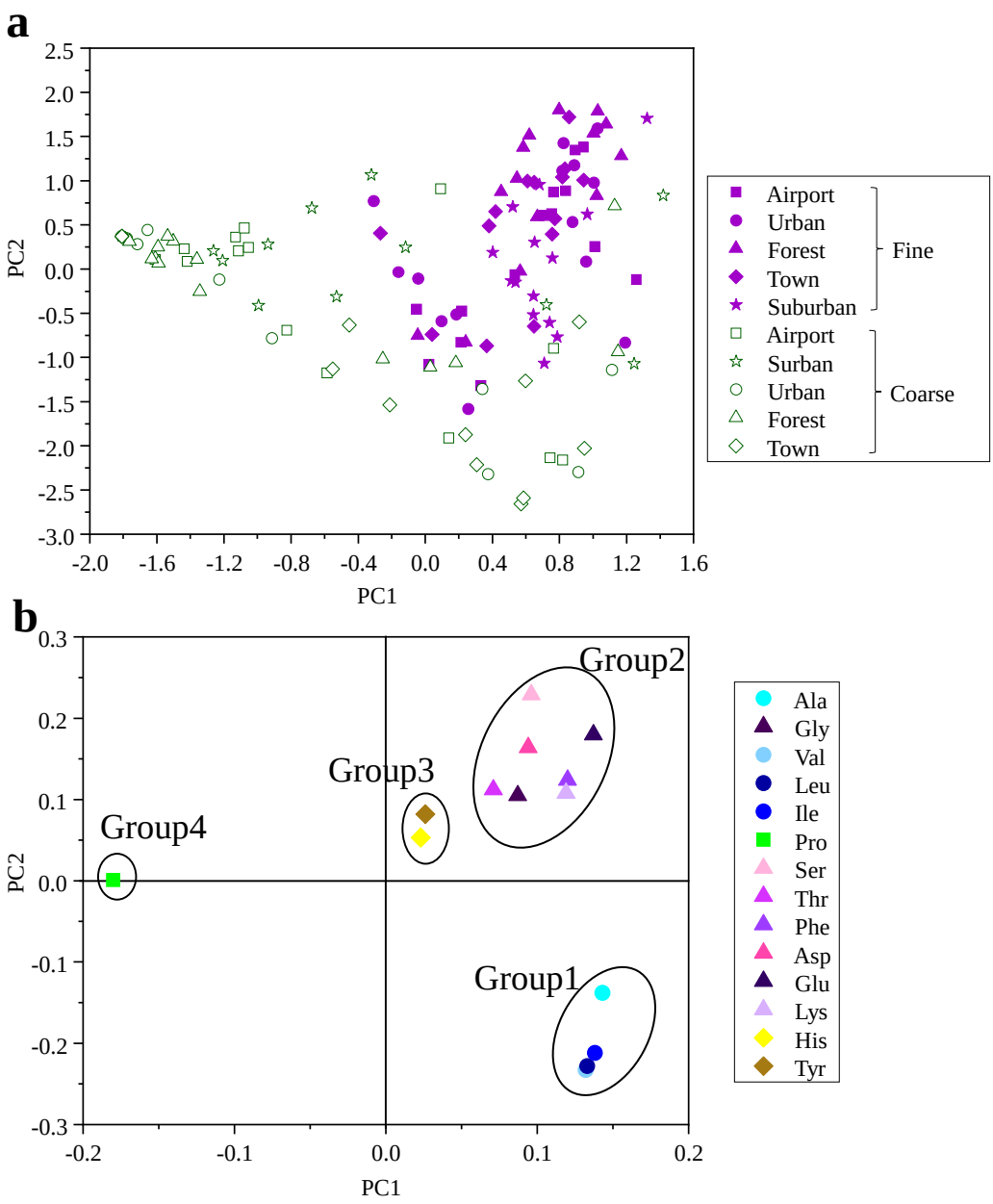


Figure 5. (a) Cross plot of the first and second component scores of PCA based on percentage composition (mol%) of hydrolyzed amino acid for fine and coarse particles. (b) Cross plot of factor coefficients of the first and second principal components of PCA. The lines enclosing each group of amino acid are arbitrarily drawn.

