Response to Anonymous Reviewer #1

We thank the referee for reviewing our manuscript and the valuable comments. Please see our reply below.

Note:

Reviewer comments are in italics.

Author responses are in normal format.

Changes that were made to the manuscript are in **bold** face.

Review of "Single-particle characterization of polycyclic aromatic hydrocarbons in background air in Northern Europe"

Passig and coauthors describe a measurement campaign at a remote site in coastal Sweden using a two-step LDI/REMPI single particle mass spectrometer designed to measure inorganic, general organic and more specific PAH particle content. Because the instrument separately records more typical LDI mass spectra and more unique REMPI PAH mass spectra, two approaches were taken to bring this compositional information together. Firstly, the LDI mass spectra were clustered using the regular neural network approach, and the corresponding REMPI PAH signatures were examined to gain insight on sources/processing. Secondly, the REMPI dataset was clustered and within those resulting PAH classes the LDI mass spectra were further examined to highlight differences between sources and processes for PAH-containing particles. Although PAHs were detected in relatively few particles in the overall dataset (which can be explained by the remote location and the dominance of aged particles), some interesting connections between PAH mass spectral patterns and the refractory core composition of the single particles can nonetheless be obtained. While the article represents a 'proof-of-concept' for the method, the features of the dataset are useful for informing future particle classifications at other sites. A few things stand out. Firstly the connection between potassium-rich particle cores and pyrogenic PAH signatures (m/z 228/252) is emerging as a useful signature for woodburning particles, even after long atmospheric processing times. Secondly, the connection between iron (detected with high sensitivity using the excimer laser here) and petrogenic PAH signatures (m/z192/206) is useful for identifying aged engine exhaust. Thirdly, more fresh soot particles associated with engine exhaust are characterized by LDI signals for calcium and alkylated phenanthrenes. This information is useful for identifying the original primary sources of these particles, even at remote sites. The discussion of limitations is also useful, as there remain potential hurdles for this type of analysis, including the difficulty in measuring substituted or heterocyclic PAHs. Overall, however, as a first examination of how to parse the complex ambient datasets generated using this new approach, the findings here are valuable for the single particle and source apportionment communities. I only have minor comments to suggest.

We thank the referee for the comments and the vital discussion.

Line 90 define continuous wave

Thank you. **Corrected.**

Line 91: "A few"

Corrected.

Line 114: It would be helpful to discuss how the vigilance factor was arrived at for the REMPI dataset

The vigilance factor of 0.7 was determined in tests of the clustering and manual checks. We added a comment on that: **"…a value that resulted in a good balance between the number of clusters that can be evaluated in manual regrouping and the recognition of prominent PAH signatures.**

Line 139: M for million

Corrected.

Line 163: Na_2^+

We apologize for the error. **Corrected accordingly.**

Line 166: Na_2Cl *for m/z 81/83*

We apologize for the error. **Corrected accordingly.**

Line 179: Was this EC/OC regrouping used to inform the final 10 classes in some way?

The final 10 classes were realized by manual regrouping after ART2a, as stated earlier in the manuscript. There was no additional regrouping for the EC/OC ratio. **We removed the misleading statement from the manuscript.**

Line 186 subscript 2.5

Changed accordingly.

Line 187 m^3

Thank you for careful check! **Corrected.**

Figure 3 part of caption unclear: top row and bottom row?

There are two different regions listed for each period in Fig. 3(a). >12h before entering the site in the first line, <12 h in the second line. **We changed "row" to "line" to avoid misinterpretation.**

Line 287 caption: "absolute number and number fraction"

Changed accordingly.

Table 2: bottom row, "Local"

Corrected.

Line 405: Refer to the name of this PAH class- HMW?

Changed accordingly.

Figure 8: Concerning the acidity aspect- it is interesting that there is no detectable signal for ammonium in these sulfate-containing particles. Although this appears to be the case for several of the PAH classes. Is detection of ammonium less efficient in this system relative to single-step LDI instruments. This would be worth discussing.

Thank you for this interesting idea and comment! As a rough trend, we find higher ammonium signals in particles with strong signals of (secondary) nitrate (e.g. Figs. 7 and S7) and nearly no ammonium in fresh particles (Fig. 9) and particles from wood combustion (Fig.6.). However, the ammonium signals in PAH-containing particles are generally low and not sufficient for a statistically sound analysis here. We discuss possible effects of the two-step method on the detection of nitrate, sulfate (also valid for ammonium) in the manuscript:

„…Thirdly, the ionization technique itself may contribute to this trend: Particles that are fully hit by the desorption laser produce more intense PAH spectra via REMPI of the plume. However, secondary nitrate or sulfate is also desorbed to a larger extent from these particles, and less amount of this material remains on the particle for detection via LDI in the second laser shot. Nevertheless, in so-far unpublished field experiments with the same setup during winter in Central Europe, we often found PAHs on more than 20% of all particles, also if strong nitrate- and sulfate signals were present, thus the instrumental aspect seems to be of minor importance here."

In several experiments, we could not find a substantial loss of efficiency for such particle components compared to single-step LDI. However, in a direct comparison between single-step LDI at 248 nm and 193 nm wavelength, we see a higher detection efficiency for nitrogen-containing compounds with the 193 nm laser (Passig et al., 2020).

***Citation**: https://doi.org/10.5194/acp-2021-722-RC1*