Response to Anonymous Referee #1

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comments (comments in italics, responses in plain font; page numbers refer to the ACPD version; figures used in the response are labeled as Fig. R1, Fig. R2,…).

Comments and suggestions:

Authors basically reported the number concentrations of FAPs as FLx, where x is channel number. As shown as figures (e.g., Fig. 6), some FLx particles have a significant fluorescent intensity at a channel other than x. It is expected that the sum of FL1, FL2, and FL3 concentrations can exceed those of all FAPs (somewhat confusing). As WIBS has a function to detect wavelength-band fluorescence, the observed data sets can create automatically seven types (= 2^3- 1) of FAPs, where there is no overlap. Perring et al. (2015) presented this approach as authors also did as a part of the results. I recommend removing the descriptions on FLx typology and rearranging the data analysis of the seven-type FAPs at the first step to interpret how the FAPs concentrations varied during the observation period. This can improve the readability of the manuscript.

Responses and Revisions:

Good suggestion. In this study, we firstly reported the FAPs as FLx because this is the traditional method used in previous studies (Gabey et al., 2011; Healy et al., 2014), and the results can hence be comparable. However, as the referee suggested, we realized that it is a better way to focus on this seven-type instead of the FLx. Therefore, we have rearranged the structure of our paper:

In section 3.1, we will briefly report the number concentration of FLx and compare with previous studies, and their correlations with BC mass fraction are also introduced.

In section 3.2, we will show the classification of seven-type and analyze the number size distributions and diurnal variations.

Comments and suggestions:

Authors suggested the presence of "some other fluorophores" through the discussion on the comparison between non-combustion related FAPs at Nanjing and FAPs observed in other different "clean background" areas. As the atmospheric environment, ecosystem, human activities, and some other factors can greatly affect the emission of bioaerosols, the concentration levels of bioaerosols can be different

among places and not be necessarily same. To the best of my knowledge, no one knows the true values of bioaerosols concentrations at Nanjing. If there is no evidence to support this message, authors should remove this sentence and modify the sentence line 322-325.

Responses and Revisions:

In principle, the number concentration of bioaerosols is assumed to be higher in rainforests like Amazon and Borneo, being dominated by the biological activities. A previous study in Nanjing (Wei et al., 2015) also reported lower bioaerosols loading of 0.04 cm^{-3} on average, although the result might not be representative due to the different instrument (UV-APS) applied and the limited sampling time (2.3 hours). We therefore hypothesize that our observation is influenced by non-biological substances. We have revised this sentence:

"The number concentrations of the identified two types of bioaerosols (0.66 cm^{-3} for type C and 0.64 cm^{-3} for non-combustion-related type), however, were still higher than those observed in clean background areas and in the previous study in Nanjing (Wei et al., 2015), indicating they may also include some other non-biological fluorophores, such as dusts."

Comments and suggestions:

Authors only classified FL3 (type C, BC, AC, and ABC) particles into non-combustion related (NCR) and combustion-related (CR). Although type A, B, and AB particles, which consist of a large part of all FAPs, they are not included in the classification. Why did authors use only the fluorescent intensity at channel 3 (I3)? A simple way to see the correlation coefficient between specific type FAPs and BC/PM ratios suggests that type A and AB (type B) should be categorized into CR (NCR). If authors use only I3 information, they do not need to deploy WIBS, and simply should do UV-APS which has almost the same function. It is pity that important and useful information is not included in the data analysis presented in this paper.

I recommend as follows.

Please explain the benefits to deploy WIBS instead of UV-APS at Nanjing in this study if you use only I3 for the classification of FAPs.

A large fraction of FAPs, type A, B, and AB, should be considered and included into the classification.

Responses and Revisions:

The advantage of WIBS is in the 2×2 excitation (280 nm and 370 nm) and emission (310-400 nm and 420-650 nm) matrix, which provides additional dimensions of data evaluation. That's the reason why we used it in this study. Our analysis focused on

FL3 channel because this channel has been validated against other independent method. For example, Huffman et al., (2012) showed the relative placement and proportion of PBAP from SEM (scanning electron microscopy) analysis were very similar to that of PBAP from UV-APS in Amazon rainforest. The good agreement (R^2=0.78) between FL3 channel (WIBS) and UV-APS was also reported (Healy et al., 2014). We are not aware of similar validation for the other channels under ambient conditions. However, we followed the referee's suggestion to demonstrate the seven-type classification in the revised manuscript and included the similar analysis for I_{FL1} and I_{FL2} in the supplement.