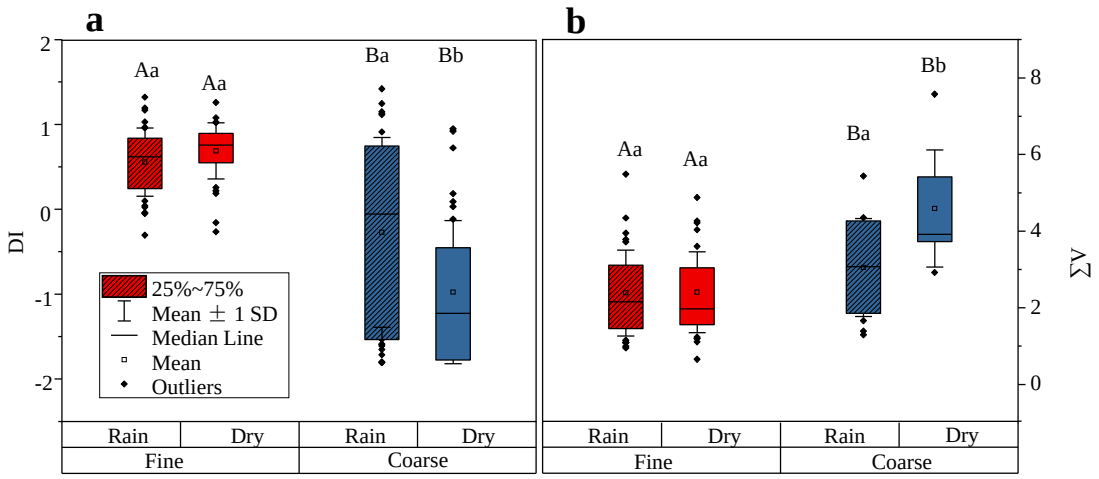


Figure 6. DI values (a) and (b) ∑V for fine (red box) and coarse (blue box) particles. The box encloses 50% of the data, the whisker is standard deviation of the data, the horizontal bar is the median, solid circles are outliers. The differences in means were statistically significant (two-way ANOVA, $p < 0.05$). Different uppercase letters denote means found to be statistically different (Tukey-HSD test) between fine and coarse particles. Different lower case letters denote means found to be statistically different (Tukey-HSD test) between rainy and dry days.

