Response to Referee 2

This manuscript describes an analytical mass spectrometry-based method to measure refractory salts of sodium and potassium or atmospheric relevance. This work represents a useful advance for atmospheric measurements of these species, which are difficult or impossible to measure with current online instrumentation and often require slower, more labor-intensive offline analysis. The manuscript is well-written and straightforward, and I recommend it be published.

We would like to thank the referee very much for giving us valuable comments and suggestions. We have revised the manuscript to address those comments and also made other corrections to improve the clarity of the presentation. The line numbers for this response letter are based on the manuscript with track changes.

(1) My main suggestion is that the authors include some context for the stated goals of measuring potassium in ambient biomass burning particles. What is biomass burning K+ associated with? Can it be associated with organic compounds, and if so, what are the prospects for detecting it? On a similar note, potassium is present in biological aerosol (Christopher Pöhlker, Bärbel Sinha, Manabu Shiraiwa, et al., 2012). Should we expect that to be measured with similar efficiency to the compounds explored in this study?

The issue raised by the referee would be important in measuring biomass burning particles. KCl is the dominant form of chloride in biomass burning aerosols (Reid et al., 2005), whereas potassium may also be present in biological particles emitted from rainforest (Pöhlker et al., 2012). We have added these points in Section 1 and also added some of the suggested references. We consider that the maximum temperature of the graphite collector is sufficiently high to decompose potassium-containing organic particles. However, the current study was focused on the detection of inorganic salts, and we have not tested the quantification of organic particles. The quantification of biomass burning aerosols will be investigated in future studies.

P2, L38-40

(2) Line 90-91. The authors should note that atomizing seawater does not produce sea spray aerosol that has the same composition of real sea spray aerosol produced by wave breaking-driven bubble bursting, e.g. (Fuentes et al., 2010). The differences may be mostly due to the presence of organics, but association of organics with some major ions may result in differences in the major ions in sea spray, which likely would not be replicated in atomized samples, e.g. see Salter et al. (2016).

We thank the referee for useful information. The molar fractions of the inorganic salts in the laboratory-generated particles may be different from those in real-world sea salt particles. We have added this point in Section 2.2.

P4, L112-115

(3) Line 253. It is interesting that no NaCl cluster ions were observed. ClNa2+ is a singly charged ion that is observed in CIMS observations of thermally desorbed particles (Lawler et al., 2014). I think those observations show that NaCl can be desorbed as an intact molecule that can react with Na^+ to form the cluster. I wonder whether it is more a consequence of the ionization scheme (EI) that no cluster molecules were observed. Can the authors comment on this possibility?

The QMS was operated in the multiple ion detection mode to measure ion signals at some selected *m*/*z* peaks. Before starting the full experiments, we measured all possible *m*/*z* signals to identify the major *m*/*z* peaks to be used for quantification (Table S1 in the Supplement). Following the referee's suggestion, we performed additional experiments to investigate possible contributions from the intact form of NaCl or its clusters. We found that ion signals at *m*/*z* 58 ($Na^{35}Cl^+$) and 81 ($Na_2{}^{35}Cl^+$) were negligibly small as compared to those at *m*/*z* 23 or 36, indicating that the contributions of the intact form of NaCl or its clusters were not significant.

P8, L195-197

(4) Table 3. It would be helpful to have the detection limits also reported in terms of total sample mass (ng).

We have added the detection limits in terms of total sample mass (ng) in Table 3.

P18, Table 3

(5) Figure 2. Can the authors comment on the wide gap in desorption time between the NaCl peaks and the Na_2SO_4 peaks? The bulk compounds differ in melting point by only about 80 K, while the difference in melting point of NaCl and $NaNO_3$ is several hundred degrees and the peaks for these two compounds show up close in time. Is the rate of temperature increase of the graphite cup strongly nonlinear or is there some other explanation? If it is possible to estimate the temperature over the heating period, that would of course be helpful to show.

The details of the laser power settings and the temperature of the graphite collector are presented in Section S2 in the Supplement. We consider that the issue raised by the referee is important. We used the two-step laser modulation to separately quantify the aerosol compounds tested in this study. While this method successfully separated SS from SN and SC, the ion signals for SN and SC showed temporal overlapping. This is somewhat unexpected considering that the difference in the bulk thermal desorption temperature between SN and SC is larger than that between SC and SS, as the referee pointed out. The cause of this discrepancy is currently unidentified. We have added this point in the last part of Section 4.1.

P17, L330-333

Other corrections:

- Fig. 3: We have corrected minor errors in calculating the mass of Cl (the isotopic fractions). We have also corrected errors in calculating the mass of K_2SO_4.
- Fig. 6: We have revised the y-axis values (the changes in the sensitivity for *m*/*z* 36 and modification of the multi-mode fitting). We have also updated the error bars.
- Table 3: The LOD value for PS has been slightly modified due to the change in the sensitivity.
- The data in the Supplement have also been updated.

Although these corrections do not alter the major conclusions, we apologize for the mistakes in the key results. We have also made minor corrections, adjustment of figure symbols (Fig. 4), and layout of tables in both the main document and Supplement.

References:

Christopher Pöhlker, Bärbel Sinha, Manabu Shiraiwa, K. T. W., Sachin S. Gunthe Hang Su Paulo Artaxo Qi Chen Yafang, M. S., Cheng Mary K. Gilles Arthur L. D. Kilcoyne Ryan C. Moffet, W. E. and Markus Weigand Ulrich Pöschl Meinrat O. Andreae, S. T. M.: Biogenic Potassium Salt Particles as Seeds for Secondary Organic Aerosol in the Amazon, Science (80-.)., 337(August), doi:10.1126/science.1123264, 2012.

Fuentes, E., Coe, H., Green, D., de Leeuw, G. and McFiggans, G.: Laboratory-generated primary marine aerosol via bubble-bursting and atomization, Atmos. Meas. Tech., 3(1), 141–162, doi:10.5194/amt-3-141-2010, 2010.

Lawler, M. J., Whitehead, J., O'Dowd, C., Monahan, C., McFiggans, G. and Smith, J. N.: Composition of 15–85 nm particles in marine air, Atmos. Chem. Phys., 14(21), 11557–11569, doi:10.5194/acp-14-11557-2014, 2014.

Salter, M. E., Leck, C., Werner, J., Johnson, C. M., Riipinen, I., Nilsson, E. D. and Zieger, P.: Calcium enrichment in sea spray aerosol particles, Geophys. Res. Lett., 43, 8277–8285, doi:10.1002/2016GL070275.Abstract, 2016.

We have added some of the suggested references.

References for this reply letter:

Pöhlker, C., Wiedemann, K. T., Sinha, B., Shiraiwa, M., Gunthe, S. S., Smith, M., Su, H., Artaxo, P., Chen, Q., Cheng, T., Elbert, W., Gilles, M. K., Kilcoyne, A. L. D., Moffet, R. C., Weigand, M., Martin, S. T., Pöschl, U., and Andreae, M. O.: Biogenic potassium salt particles as seeds for secondary organic aerosol in the Amazon, Science, 337, 1075–1078, https://doi.org/10.1126/science.1223264, 2012.

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: Intensive physical properties of biomass burning particles, Atmos. Chem. Phys., 5, 799–825, https://doi.org/10.5194/acp-5-799-2005, 2005.