Reply to Reviewer 1

We gratefully thank the reviewer for the careful manuscript reading, and the constructive comments which were helpful to improve the quality of our manuscript. Our point-to-point replies are given below in italics and in blue following the original comments:

General Comments

The authors present a comparison of the mass spectra obtained from the laser desorption ionization of atmospherically relevant particle types using ns and fs laser systems in a LAAPTOF single particle mass spectrometer. Although a similar study of has been presented previously by Zawadowizc (2015), this manuscript dealt with a different instrument geometry, and therefore the study presented here has the potential to contribute to the understanding of laser-particle interactions in single-particle mass spectrometry.

However, the authors fail to emphasize the key difference in geometry between the LAAPTOF and the PALMS instrument in the previous study i.e. the counter propagate vs orthogonal arrangement of the excimer laser with respect to the particle beam axis. This difference in geometry is likely to influence how the ablation process proceeds and will also influence the interpretation of the spectral characteristics for the reasons stated in the specific comments below.

It is correct that in this study we used a different geometry for laser ablation compared to the previous study by Zawadowizc et al., 2015, but furthermore it was our aim to study different particle types (e.g. pure organic, salts and core shell) for different power densities to get a better understanding of the light particle interaction. The principle difference is indeed that in our set up the particles interact with different intensities of the laser beam. However, we did obtain only reasonable signal intensity if the particles were hit close to the focus of the laser beam, and selected those mass spectra that had not less than 90% of the maximum total ion intensity. Due to this procedure we ensured that the laser intensity acting on the particle was reproducible and close to the maximum possible. Mass spectra of particles that were hit only partially, or only partially ionized, e.g. if they were not close enough to the focus, were omitted. However, we cannot determine exactly how close to the focus position the particles were ionized. We did vary the laser focus to the left/right and up/down and determined the diameter of the particle beam to 1-2 mm, depending on particle type, while the diameter of the laser focus was calculated for all wavelengths to range between 81-487 µm as listed in Table S4. We added the following sentence to the introduction:

"Please note that for this work the geometry of ablation/ionization laser beam particle interaction was not orthogonal as for the experiments described by Zawadowicz et al. (2015), but almost collinear as this was favoured by the design of the LAAPTOF."

In addition, the manuscript has some major deficiencies which need to be addressed. With the exception of the ion intensity comparison of the two systems, the key conclusions offered in the abstract in this manuscript are not supported in the data or discussion. Namely:

- There is no supporting data for the conclusions regarding the reproducibility of spectral patterns.
- The methods used for quantifying the fraction of spectra types is not provided.
- The conclusion that 'fs-laser ablation produce spectra with larger ion fragments and ion clusters, as well as clusters with oxygen, which does not render spectra interpretation more simple compared to ns-laser ablation' is only supported by a single hand-picked spectra of each particle type.
- There is no evidence or discussion of the claim in the abstract that quantification remains difficult due to the incomplete ablation of the particle. Evidence of a rigorous statistical comparison of the mass spectral patterns is required.

As discussed above we selected for our analysis mass spectra with at least 90% of the maximum total ion intensities obtained for each particle type, which led to a selection of 30-40 % of the total of 200-600 individual spectra obtained for each particle type, hence 60-240 spectra. From these spectra we selected two typical average spectra classes by a fuzzy c-mean algorithm available within the LAAPTOF data analysis software. For each class of mass spectra we selected 10 representative spectra showing all main characteristics and applied an additional mass axis calibration for each spectrum.
An example demonstrating the reproducibility and representativeness of the selected spectra has been added in the supplementary section for one particle type (Figure S3- S6).

We added the following text to section 3.1 of the manuscript:
"The mass spectra that are discussed in this section were selected to be representative for each particle type in the following manner. From the typically 200-600 useful single particle mass spectra measured for each particle type only those 30-40% (60-240 spectra) with at least 90% of the maximum total ion intensities were selected to ensure optimal hit of the particles by the ablation and ionization laser. These remaining spectra were classified using the fuzzy c-mean algorithm available in the LAAPTOF data analysis software. This resulted in typically two classes of mass spectra per particle type. For each class of mass spectra we manually selected 10 spectra representing all main characteristics and applied an additional mass axis calibration for each spectrum. These 10 spectra showed correlation coefficients of r = 0.7-0.9. An example demonstrating the reproducibility and representativeness of this selection process is given in the supplementary section (cf. Figures S3-S6)."

Consequently, we consider our conclusions that fs-laser ablation produces spectra with larger ion fragments and ion clusters, as well as clusters with oxygen compared to ns-laser ablation to be based on representative mass spectra.

Mainly in section 3.2.2 and in the conclusions we discuss the potential quantification abilities of the fs laser ablation single particle mass spectrometer. Our study shows that there is only relatively small difference in total ion intensities between ns- and fs-laser ablation and ionization (section 3.2.1). Furthermore, the experiment with the core shell particles clearly show no increase in signal from the core for the fs-laser (3.1.5-6). We therefore believe our conclusion that the quantification of ablated material remains difficult due to incomplete ionization of the particle to be justified.