Comments and suggestions:

PAHs emitted with BC through the incomplete combustion are originally in gas phase and subsequently can be scavenged by the preexisting surface of aerosol particles. Therefore, BC is one the carriers of PAHs. It is the fact that almost all of PAHs share the emission sources with BC. However, all the particles associated with PAHs cannot be combustion-generated, are just combustion-related. I recommend modifying the terminology of "combustion-generated".

Responses and Revisions:

Suggestion approved. We replaced "combustion-generated" by "combustion-related" in the revised manuscript.

Comments and suggestions:

Authors analyzed in detail the size-dependence of FL3 fraction classified by I3. To the best of my knowledge, Figure 9 is one the most important results in this study. Positive correlation of BC/PM and FL3 fraction was clear for the size range of 1-2 μm. I have some questions on the interpretation of the results as follows.

How did authors set the threshold value of I3, Icri? I'm confusing to see some findings in Figure 9 such as that the FL3 fraction for the size range of 4-5 μm with I3 > 18 was very weakly correlated with BC/PM and that the FL3 fraction for the size range of 5-15 μm with I3 > 18 (< 80) was positively but very weakly correlated with BC/PM. The former suggests the FL3 fraction for the size range of 4-5 μm with I3 > 18 can include the CR particles. The latter does that the FL3 fraction for the size range of 5-15 μm with 18 < I3 <80 can include the NCR particles. Especially, I could not understand that authors identify the FL3 particles for the size range of 5-15 μm with 18 < I3 <80 as CR particles. Please describe or guess what such huge combustion-related particles are. If not, we, the readers of this paper, will be confused.

Responses and Revisions:

In this study, we adopted the $M_{BC}/PM_{0.8}$ to assist the determination of I_{cri} because bioaerosols and combustion-generated FAPs are of different origins. Different I_{cri} values were scanned until the corresponding FAPs (intensity > I_{cri}) fraction showed a non-positive correlation with $M_{BC}/PM_{0.8.}$

We calculated the correlation coefficient for each I_{cri} in different size ranges. In practice, the correlations for these two groups of aerosol particles (4-5 μm, I_3>18 and 5-15 μm, 40 >I_{FL3}>18) are actually quite different. As shown in Fig. R1, a stronger correlation was found for the particles in the size range of 5-15 μm (R^2=0.98) than for particles in the size range of 4-5 μm (R^2=0.43). Thus we assume the particles in the size range of 4-5μm with I_3>18 are NCR particles.

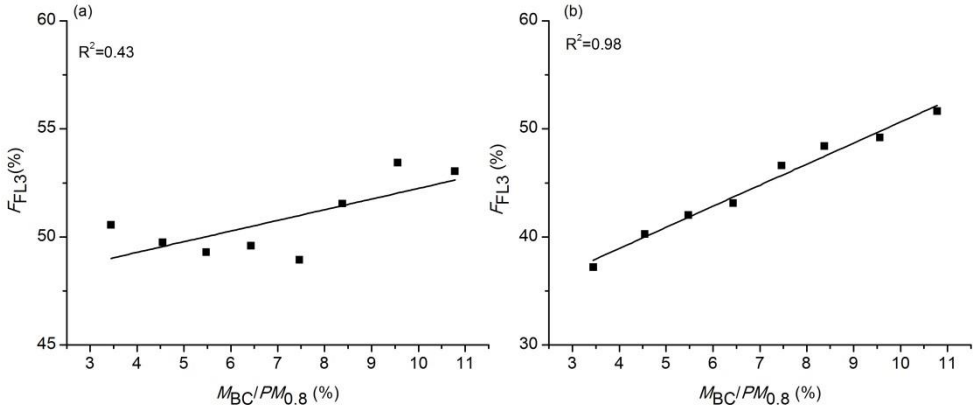

Figure R1. Correlations between FL3 fractions and $M_{BC}/PM_{0.8.}$ (a) Particles in the size range of 4-5 μm with I_{FL3}>18. (b) Particles in the size range of 5-15 μm with 40 >I_{FL3}>18.

