A new method to quantify mineral dust and other aerosol species from aircraft platforms using single particle mass spectrometry

Major Comments:

Previous attempts to scale SPMS data to tandem measurements should be describe in more detail in the introduction and in section 3.6. The authors described the work of Qin et al., (2006) as an attempt to scale SPMS data with pre-defined quantitative concentration obtained in controlled conditions (P13L26) , when it was in fact scaled to co-located APS measurements (with an hourly average). The same approach was used more recently to obtain mass concentration with the ATOFMS (Gunsch et al., 2018) which should also be referenced as an example of obtaining absolute concentration by size scaling. On the other hand, Marsden et al., (2016) compared data rates from a LAAPTOF with an APS and concluded an over-estimation in the relative fraction of sea-spray aerosol with respect to mineral dust due to instrument function and did not attempt to derive absolute concentration because of unquantified uncertainties. Subsequently, Shen et al., (2018) has defined composition resolved overall detection efficiency (ODE) for the LAAPTOF and has demonstrated that number fraction of compositional classes in ambient data could be incorrect by an order of magnitude in the uncorrected data (Shen et al., 2019).

Although all the above studies involved ground data, the same principals would apply to aircraft versions of these instruments. It maybe the unique design of the PALMS instrument does not suffer from such composition bias, but no evidence is offered in this manuscript. The chemical bias is described here as 'minimal' (P4L29) due to the particle hit rate of 90%, but does this apply to all particle types at all sizes? There is no reference to data. This discussion is necessary if the method is transferred to other instrument designs as the number fractions bias will be scaled to the absolute concentration. Marsden et al., (2018) showed that the spectral hit rate of mass selected mineral dust can vary by a factor of 2 due to mineralogy (not size transmission), therefore size scaling alone is insufficient. The absorbing characteristics of the particle at the ablation wavelength is an important factor. This should be discussed in the introduction, method and conclusion.

Another area of concern is the lack of discussion surrounding particle classification techniques and errors that arise due to matrix effects and complex particle mixing state. The PALMS system has a well-established classification scheme that need not be reviewed in detail here, but some acknowledgement of different result produced by different techniques should be offered with respect to the literature, particularly regarding ion mode of the TOFMS.

Hatch et al., (2014) showed that particle ageing can affect ATOFMS hit-rates and signal fractions in spectra of ambient particles. The core shell structure of coated particles was an important consideration when interpreting instrument response to organics and sulfate . I think this work should be referenced in Section 3.7 and some discussion of how well laboratory generated proxies represents internally mixed ambient particles using the relative ionisation efficiency method. Is a binary system (organic vs sulfate) sufficient in ambient particles with complex mixing state and structure? Marsden et al., (2019) argued for a ternary system with internally mixed dust. Also, a comparison of organic concentrations is missing in section 4.1 (A comparison of sulfate is given). This important as it was the comparison organic comparison with AMS that was the most uncertain in Hatch et al., (2014).

Finally, please consider revising the structure of the methods section. For example, is a detailed description of the campaigns necessary for the understanding of this method? Would a table featuring the important parameters be sufficient? A summary paragraph under the section 2 main header would be helpful.

Minor Comments:

P1L20 The abstract could be consolidated, the particle types/classes are partially repeated from the paragraph above.

P1L34 The use of a virtual impactor to enhance sampling statistics is not demonstrated or discussed in any depth. Please add a section on this or remove form the abstract.

P2L13 This sentence could suggest (to a non-expert) that a single particle is ionised.

P2L30 Shen (2019) does discuss uncertainties in derived concentrations and also includes mineral dust.

P2L35 There are several topics of discussion in this paragraph that do not sit well together.

P3L18 There is a jump between mass concentration measurement and particle number counting in this paragraph that makes it a little incoherent.

P4L7 What particle size spectrometers? Not yet introduced.

P4 L10 The AMS instrument has not been introduced or defined.

P4 L11 SAGA inlet filters has not been introduced or defined.

P4L13 There is switch to a different campaign mid-paragraph.

P4L29 Is there a data or a reference for the hit-rate performance? How minimal is the chemical bias on the PALMS system.

P4L33 A summary of the post-processing method would be useful here.

P5L31 “The atmosphere consists of an external mixture of particle types” Is this conclusion or an argument? Maybe reword this sentence.

P9L26 Can you give a reference for the abundance of pure hematite in the atmosphere?

P14L25 Is the organic signal fraction calculated from peak area? Which peaks were used to do the calculation?

P15L10 An explanation of why mixing with sea-salt and mineral dust is not included. Potential matrix effects?

P16L5 I find the description of the mineral dust concentration (section 4.2) rather brief for a paper that has mineral dust in the title.

P16L15 The opening paragraph to the summary should be specific about what is new about the method i.e. the integrated size bins.

P17L14 What are concentration products?

P17L18 Not sure what are recommendation and what are general conclusions in this list.

References

Gunsch, M. J., May, N. W., Wen, M., Bottenus, C., Gardner, D. J., Vanreken, T. M., Bertman, S. B., Hopke, P. K., Ault, A. P. and Pratt, K. A.: Ubiquitous influence of wildfire emissions and secondary organic aerosol on summertime atmospheric aerosol in the forested Great Lakes region, Atmos. Chem. Phys., 18(5), 3701–3715, doi:10.5194/acp-18-3701-2018, 2018.

Hatch, L. E., Pratt, K. a., Huffman, J. A., Jimenez, J. L. and Prather, K. a.: Impacts of Aerosol Aging on Laser Desorption/Ionization in Single-Particle Mass Spectrometers, Aerosol Sci. Technol., 48(10), 1050–1058, doi:10.1080/02786826.2014.955907, 2014.

Marsden, N., Flynn, M. J., Taylor, J. W., Allan, J. D. and Coe, H.: Evaluating the influence of laser wavelength and detection stage geometry on optical detection efficiency in a single-particle mass spectrometer, Atmos. Meas. Tech., 9(12), 6051–6068, doi:10.5194/amt-9-6051-2016, 2016.

Marsden, N. A., Flynn, M. J., Allan, J. D. and Coe, H.: Online differentiation of mineral phase in aerosol particles by ion formation mechanism using a LAAP-TOF single-particle mass spectrometer, Atmos. Meas. Tech., 11(1), 195–213, doi:10.5194/amt-11-195-2018, 2018.

Marsden, N. A., Ullrich, R., Möhler, O., Eriksen Hammer, S., Kandler, K., Cui, Z., Williams, P. I., Flynn, M. J., Liu, D., Allan, J. D. and Coe, H.: Mineralogy and mixing state of north African mineral dust by online single-particle mass spectrometry, Atmos. Chem. Phys., 19(4), 2259–2281, doi:10.5194/acp-19-2259-2019, 2019.

Qin, X., Bhave, P. V. and Prather, K. A.: Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements, Anal. Chem., 78(17), 6169–6178, doi:10.1021/ac060395q, 2006.

Shen, X., Ramisetty, R., Mohr, C., Huang, W., Leisner, T. and Saathoff, H.: Laser ablation aerosol particle time-of-flight mass spectrometer (LAAPTOF): Performance, reference spectra and classification of atmospheric samples, Atmos. Meas. Tech., 11(4), 2325–2343, doi:10.5194/amt-11-2325-2018, 2018.

Shen, X., Saathoff, H., Huang, W., Mohr, C., Ramisetty, R. and Leisner, T.: Understanding atmospheric aerosol particles with improved particle identification and quantification by single-particle mass spectrometry, Atmos. Meas. Tech., 12(4), 2219–2240, doi:10.5194/amt-12-2219-2019, 2019.