Specific comments

P1, L23. Reproducibility is not specifically discussed in this manuscript.
An example demonstrating the reproducibility and representativeness of the selected spectra has been added in the supplementary section for one particle type (cf. Figures S3-S5). One example shows two raw mass spectra of PSL 500 nm particles for two different measurements of the same energy per pulse and the same focus position resulting in the same characteristic spectra for both measurements. Furthermore, 20 mass spectra for 20 different particles are compared showing the same spectral characteristics.

Hence we consider it justified to speak of "reproducibility of mass spectral signatures" in the abstract. Furthermore, we have added the following lines to the conclusions.

"Please note that between 30 to 40% of the spectra obtained using the fs-laser have the same spectral features, which demonstrates the reproducibility within a single type of measurement and which is a good basis to compare results for different measurement conditions."

P2, L64. Do you mean a solid particle or fixed target/substrate? Please clarify.
Here we mean the interaction of light with a solid particle as becomes evident in the following sentences in this section.

P3, L96. This is only applicable to positive Cl^+ ions. Cl ions are readily observed in negative in mode due to high electron affinity.
We agree and have modified the sentence as follows: "Overall, they observed similar mass spectra in both ns- and fs-laser ablation, but also showed that ions with high ionization energy such as Cl^+ are more easily generated by the fs-laser due to its higher power density."

P3, L199 and P4, L1. Were the beam diameter and focal length/position measured or calculated?

All ionization laser beams were focused using the same lens. The focal length of the lens was measured for all wavelengths and the beam diameter at focus or interaction position was calculated. This information is now given in sections 2.1., 2.2., and in the supplementary section (cf. Table S4).

We have added the following text to section 2.1:
"We did vary the laser focus to the left/right and up/down and determined the diameter of the particle beam to 1 - 2 mm, depending on particle type. The ns-laser beam is slightly defocused at the position (F1) increasing the particle-laser interaction area, and the defocused beam diameter is 99±31 µm where it encounters the aerosol particle (F1, Fig. 1). The focus position of the excimer laser is at 20 cm from the lens, and ionization happens 3 - 4 cm after the

focus position, for F2 and F1, respectively. This is the distance from focus point to the center of the ion extraction region from where the ions are extracted into the mass analyser. The movable lens can be used to shift the focus position from F1 to F2 where the defocused beam diameter is 81±7 µm resulting in higher power densities acting on the particles. Please note that the position of the ionization region is quite well defined in this case, close to the center of the ion extraction zone, due to the scattering signal of the second detection laser whereas for the experiments with the fs laser we had to apply a different procedure to define this (see section 2.2 and 3.1). Variation of the focus position allows to vary the power density by a factor of ~1.5 for otherwise similar conditions, for F1 and F2, respectively."

We have added the following text to section 2.2:
"To define the ionization region for this case also close to the center of the ion extraction region a procedure selecting those mass spectra with more than 90% of the maximum total ion intensities was applied (cf. section 3.1)."

"For the wavelength of 800 nm the laser beam diameters are 487±77 µm and 246±36 µm at the positions F1 and F2, respectively. The focal positions were varied to study the effect of power density on the mass spectra. The power densities at F2 are ~3.5 times higher than at F1."

P4, L3. Do you mean the excimer focal position? How do you know ionization happens 3-4cm after the focal position with a counter propagate geometry? Can you comment on the depth of field of the focusing? Is it more likely that ionization takes place before the focal position? Does the position of ionization depend on the absorbing properties and ionization threshold of the material with a counter propagate geometry?

Yes, we mean the focus position of the excimer laser. The ionization happens typically 2 cm before the focus point of the excimer laser in the counter direction of the particle beam close to the position of the second detection laser. Hence, the ionization happens before the focus point, which improves the hit rate due to the larger laser beam diameter. We have shifted the focus position up to 4 cm away from the ionization region to study the impact on the mass spectra. Please note that the position of the ionization region is quite well defined in this case, close to the center of the ion extraction zone, due to the scattering signal of the second detection laser which triggers the ionization laser beam. Between scattering and ionization a particle travels 500 µm depending on its size, shape, and density. For the experiments with the fs laser we don't have this additional information and applied a different procedure to define this (cf. section 3.1). The position of ionization shouldn't depend strongly on the absorbing properties and ionization threshold of the material as it is defined by the laser triggering (ns-laser) and the dimensions of the ion extraction region (fs-laser).