Figure R2 shows the particle number size distributions from different sources. Our measurements revealed a coarse mode (D >1 μm) pattern that is similar to biomass burning particles (Hungershoefer et al., 2008). Both of them are dominated by the particles in the size range of 1-2 μm, with the fractions of 90% and 80% of the total number concentrations, respectively. On the contrary, particles from diesel vehicle emissions (Morawska et al., 1998) showed a different distribution in the coarse mode, and the contribution of particles in the size range of 1-2 μm was only 37%. Pöhlker et al. (2012) reported that interferent like PAHs, is particularly enriched on the surface of soot particles from biomass burning. Therefore a possible origin of these CR particles might be biomass burning.

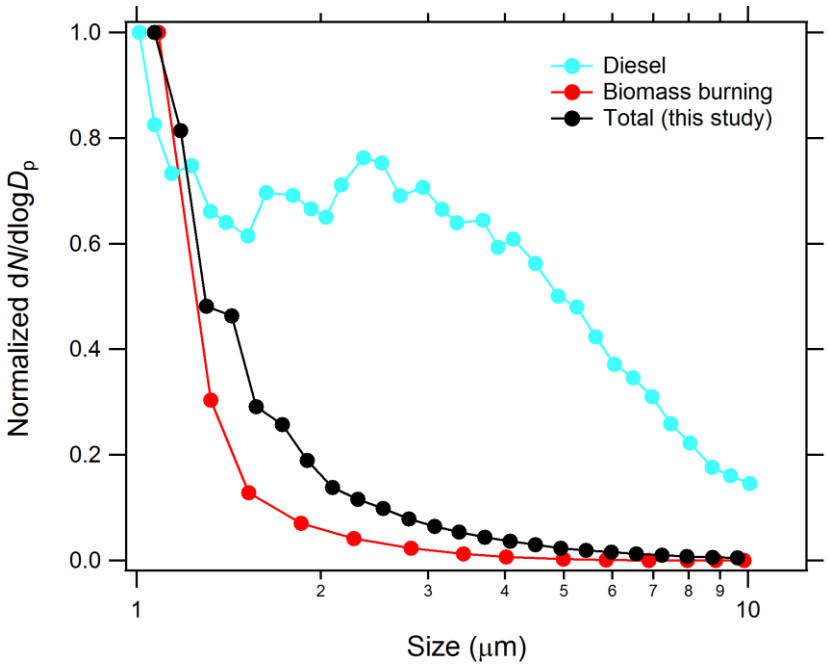

Figure R2. Comparisons of particle number size distributions from different sources.

Comments and suggestions:

In the section 3.1, authors showed the presence of CR particles which are FL2-related (type B, AB, BC, and ABC) and have the size of 4-5 μm. As the size ranges of CR particles defined in the section 3.3.2 were limited to 1-2 μm and 5-15 μm, the definition is inconsistent with the fact shown in the section 3.1. This can confuse the reader of this paper. Please recheck the assumptions and results and make the descriptions clearer.

Responses and Revisions:

The number size distribution of FL2 channel showed a peak at 3-4 μm, which was mainly contributed by type B particles (58%, Fig. R3b). Meanwhile, this peak showed a good correlation with $M_{BC}/PM_{0.8}$ (r=0.58). Therefore, the CR particles in FL2 channel actually indicated type B particles in 3-4 μm. We have included this info in the revised manuscript.

For the FL3 channel, there was no positive correlation between particles in the size range of 3-4 μm and $M_{BC}/PM_{0.8}$. We hence assigned these particles to NCR particles, which is different from FL2 channel. Also the good correlation suggested that the dominate CR particles are located between 1 and 2 μm in FL3 channel (r=0.82).

