Design, characterization, and first field deployment of a novel aircraft-based aerosol mass spectrometer combining the laser ablation and flash vaporization techniques

Hünig et al.

Replies to the comments by Anonymous Referee #2

General Reply:

First of all, we would like to thank Referee #2 for reviewing our manuscript and for his/her diligent and helpful comments, which significantly contribute to an improvement. In the following we will comment on the individual points.

The reviewer comments are written in this font style and color.

Our answers are written in this font style and color.

Changes to the revised version of the manuscript are printed in red.

Review of *Design, characterization, and first field deployment of a novel aircraft-based aerosol mass spectrometer combining the laser ablation and flash vaporization techniques* by *Hünig et al.*

Anonymous Reviewer

October 2021

1 Summary

In this work, Hünig et al. describe, for the first time, the design and characterization of ERICA. At the time of this review, ERICA is a unique instrument, but it does combine two well-known methods: (1) single-particle mass spectrometry using laser ablation to (partially) vaporize single particles and ionize their constituents, and (2) an AMS-style instrument that flash vaporizes the non-refractory component of aerosol using a hot tungsten filament and creates ions using electron impact. Method 1 will be referred to as ERICA-LAMS, and Method 2 will be referred to as ERICA-AMS, per the authors' designation. ERICA LAMS uses two time-of-flight mass spectrometers to analyze the positive and negative ions from a single particle; ERICA-AMS uses a compact-time-of-flight mass spectrometer to analyze positive ions. Both ERICA-LAMS and

ERICA-AMS share a common aerosol focusing inlet (AFI), which is pressure-controlled and has been written about in a separate publications (Molleker et al., 2020). After exiting the AFI, the particles are sized by measuring the particle time-of-flight between two particle detection units (PDU1 and PDU2). Optical sizing was experiementally achieved for PSL between 80 nm and 5.145 µm Particles detection by PDU2 triggers a 266-nm quadrupled Nd:YAG ablation laser to fire (max repetition rate 8 hz−1, ~4 mJ/pulse). Particles that are not detected by PDU2 or are missed by the ablation laser are collected ~55 cm from the exit the AFI, and ~30.1 cm downstream from the ablation laser spot.

The authors give much attention in the paper to the particle beam diameter and the effective laser / vaporizer diameters. All are fitted parameters, which are fitted to a convolution of two functions–a top hat function for the effective laser / vaporizer width and a 2D Gaussian function for the particle beam width. In ERICA-LAMS, the particle beam width ranges from ~30-40 µm for 335 nm AN particles to ~100-200 µm for all particles >400 nm to >500 µm for 103 nm PSL. For particles ≥208 nm, the particle beam diameters are smaller than the effective laser diameters in PDU1 and PDU2. For ERICA-AMS, particles with diameters > 91 nm have particle beams smaller than the effective diameter of the vaporizer, which, unlike the effective laser diameters, is similar to the physical dimensions of the vaporizer (3.8 mm).

The most userful meaasured parameters in the paper are the detection efficiency (DE) and the abation efficiency (AE). The former measures the number of particles detected by the PDUs compared to a separate measurement of particles counts by a CPC or OPC; the latter is the number of particles that has mass spectra divided by the number of particles that trigger PDU2. The DE analysis shows that, under ideal conditions (e.g., idea beam position, which changes as a function of size), the DE for PSL is above 0.6 for particles ≥208 nm; however, for real-world particles the DE is generally lower across all sizes measured. Finally, the AE for real-world urban particles was presented. The AE has a maximum value of 0.52 @ 218 nm; however, the authors also found that the AE is a steep function of size, and hovers around 10-20% for particles below ~200 nm and above ~300 nm.

The paper finished with some example laboratory particles, as well as some example particles and science from the first aircraft deployment.

Overall, this paper is very well written and very well thought out. The scope of the paper also fits very well within the scope Aerosol Measurement Techniques. At the time of this review, ERICA is a completely unique instrument; thus, a detailed description and characterization paper is well-timed and necessary for future publications. This reviewer only has a few comments, which are outlined below.

We thank the reviewer for this generally positive rating of our manuscript.