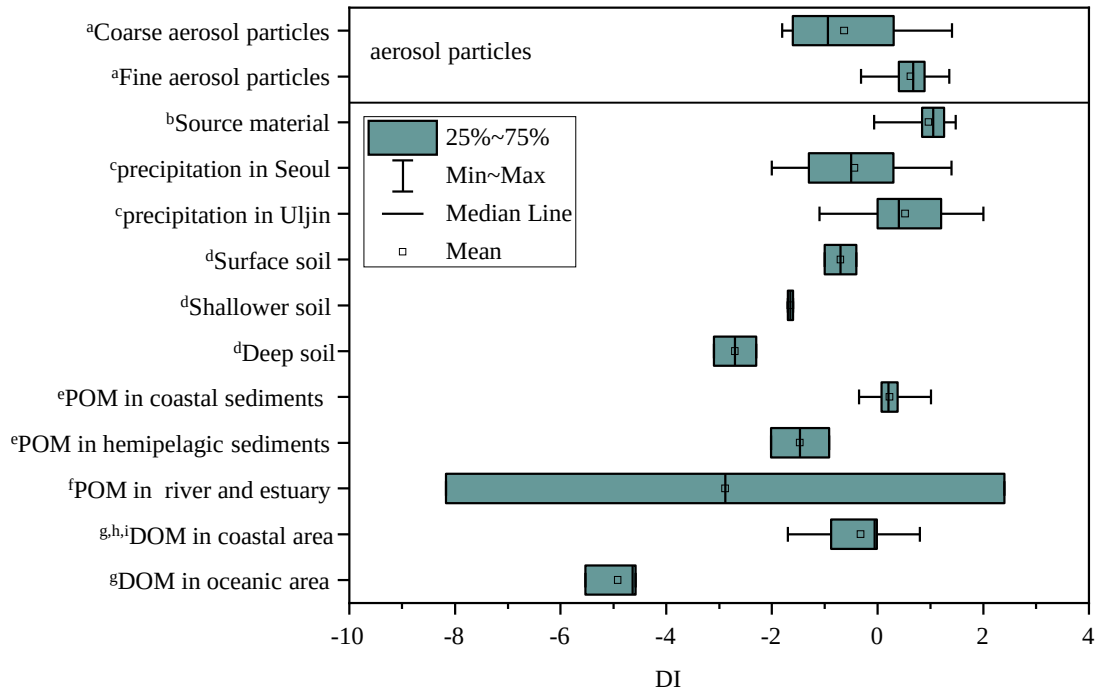
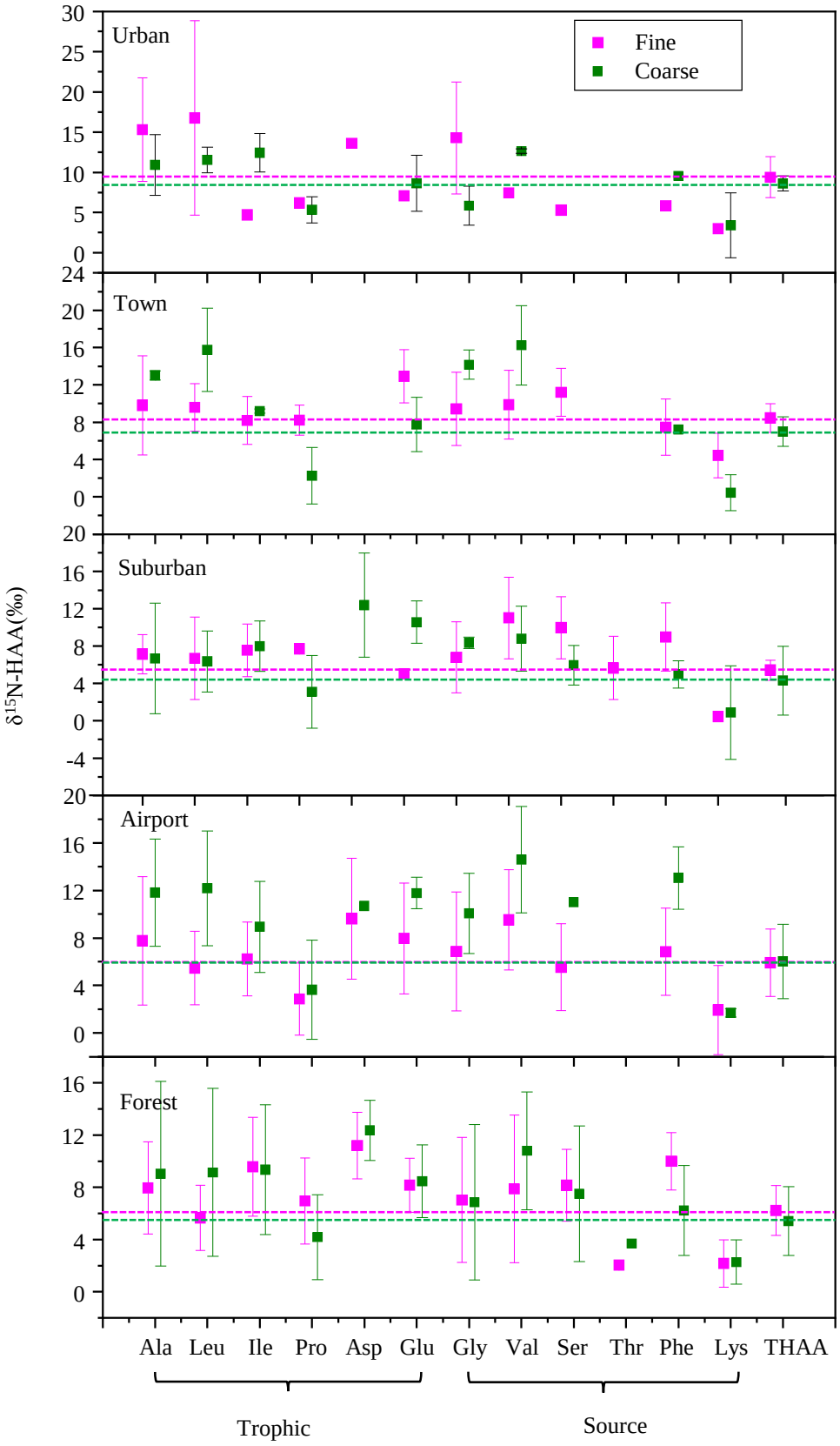


Figure 7. DI values of fine and coarse particles in comparison to other studies. a: this study. b: source materials including phytoplankton, bacteria, zooplankton and sediment trap material from Dauwe et al., 1999. c: Yan et al., 2015. d: Philben et al., 2015. e: particle organic matter from Mccarthy et al., 2007. f: Wang et al., 2018. g: Yamashita and Tanoue, 2003. h: Chen et al., 2016. i: Ji et al., 2019.