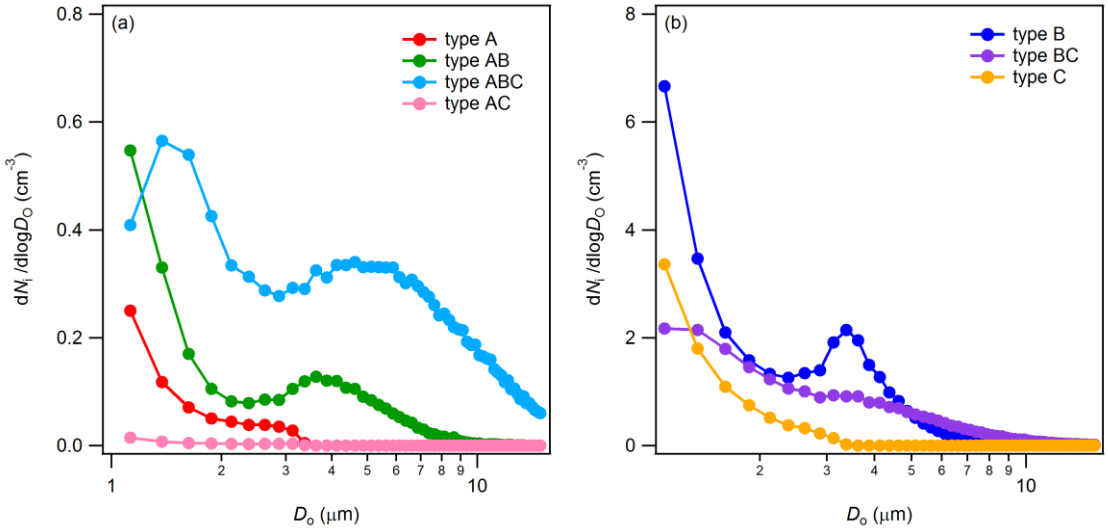

Figure R3. Mean number size distributions of (a) type A (red), type AB (green), type AC (pink) and type ABC (light blue); (b) type B (blue), type BC (purple) and type C (dark yellow).

Comments and suggestions:

Introduction: Line 56-57: Some of microorganisms cannot be cultivated. Please include this factor in the Introduction.

Responses and Revisions:

Suggestions approved. We have added this in the revised paper:
"These methods are time-consuming and their results may differ depending on the cultivation condition and procedures, especially considering the ubiquity of microorganisms that cannot be cultivated (Oliver, 2005; Pöhlker et al., 2012)."

Comments and suggestions:

Line 60-74: This paragraph is lengthy. Some details of the technical specification of commercial are not necessarily included in "Introduction" and those of WIBS should be moved into the experimental section. Why did authors include only the commercial one? Some custom-made UV-LIF instruments have ever been developed in previous studies such as Pan et al. (2009; 2011), Taketani et al. (2013), and Miyakawa et al. (2015). For the purpose to introduce the previous studies, authors should include more widely the UV-LIF techniques.

Responses and Revisions:

We have modified this in the revised paper:
"Since most biological materials contain fluorophores, instruments based on the

fluorescence detection, such as UV-APS (Ultraviolet Aerodynamic Particle Sizer; Brosseau et al., 2000), WIBS (Wideband Integrated Bioaerosol Spectrometer) and other custom-made instruments based on LIF (laser/light induced fluorescence) technology (Pan et al., 2009; Taketani et al., 2013; Miyakawa et al., 2015) have recently been developed for automatic online measurements of PBAPs..."

Comments and suggestions:

Instruments: What is the upper limit of the particle number concentrations that WIBS-4A can accurately measure? Based on OPC-like techniques, very high concentrations can affect the counting efficiency through the coincidence error. Please clarify whether WIBS-4A works well in such highly polluted region.

Responses and Revisions:

WIBS-4A can measure particles up to ~2×10^4 L^{-1}. Our measurements showed that the number concentration of FAPs was ~ 1.5×10^4 L^{-1} in Nanjing, which is within the upper limit. Meanwhile, the results showed a good agreement between WIBS and APS（R^2=0.9）at another polluted regional site around Beijing, indicating its application in highly polluted regions.

Comments and suggestions:

Line 144-146: The "ratio" approach can minimize the effects of some processes such as diurnal variations of PBL height and air mass dilution. To the best of my knowledge, this should be valid assuming no additional formation and loss process for both numerator and denominator species. Please clarify whether this assumption is valid.

Responses and Revisions:

The effects of variations of PBL height and air mass dilution should be similar for all kinds of species. For example, if we assume the values of M_{BC} and $PM_{0.8}$ are A and 10A, respectively. The mass fraction of BC ($M_{BC}/PM_{0.8}$) was 10% (A/10A=10%), and this fraction won't change due to the effect of PBL dilution in the case of no additional formation/loss processes for BC and fine particles. However, if there is a combustion source nearby, which can contribute the same additional amount of BC (A). Then the value of $M_{BC}/PM_{0.8}$ is 18% ($\frac{A+A}{10A+A}=18\%$), and this enhancement can reflect the combustion emission process. In other words, the additional source will strongly influence the numerator, while the denominator won't change a lot, resulting in the significant variation of ratio (relative fraction). Back to our case, we compared

the number fraction of FAPs with $M_{BC}/PM_{0.8}$, which both minimize the PBL influence, and the good correlation indicates a large contribution of combustion-generated aerosols to FAPs.