2 General Comments

1. Section 3.1–It is unclear to this reviewer if the "razor blade" is integrated into the system like the "knife edge" in the PALMS instrument. If so, it is also unclear if ERICA uses the knife-edge to re-position the papers during flight, where they might have moved due to vibrations from the aircraft.

"For characterization of the laser beams of the PDUs and the ablation laser outside the vacuum chamber, a razor blade was moved stepwise perpendicularly into the respective laser beam (with steps of 0.01 mm)."
changed to:
"For characterization of the laser beams of the PDUs and the ablation laser, a razor blade was moved stepwise perpendicularly into the respective laser beam (with steps of 0.01 mm). These characterization experiments were performed in a separate measurement setup."

2. Section 3.3: It is unclear to the reviewer if the "effective laser radius" being much larger than the physical dimensions of the laser is supported by Mie theory (as was done for 108 nm particles). Is this true? Is this akin to a "scattering cross section?" If so, the authors should support that with some calculations in the supplemental. Otherwise, the authors risk comparing the physical beam diameters to a laser diameter that is fitted (as opposed to measured) and perhaps physically unrealistic.

(Numbers of sections and figures refer to the revised manuscript.)

The different definitions of w_0 (1/e²-radius, determined by the knife-edge experiment) and the effective laser radius $r_{eff,L}$ (determined by the ADL scan measurements) have to be considered:

A knife-edge moved into the laser beam allows only the intensity of the open half plane to pass. The power measured on the detector is the integral of the intensity over the unshaded area. The integral is the Gaussian error function (see Sect. 3.2.1 and Sect. S2.1 in the supplement). The beam radius is defined as the difference of the position where the transmission is 16 % and 84 %. In the case of a Gaussian beam, the beam diameter thus determined coincides with the $1/e^2$ width of the intensity distribution (Eichler et al., 2004).

The effective laser beam radius $r_{eff,L}$ is the laser beam radius wherein a particle is registered (see Sect. 3.1.1). The effective laser beam radius was determined by the ADL position scans (convolution of the particle beam and the effective laser beam; see also Molleker et al., 2020) and depends on the particle size. Larger particles scatter the laser light more than smaller particles, resulting in a larger $r_{eff,L}$ value for larger particles. Thus, a $r_{eff,L}$ value larger the w_0 value is possible. It means, the intensity at the distance $r_{eff,L}$ is below 1/e² of the maximum intensity, but the intensity of the scattered light is still sufficient for a particle to be detected. However, $r_{eff,L} = 4.687 \times w_0$ yields unrealisticly low values for the intensity distribution of a Gaussian beam. Possibly the beam shape does not follow a Gaussian distribution at the edges. We added the lines: „This calculation is valid for a Gaussian beam profile, which is most likely not true on the edges of the distribution, and can thus

only be seen as a rough approximation." in Sect. S5.1 in the supplement and „[...] according to a rough estimation (see Sect S5.1 in the supplement)." in the main paper (Sect. 3.1.2).

The calculated response functions of the Mie curve (see Sect. S5.1 in the supplement) increase with particle size (See Fig. S11). However, it cannot fully explain the shape of the $r_{eff,L}$ curves. In addition, I_{rel} seems to be too small for small particles ($d_{va} < 200$ nm) to be detected. However, measurements show (see Figs. 8, S9, and S21) that particles $d_{va} < 200$ nm can be optically detected and ablated.

3. Fig.10: I am slightly confused how it is possible that PDU2 can have higher values than PDU1. Can the authors comment on this?

(Number of figures refer to the manuscript submitted for review.)

Due to the fact that the ADL position where the optical detection efficiency has its maximum deviate (also for different particles sizes differently) to the adjusted particle beam axis (see Fig. S13), the DE_{KTM} values at PDU2 can be higher than at PDU1. This means for these particle sizes that the particle beam might be better adjusted to PDU2 than to PDU1.

In Fig. S13, the measurements with AN particles with particle sizes between 200 nm and 400 nm show that at PDU2 the x_0 offset is smaller than at PDU1. This might result in a higher DE_{KTM} for measurements at PDU2.

4. Section 3.4: Because ERICA has both an optical DE for PDU2 and an AE, it would be helpful for the authors to explicitly show a DE for ablation. This wold help the readers understand biases in ERICA number fractions etc.