1255 Figure 8. δ^{15}N-HAA patterns of fine and coarse aerosol particles in urban, town, suburban, airport and forest sites.

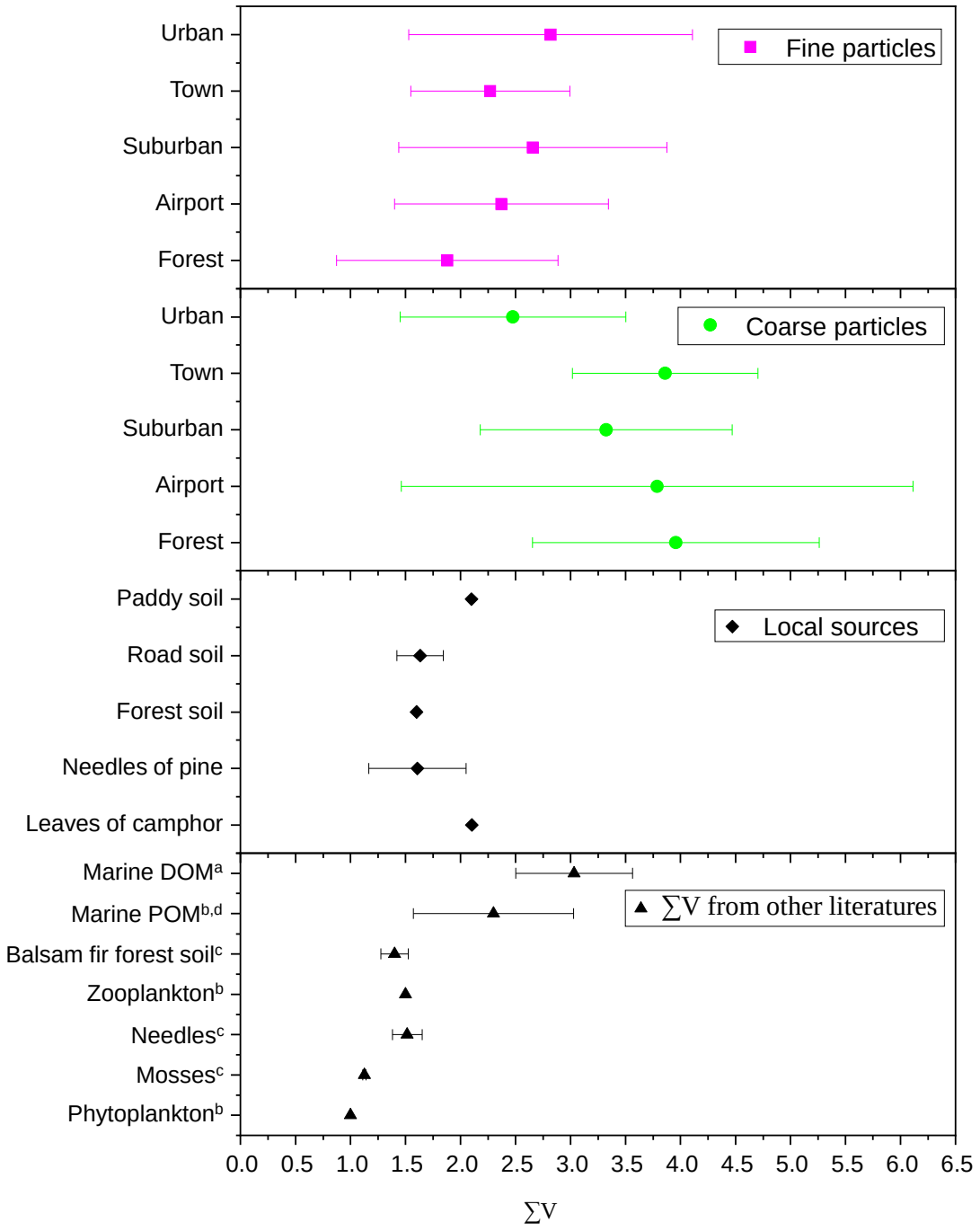


Figure 9. $\sum V$ values for fine and coarse particles in comparison to local natural sources and other studies. a: Calleja et al., 2013. b: Mccarthy et al., 2007. c: Philben et al., 2018. d: Batista et al., 2014.