Comments and suggestions:

Line 184-195: Miyakawa et al. (2015) did not use similar technique. They used a multivariate analysis of the temporal variations of number concentrations of 8 type FAPs. This sentence is very confusing. This previous study should be included in "Introduction", because the results shown there closely relate to this study.

Responses and Revisions:

We have now included this technique in the introduction:
"Since most biological materials contain fluorophores, instruments based on the fluorescence detection, such as UV-APS (Ultraviolet Aerodynamic Particle Sizer) (Brosseau et al., 2000), WIBS (Wideband Integrated Bioaerosol Spectrometer) and other custom-made instruments based on the LIF (Laser induced fluorescence) technology (Pan et al., 2009; Taketani et al., 2013; Miyakawa et al., 2015), have recently been developed for online measurements of PBAPs."
The data analysis method has now been included in section 3.1:
"Miyakawa et al. (2015) had used factor analysis based on carbon monoxide, elemental carbon and other markers (using concentration instead of ratio) to identify "combustion-type" and "dust-type" aerosols in urban areas."

Comments and suggestions:

Line 200-212: Please clarify what fluorescent compound I and II are. Are they representative compound for the combustion- and non-combustion-related aerosols? Unless they are, I have an impression that authors picked up some compounds to well account for the observation results.

Responses and Revisions:

Compound I and II are tryptophan and pyrene, respectively. The former one is an amino acid (biological compound) and the latter one belongs to the group of PAHs (combustion-related compounds). In principle, we preliminarily distinguish compounds according to their disparate excitation-emission matrix profile.

Comments and suggestions:

Line 213-230: As noted in "Major comments", if you use only I3 signal, the information on type A, B, and AB particles should be ignored. Please consider some modification to the approach (See the "Major comments" for details).

Responses and Revisions:

We now have added FL1 and FL2 channel classification in the supplement.

Comments and suggestions:

Some sentences should be modified according to the revision. The last paragraph should be removed or moved to the discussion part, because all the descriptions are speculative, not suggested solely based on this study, and should not be discussed in Summary.

Responses and Revisions:

The last section of the last paragraph includes some conclusive remarks based on the findings (observations and data retrieval/evaluation methods) of our study, constraining current technical shortcomings and perspective. We think this is well suited in the conclusions. This way, we now re-titled this section as "Conclusions".

Comments and suggestions:

Line 63-64: UV-APS use the UV-laser for exciting the particles, so here UV-Laser induced fluorescence (UV-LIF) is correct.

Responses and Revisions:

Corrected.

Comments and suggestions:

Line 79: Miyakawa et al. (2015) deployed a custom-made UV-LIF instrument (not UV-APS and WIBS).

Responses and Revisions:

We now better explicate in the revised manuscript:
"Since most biological materials contain fluorophores, instruments based on the fluorescence detection, such as UV-APS (Ultraviolet Aerodynamic Particle Sizer; Brosseau et al., 2000), WIBS (Wideband Integrated Bioaerosol Spectrometer) and other custom-made instruments based on the LIF (laser/light induced fluorescence) technology (Pan et al., 2009; Taketani et al., 2013; Miyakawa et al., 2015) have recently been developed for automatic online measurements of PBAPs…."

Comments and suggestions:

Line 107: Is the silica gel dryer TSI's one or custom-made? If this is TSI's one, particle transmission efficiency for the coarse mode particles is not so good depending the sampling flow rate. If custom made, please clarify how authors locate it in front of WIBS-4A. The direction of flow in the dryer should be parallel to the sampling line.

Responses and Revisions:

The silica gel dryer is custom-made. It was installed vertically above the WIBS-4A. So the particle loss due to the gravity settling can hence be neglected. In the revised manuscript, we have clarified this:
"A 0.75 inch stainless-steel tube inlet was installed ~3 m above the roof, and sample air was dried by a vertical silica gel drier prior to entering the WIBS."

Comments and suggestions:

Line 118: Why did authors show approximate value of the size of a PSL particle (~2 μm)? Please provide the exact sizes and type (Sample bottle has) of PSL particles given by Duke Scientific.

Responses and Revisions:

We have included this in the revised manuscript:
"During the measurement period, we used 1 μm and 2 μm fluorescent and non-fluorescent PSL microspheres (3K-990, B0100, 4K-02 and B0200, Duke Scientific, Inc.) for calibration."