Due to the limited repetition rate of the UV laser, a DE for ablation that depends on the particle concentration outside the instrument turns out to be not useful in this context. This is especially the case for high particle concentrations outside the instrument (>12 particles cm^{-3}), which exceed the temporal resolution of the UV laser.

5. Section 4: Towards the end of the paper, the authors compare ERICA-LAMS data to ERICA-AMS data on the same plot. This caused this reviewer to of biases between the measurements that should be addressed before having a combined interpretation of the LAMS and AMS results. The major bias, as understood by this reviewer from the figures in this paper, is that the "number fraction" will be highly dependent on the size and composition of the particles present. These should somehow be weighted accordingly–by internal DE curves or by normalizing to external quantitative measurements. No discussion of this correction is present in

the current manuscript–this reviewer strongly suggests that the authors address that in this manuscript, as it will affect all future work from this instrument.

(Numbers of sections and figures refer to the manuscript submitted for review.)

In Section 4, it is not intended to be a comparison to highlight the differences of the ERICA-LAMS and the ERICA-AMS, but to demonstrate the possibility of obtaining complementary information and that this information can be merged. Therefore, not the differences are discussed here. In order to prevent the reader's expectation of a discussion on the differences, Fig. 17 was separated into 3 panels. (See also our reply to RC1)

In the revised manuscript, we revised the presentation of a new and future mode of an Optically Triggered AMS (OT-AMS) of the ERICA. With this mode, it might be possible to investigate residuals from the LDI process with the TD-EI method to investigate the biases. The work on the OT-AMS mode is in progress and the results are substance of an upcoming publication. In our publication here, we solely present the ability of particle detection of the ERICA-LAMS and the ERICA-AMS:

„For the same point in time, a data acquisition card is triggered and, similar to the procedure with a light scattering probe on the AMS (Cross et al., 2007; Freutel, 2012), the single particle mass spectrum is recorded. In this way it is possible to quantify the non-refractory components of a single particle. In addition, the size information of the measured single particle is obtained by means of the particle flight time between the two PDUs. Here, a future characterization of interest is the ablation laser's effect to the particles that are only partly ablated and the residuals reach the vaporizer of the ERICA-AMS. For this purpose, a method has to be developed to ensure the linkage of the results to the very same particle. Such a procedure needs more implementations and further laboratory studies."

was changed to

„For the same point in time, the data acquisition card is triggered and the single particle mass spectrum is recorded. For the ERICA this mode is called optically triggered AMS (OT-AMS) mode. With the method of the OT-AMS mode, it is possible to quantify the non-refractory components of single particles when the ablation laser is in idle mode. This method is similar to the procedure with a light scattering probe on the AMS (Cross et al., 2007; Freutel et al., 2013). In addition, the size information of the measured single particle is obtained by means of the particle flight time between the two PDUs. One possible future investigation by means of the OT-AMS mode is the ablation laser's effect on the particles that are only partly ablated and where the residuals reach the vaporizer of the ERICA-AMS. This investigation is only possible with the unique feature, the serial configuration of SMPS and AMS, as in the OT-AMS mode. A method has to be developed to ensure the linkage of the results to the very same particle. Such a procedure needs more implementations and further laboratory studies. "

3 Minor Comments

1. P2L40: Since each paper should stand on its own–a brief description of the Dragoneas paper should be described here. That way the reader does not have to download a separate paper to fully understand your methods.

Dragoneas et al. (2022), meanwhile completed and ready for submission, includes the detailed technical description of the electronics and the hardware of the ERICA. All for understanding necessary details are included in the manuscript. However, the sentence in P2L40 was revised.

"The adopted techniques for automatizing the operation are detailed in the companion paper by Dragoneas et al. (2022)."

was changed to

"The adopted techniques for automating the operation of the ERICA (including pressure and temperature control), details on the electronic hardware, the mechanical adaption, the inlet system, the electrical distribution, and the remote control, are detailed in the separate paper by Dragoneas et al. (2022)."

2. P3L24: "A large fraction" here is largely meaningless without some general numbers or statistics.

To give an idea of the amount of the "large fraction", the idle time of the ablation laser was emphasized. It has to be noted that the losses depend also on the ambient aerosol concentration (in the detectable size range).