P4, L129. What is the diameter of the focal point of the fs system?
We calculated the laser beam diameters at the focus point and other positions for all wavelengths of the fs and ns-laser system. This calculation and the results are added to the supplementary information of the revised manuscript:

Table S4: The Laser beam diameters calculated for the different focus positions and different wavelengths

Laser and Wavelength	Beam Diameter at Position F_2 (µm)	Beam Diameter at Position F_1 (µm)	Beam Diameter at Focus Position (µm)
fs-laser 800 nm	*246±36*	*487±77*	*42±9*
fs-laser 266 nm	*182±32*	*270±32*	*38±9*
ns-laser 193 nm	*81 ±7*	*99±31*	*37±2*

P4, L141. Can the authors comment on the stability/reproducibility of the focal length, the depth of field and the effect on power density? How is the power density different at F1 than F2? Surely the densities are the same and the focal position has just shifted upstream in the particle beam. Why do the authors vary the focal length? The objectives and conclusions of this operation are not stated in the manuscript.
The beam pointing stability is better than 0.25 µrad (rms) for the fs-laser as specified by the manufacturer, and thus also focal length, depth of field, and power density are very stable. The power density is varied by changing the beam diameter of the defocused beam. The focus position was varied to study the variation of power density without

changing other parameters. We can vary the power density by changing the pulse energy or by changing the focal position. The focus position was changed by changing the lens position from F1 to F2; the beam diameter is larger at position F1 compared to F2 and hence, the power density at F2 is larger than at F1. This is now mentioned in sections 2.1 and, 2.2., and the results are discussed in section 3.2.1.

P5. L171 and throughout the manuscript. How were the mass spectra assigned to a spectra type?
This was explained above and is detailed now in section 3.1. of the revised manuscript: "The mass spectra that are discussed in this section were selected to be representative for each particle type in the following manner. From the typically 200-600 useful single particle mass spectra measured for each particle type only those 30-40% (60-240 spectra) with at least 90% of the maximum total ion intensities were selected to ensure optimal hit of the particles by the ablation and ionization laser. These remaining spectra were classified using the fuzzy c-mean algorithm available in the LAAPTOF data analysis software. This resulted in typically two classes of mass spectra per particle type. For each class of mass spectra we manually selected 10 spectra representing all main characteristics and applied an additional mass axis calibration for each spectrum. These 10 spectra showed correlation coefficients of r = 0.7-0.9. An example demonstrating the reproducibility and representativeness of this selection process is given in the supplementary section (cf. Figures S3-S6)."

P7, L243. Silicate particles predominantly come from mineral dust not sea spray. SiO4 is an anion in crystalline orthosilicates and is not an appropriate description of silicate composition.

We agree; this is an obvious error. We have modified the sentence to: "Recent studies with a LAAPTOF by Marsden et al. (2016) of silicate rich ambient dust particles featured similar mass spectral peaks, namely from Si^+, SiO^+, and O^-, SiO^-, SiO_2^- ions."

P7, L256. The work cited used Silicon substrate with organic and inorganic solutions and the claims regarding the fragmentation/ clusters were relating the compounds in solution not the silicon. Please be careful not to confuse clusters with fragments.

Kato et al. (2007) have observed more atomization, and cluster formation in fs-laser, ablation and more fragmentation in ns-laser ablation. The clusters (with n=1 to 6) were observed from the silicon substrate and not from the solution.

P10, L361. It should be pointed out that the conclusions are with respect to SPMS with a counter propagate geometry.
We agree and have modified this sentence. "Generally, ns-laser spectra for the same particle type exhibit higher reproducibility of the spectral pattern than fs-laser spectra with the LAAPTOF in counter propagating geometry".

P10, L361. Do you mean reproducibility of average ion intensity or spectral pattern?
We mean the reproducibility of spectral pattern. With the ns-LAAPTOF we can observe a higher reproducibility of the spectral pattern.

P10, L369. Cl- was observed in negative ion spectra. See comment above.

Thanks for this hint: The sentence was modified to: "For NaCl particles, only in fs-laser spectra high ionization energy species like Cl^+ or N^+ were detected."

Technical Corrections

P2, L92. GmbH not Gmbh.
Corrected.

P10, L372. Sentence structure/word order.
For NaCl particles, only in fs-laser spectra high ionization energy species like Cl^+ or N^+ were detected. Fs-laser ablation also led to formation of oxides, for e.g. core-shell particles, silica particles, and silver oxides for the gold-silver core-shell particles.

Figure1 Inset. It is not clear what the position label, defocus label and arrow are referring to.
The inset picture is modified and labels are marked clearly.

Figure 2. It is not clear what the wavy line represents.

It is an input data signal, and is marked on the schematic diagram. This diagram explains the pre-trigger data acquisition technique. The figure caption has been modified to: "Figure 1: Pre-trigger sampling mechanism of the data acquisition system. The data (input signal, the dotted wavy line) arriving before the trigger event (pre-trigger samples) are saved in the temporary memory of the data acquisition card and then combined with the trigger samples"

Figures 3-9. Please state the estimated power density or laser setting at which these spectra were acquired.

The pulse energies and power densities were added to each figure caption.

Figures 9 and 10. Please state how many particles were averaged and what the error bars represent. The error bars are difficult to see and the quality of the graphics are generally poor.

The averaged intensities are calculated for 10 representative spectra of each particle type and at each power density. The error bars are standard deviations of the average intensity. Both the graphs Figure 9 and 10 were modified for better visibility. The caption of Figure 10 was modified to: "Figure 10: Variation of average total ion intensity with respect to the size of PSL particles. The total ion intensities were averaged for 10 representative spectra of each particle type. (Particle diameters: 500 nm, red circles, and 1000 nm, green triangles). (a, b) at focus position F2 and (c, d) at focus position F1."