Comments and suggestions:

Line 130: PM800 is confusing. We traditionally label the subscript of PM (particulate matter) based on the size cut in "micrometer". Please modify PM800 into PM0.8.

Responses and Revisions:

Corrected.

Comments and suggestions:

Figure 10: I feel this figure is meaningless because Tables 2, 3, and 4 covers what this figure illustrates.

Responses and Revisions:

Yes. We have deleted this figure in the revised manuscript.

References

Brosseau, L. M., Vesley, D., Rice, N., Goodell, K., Nellis, M., and Hairston, P.: Differences in Detected Fluorescence Among Several Bacterial Species Measured with a Direct-Reading Particle Sizer and Fluorescence Detector, Aerosol Sci. Technol., 32, 545-558, 10.1080/027868200303461, 2000.

Gabey, A. M., Stanley, W. R., Gallagher, M. W., and Kaye, P. H.: The fluorescence properties of aerosol larger than 0.8 μm in urban and tropical rainforest locations, Atmos. Chem. Phys., 11, 5491-5504, 10.5194/acp-11-5491-2011, 2011.

Healy, D. A., Huffman, J. A., O'Connor, D. J., Pöhlker, C., Pöschl, U., and Sodeau, J. R.: Ambient measurements of biological aerosol particles near Killarney, Ireland: a comparison between real-time fluorescence and microscopy techniques, Atmos. Chem. Phys., 14, 8055-8069, 10.5194/acp-14-8055-2014, 2014.

Huffman, J. A., Sinha, B., Garland, R. M., Snee-Pollmann, A., Gunthe, S. S., Artaxo, P., Martin, S. T., Andreae, M. O., and Pöschl, U.: Size distributions and temporal variations of biological aerosol particles in the Amazon rainforest characterized by microscopy and real-time UV-APS fluorescence techniques during AMAZE-08, Atmos. Chem. Phys., 12, 11997-12019, 10.5194/acp-12-11997-2012, 2012.

Hungershoefer, K., et al.: Modelling the optical properties of fresh biomass burning aerosol produced in a smoke chamber: results from the EFEU campaign, Atmos. Chem. Phys., 8, 3427-3439, 10.5194/acp-8-3427-2008, 2008.

Miyakawa, T., Kanaya, Y., Taketani, F., Tabaru, M., Sugimoto, N., Ozawa, Y., and Takegawa, N.: Ground-based measurement of fluorescent aerosol particles in Tokyo in the spring of 2013: Potential impacts of nonbiological materials on autofluorescence measurements of airborne particles, J. Geophys. Res. Atmos., 120, 1171-1185, 10.1002/2014jd022189, 2015.

Morawska, L., Bofinger, N. D., Kocis, L., and Nwankwoala, A.: Submicrometer and Supermicrometer Particles from Diesel Vehicle Emissions, Environ Sci Technol, 32, 2033-2042, 10.1021/es970826+, 1998.

Oliver, J. D.: The viable but nonculturable state in bacteria, J Microbiol, 43, 93-100, 2005.

Pan, Y.-L., Pinnick, R. G., Hill, S. C., and Chang, R. K.: Particle-Fluorescence Spectrometer for Real-Time Single-Particle Measurements of Atmospheric Organic Carbon and Biological Aerosol, Environ. Sci. Technol., 43, 429-434, 10.1021/es801544y, 2009.

Pöhlker, C., Huffman, J. A., and Pöschl, U.: Autofluorescence of atmospheric bioaerosols – fluorescent biomolecules and potential interferences, Atmos. Meas. Tech., 5, 37-71, 10.5194/amt-5-37-2012, 2012.

Taketani, F., Kanaya, Y., Nakamura, T., Koizumi, K., Moteki, N., and Takegawa, N.: Measurement of fluorescence spectra from atmospheric single submicron particle using laser-induced fluorescence technique, J. Aerosol Sci., 58, 1-8, http://dx.doi.org/10.1016/j.jaerosci.2012.12.002, 2013.

Wei, K., Zheng, Y., Li, J., Shen, F., Zou, Z., Fan, H., Li, X., Wu, C.-y., and Yao, M.: Microbial aerosol characteristics in highly polluted and near-pristine environments featuring different climatic conditions, Science Bulletin, 60, 1439-1447, 10.1007/s11434-015-0868-y, 2015.