„A large fraction of the particles is not ablated by laser pulses, either because the laser pulses miss the particles, or because the particles are too small for the optical detection. However, even most particles amenable for laser ablation, which pass through the ablation region, remain undestroyed, because the laser is firing at a limited maximum repetition rate of 8 pulses per second."

was changed to (see also reply to RC1):

"It is assumed that a large fraction of the sampled particles will not generate a single particle spectrum. The major reasons for this effect are: First, the particles are not ablated, because the laser is firing at a limited maximum repetition rate of 8 pulses per second. During the idle time of the Nd:YAG laser, particles remain unablated, even if they are successfully detected by the units PDU1 and PDU2. This actually is by far the largest fraction of the sampled particles emerging from the ADL. If, for example, the ambient number density of particles with diameters above the optical detection limit is 100 cm^{-3}_{Std}, then, at most only 5.4 % (8 shots per second and sampling volumetric flow rate of 1.48 $cm^3 s^{-1}$) of the detectable particles are hit by the laser. Second, the particles are too small for optical detection. Third, particles for which the calculation of the trigger failed continue their travel towards the ERICA-AMS vaporizer. Fourth, particles that primarily consist of materials that are transparent at a UV wavelength of 266 nm, such as pure sulfuric acid, are hard to ablate (Murphy et al., 2007). We selected a UV laser with 266 nm wavelength due to smaller dimensions of the laser and the fact, that chemical substances show less fragmentation compared to ablation with

shorter wavelengths (Thomson et al., 1997). In general, however, it is also possible to implement excimer lasers operating at shorter wavelength to ablate pure sulfuric acid droplets. Also, pure sulfuric acid is detected by the ERICA-AMS. Thus, even most particles amenable for laser ablation, which pass through the ablation region, remain undestroyed. Another reason why a spectrum is not triggered over a signal threshold for recording is a low number of generated ions during the LDI process."

3. P3L34: Is the lens and geometry in ERICA the same as the lens in XU et al.?

Yes, see also Sect 2.2.

"The detectable particle size range (d_{va}) of the ERICA-LAMS is between ~180 nm and 3170 nm (see Sect. 3.3.3). However, the signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5 μm (see Sect. 3.2). The detectable particle size range of the ERICA-AMS is assumed to be the same as published by Xu et al. (2017) for the deployed lens type.: ~120 nm to 3.5 μm."

was changed to (Numbers of sections and figures refer to the revised manuscript; see also reply to RC1 and RC3):

"The particle size range within the 50 % cut-off in detection efficiency (d_{50}) of the ERICA-LAMS is between 180 nm and 3170 nm (see Sect. 3.2.2). The signal-to-noise ratio of optical particle detection is sufficient for particle time-of-flight calibration between 80 nm and 5000 nm (see Sect. S4 in the supplement). For the ERICA-AMS, the detectable particle size range is determined by the transmission and focusing properties of the aerodynamic lens. For the ADL used in our instrument, Xu et al. (2017), who used this lens in combination with an ACSM (Aerosol Chemical Speciation Monitor), determined a transmission range from ~120 nm to 3500 nm. We assume that the detectable particle size range of the ERICA-AMS matches this transmission range."

4. P8L29: At what aerosol concentration (number and volume / mass), does ERICA-LAMS affect ~30% of the particles? This should be spelled out for the reader? I assume it could affect some areas of the Upper Troposphere.

Here we show two cases: The first, where we have maximum losses at the ERICA-AMS (theoretically 100% for particle detection rates < 8 particles s^{-1}, approx. 5 particles cm^{-3} within the detectable size range with a flow into the instrument of 1.48 cm^3 s^{-1}), and the second, the typical case in the BL (5.4% for particle detection rates >100 particles s^{-1}, approx. 68 particles cm^{-3} within the detectable size range).

By calculation, 30 % losses in the particle numbers equal (1/0.3)×8=27 particles s^{-1}, approx. 18 particles cm^{-3}. In the UTLS (>15 km), we measured a particle detection rate of between 5 and 800 particles s^{-1}. Thus, for these measurements, losses for the mass concentration of up to 100 % have to be considered and the uncertainty of 30% has to be adapted.

"However, the losses can be neglected considering the commonly assumed uncertainty of 30 % in AMS instruments."

was changed to:

"However, the losses (in mass) are small considering the commonly assumed uncertainty of 30 % in AMS instruments (Bahreini et al., 2009). By calculation, 30 % losses for the particle numbers equal 27 particles s^{-1}, (~18 particles cm^{-3}). In the upper troposphere and lower stratosphere (UTLS; >15 km), we measured a particle detection rate of between 5 and 800 particles s^{-1}. Thus, for such measurements, losses for the mass concentration of up to 100 % have to be considered and the uncertainty of 30 % has to be adapted."

5. P10L18: That the aerodynamic diameters of AN are similar to PSL suggest that they are spherical and of similar density. This not entirely surprising because AN is notoriously difficult to effloresce; however, the authors state that effective laser radius for AN do not match PSL because the AN are non-spherical. Can you reconcile these two statements?

(Numbers of sections and figures refer to the revised manuscript)

The reviewer is right. The statement that $r_{eff,L}$ (Sect. 3.1.2) does not match PSL because of the non-spherical shape was removed

"The AN measurement results do not agree with the results of the measurements with PSL particles, possibly due to a non-spherical shape and a different refractive index of AN as compared to that of PSL."

was changed to:

"The AN measurement results do not agree with the results of the measurements with PSL particles, possibly due to a different refractive index of AN as compared to that of PSL."

6. P13L32: I'm not sure that "$w_{0,dia}$" is not the most meaningful measurement for overlap. Unlike the signal in PDU1 and PDU2, the intensity of the ablation laser will be essential to the interpretation of the mass spectra–especially for large or coated particles. Thus, a measure of the overlap between the particle beams and where the ablation laser is sufficiently powerful is indeed important to report.

As described for $S_{detect,L}$ (P12L36; refer to the manuscript submitted for review), the laser intensity of a Gaussian beam profile provides intensities larger than zero also for radial distances above w_0 and the scattered light might be sufficient for particles to be detected (see also comment on 2.2). However, $w_{0,dia}$ is supposed to be an approximation. Of course, this approximation is good enough to be shown here, as the reviewer also agrees.

7. P13L35: I don't think I saw any evidence that the 80 nm and 5145 nm
   particles were ablated and detected by the MCP. Is this true? If so,
   perhaps a AE_{max} could be shown for PSL particles much like DE_{max}
   was?

(Numbers of sections and figures refer to the revised manuscript)

The reviewer is right. Fig. S20 in the supplement shows the size distribution from a research flight during the second aircraft field campaign of StratoClim on 08.08.2017. Here, mass spectra from particles in a size range of between 100 nm and 3700 nm were obtained.

The range from 80 nm to 5245 nm is the size range of the particle size calibration. This is the maximum possible size range where particles are detected by the PDUs (see Sect. S3 and S4 in the supplement) and is theoretically the maximum possible size range for ablated particles.

8. P18L21: This reviewer is not an AMS expert–but, as written, it sounds
   like all RIEs are relative to the nitrate IE. So, why does nitrate have an
   RIE of 1.1?

This is correct. It is explained in Canagaratna et al. (2007): "The RIE values usually used in AMS ambient concentration calculations are 1.4 for organic molecules and 1.1, 1.15, and 3.5–6 for NO3, SO4, and NH4 moieties, respectively. These values are based on many calibrations of laboratory-generated aerosols. The RIEs for NO3 is greater than 1 to account for the fact that although only m/z 30 and 46 are used to track NO3 ion signal during calibrations, NO3 signals at other ion fragments are included in the fragmentation table that is used for calculating NO3 concentrations (Allan et al., 2004; Hogrefe et al., 2004b)."

9. P19L9: As written, it is unclear if it is most desirous to have a "small air
   beam sample" over no air beam sample.

From a measurement statistical point of view an airbeam of zero would be the optimum. However, in practical "no air beam sample" would not be feasible, due to the instrumental design.

"A small airbeam signal is thus desirable, e.g., to reduce the detection limit of aerosol species."

was changed to

"An airbeam signal as small as possible is thus desirable, e.g., to reduce the detection limit of aerosol species."

10. P20L34: Can an estimate of the UT and LT altitude / altitude ranges be
    added to Fig. 17?

The cold point tropopause (17 km) was added as blue dashed line in Fig. 15 (revised version of the manuscript).

11. P22L25: It seems to this reviewer that different removal rates of EC and
    C$_{total}$ suggests that the particles are not well mixed–because they would
    then be removed at the same rates.

We actually do not know the removal rates or the whether the different particle classes are vertically well mixed. In this instrument-focused paper we only describe the observation, in order to highlight that ERICA-LAMS is capable of doing such differentiated measurements in the real atmosphere. The paragraph was revised (see also reply to RC1)
"This indicates within the limitations of the applied methods that the composition of the sampled aerosol is well mixed within the particle boundary layer and in the free troposphere, although C_{total} changes. Thus, the EC particle number fraction cannot be used to define the particle boundary layer. In the ATAL, EC particles seem to play a minor role in the composition of the aerosol, while for the convective outflow levels the data suggest an increase in EC as result of detrainment."
was changed to:
"This indicates, within the limitations of the applied methods, that the EC particle type is well mixed within the boundary layer and in the free troposphere, although C_{total} changes. In the ATAL ($>$ 16 km), EC particles seem to play a minor role in the composition of the aerosol, while for the convective outflow levels ($<$ 16 km), the data suggest an increase of the EC particle number fraction as result of detrainment."

12. P22L36: Are these EC particles from coagulation? They seem quite high
    to be primary particles.

The EC particles are termed ‚primary', since they are not secondary formed (i.e., not formed from gaseous substances by chemical reaction or by accumulation of reaction products on condensation nuclei). We cannot state whether the EC particles were emitted at these altitudes and grew by coagulation or whether they were transported vertically. This would require more detailed meteorological analyses, e.g., considering air mass trajectories, to see where/how far potential sources might be. This is beyond the scope of the paper. The presented results regarding EC and C_{tot} merely serve to demonstrate ERICAs range of capabilities.

13. P23L5: The authors often differentiate the EREICA-AMS data by say
    "the non-refractory components." This is misleading because ERICA-
    LAMS also measure the non-refractory components.

(Number of pages, lines, and sections refer to the manuscript submitted for review)

The reviewer is right that the ERICA-LAMS is capable to measure non-refractory and refractory components whereas with the ERICA-AMS only non-refractory components can be measured. However, we cannot distinguish, whether sulfate as measured by the ERICA-LAMS is non-refractory or refractory.

Following sentence was added in Sect. 4 (P20L40):

„It has to be noted that the ERICA-LAMS is capable of measuring sulfate species of non-refractory and refractory types, but cannot distinguish between both types."

The sentence (P23L5) „For the non-refractory components, the cations are detected with a C-ToF-MS.“ was removed

In P23L9 „The cations generated by the TD-EI technique are detected with a C-ToF-MS“ was added

14. Figures: It is really hard, especially with the errors bars to differentiate the filled circles from the filled squares. Perhaps switch to filled and open squares?

The markers were changed to non-filled markers to estimate the uncertainty bars. In addition, the markers were enlarged for better differentiation.

15. Figure 10: Using 50% of the max is a bit strange in this plot–it results in PDU1 having larger D50s than PDU2, which is counter-intuitive given that PDU2 has better detection efficiencies.

The reviewer is right. Due to the relatively low maximum DE_{KTM} value for PSL measurements at PDU2 (0.53) compared to PDU1, the found d_{50} values at PDU2 (160 nm and 750 nm) are very small and misleading. An alternative would be another definition of d_{50}: 50% absolute.

We still hold the view that 50% of the maximum should be used as a parameter. Because of the small efficiencies and because of the large variation of the measured values, the d_{50} values (interpolated from them) have a large uncertainty and the values determined of 190 nm and 160 nm (the same for 745 nm and 750 nm) are within their uncertainties. Therefore, only the d_{50} values determined from the measurements at PDU1 are shown in Fig. 7a. The corresponding paragraph in Sect. 3.2.2 has been amended:

"In Fig. 10a, the detection efficiency DE_{KTM} of PSL particles is plotted as a function of the particle size d_{va}. The graph shows an increase with particle size until a maximum for DE_{KTM} of 0.74 for a particle size of 410 nm. By interpolation, the lower d_{50} values are 190 nm at PDU1 and 160 nm at PDU2. As upper d_{50} values we found 745 nm at PDU1 and 750 nm at PDU2. Furthermore, d_{50} is pronounced differently for particles with optical properties other than PSL such as AN." (Number of figures refer to the manuscript submitted for review)

was changed to

"In Fig. 7a, the detection efficiency DE_{KTM} of PSL particles is plotted as a function of the particle size d_{va}. The graph shows an increase with particle size up to a maximum for DE_{KTM} of 0.74 for a particle size of 410 nm. By interpolation, the lower d_{50} value at PDU1 is 190 nm and the upper d_{50} value is 745 nm. Due to the relatively low maximum DE_{KTM} value for PSL measurements at PDU2 (0.53) compared to PDU1, the found d_{50} values at PDU2 (160 nm and 750 nm) are misleading. In Fig. 7b it can be seen that d_{50} is pronounced differently for particles with optical properties other than PSL such as AN." (Number of figures refer to the revised manuscript)

16. Figure 11: Can you make the right side of this plot a log-scale (and also possibly the left?). It is hard to see if you're getting spectra for any particles below ~120 nm or above ~1 µm.

Right axis was changed to log-scale.

17. Figure 12: Why do you have a large Na^+ peak in your PAH spectra? Is your mass scale possibly off?

The spectrum showed a sodium contaminated BaA particle. It was replaced by a not contaminated one. It should be noted that Na produces a distinct peak even at very small Na fractions because of its low 1st ionization energy.

4 Technical Comments

- P1l11: What does "ERC" stand for?

  ERC stands for 'European Research Council'. The parenthesis was changed from
  "(i.e., ERC Instrument for Chemical composition of Aerosols)"
  to
  „(ERC Instrument for Chemical composition of Aerosols; ERC: European Research Council)"

- P1L15: Perhaps "*The same* aerosol sample can be sampled with both methods *simultaneously*?

  "The aerosol sample can be analyzed with both methods, each using time-of-flight mass spectrometry."
  was changed to
  „The same aerosol sample can be sampled with both methods simultaneously, each using time-of-flight mass spectrometry."

- P1L20,25,26: The acronyms ADL, B-ToF-MS an C-ToF-MS are defined here, but are not used again in the abstract. The abstract should generally stand alone, and therefore these acronyms can be omitted, but need to be defined at their first use in the main section of the paper.

  Done

- P1L36: You probably can delete the comma after "anthropogenic-"

  Done

- P2L19: Perhaps use "e.g.," instead of "beside others by."

  Done

- P13L33: This reviewer is not sure "However" is the right word here–this statement does not seem to be related to the previous sentence.

  „ However, $S_{ablation}$ smaller than 1 indicates that 1σ of the particle beam is within the $w_{0,dia}$ of the ablation laser spot."
  was changed to
  „ At least, $S_{ablation}$ smaller than 1 indicates that 1σ of the particle beam is within the $w_{0,dia}$ of the ablation laser spot. "

- P16L10: It is hard to understand ion peak threshold as currently described. It might be easier to understand by splitting this statement up into two or more sentences.

  „The ion peak area threshold is defined as the ion peak area at m/z, which are usually unoccupied (m/z 2 to m/z 6 for cations, m/z 2 to m/z 11 for anions), below which 99% of the baseline noise is present (Köllner et al., 2017)."

  was changed to (see also reply to RC1)
  „The ion peak area threshold is defined as the ion peak area at m/z, on which during ambient measurements typically no signals occur (m/z 2 to m/z 6 for cations, m/z 2 to m/z 11 for anions). To determine the ion peak area threshold, the normalized cumulative signal intensity distributions for each usually unoccupied m/z were made and the overall 99 % threshold was determined (Köllner et al., 2017). Below this ion peak area threshold, 99% of the baseline noise is present (Köllner et al., 2017). The result for cations and anions is an ion peak area threshold value of 7 mV·sample."

- P19L19: You can probably delete "especially" in this line.

  Done

- P22L25: The statement "within the limitations of the applied method" is parenthetical and needs commas around it.

  Done

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