Answers to referee #2

p601, ln 10, please give the readers an indication as to the relative abundances of neutral species to charged, based on measurements. This is important because it gives some context as to the significance of the ambient ion measurement technique described here. A person not aware of the relative abundance of neutral molecules vs. ambient ions may not realize that the former far outweighs the latter based on observations by Eisele and colleagues. I note that on p615 this point is raised : : : I suggest that this should be moved to this paragraph in this paragraph that starts on ln 7 since this issue of neutrals vs. ions is raised here.

The abundance of ions in atmosphere is dependent on ionization rate and the sink of the ions. Ionization rate depends mainly on radon decay (changes with the change of mixing layer height) and cosmic radiation (rather constant in single measurement point). The main sink processes are the coagulation on pre-existing aerosols and recombination of ions. The first steps of ion formation is kinetically limited and thus the first ions are from most abundant air molecules, N2, O2, CO2, H2O. First steps are followed by cascade of collisions and finally charge will be associated with species that have the highest proton affinity (positive charges) and electron affinity (negative charges). Air composition plays an important role on how charge distribution between different species, e.g. at night time charges is distributed between several hundred species, but after sun rise and sulphuric acid form and the majority of the charge is associated with sulphuric acid (monomer, dimer, trimer). Therefore, it is not straight forward to give a charged/neutral ratio that the referee has asked for, since it depends strongly on the species in question. However, the total ion concentration is about ~10^3 ions/cm3 and the concentration of air molecules is 10^{19} cm^{-3} (pressure 1 atm and temperature 298 K). If assuming that all charge is carried by sulphuric acid and neutral sulphuric acid concentration is about 10^7 cm^{-3}, the charged to neutral ratio for sulphuric acid is ~10^{-4}.

ACTION: new sentence will be added to paper

For sulphuric acid the charged fraction during the concentration maximum (10^7 cm^{-3}) is around 10^{-4}.

p602, ln 25: Since the main purpose of this instrument is in "bridging the gap" between gas and particle phase measurements, it would seem appropriate to mention the m/z range of this instrument in this part of the document, along with some estimate of the equivalent mobility diameter range at large values of m/z.

Referee is correct, in this section we should mention the measurement range, although we discuss it later.

ACTION: new sentence will be added

The mass range of the instrument is set to be 8 – 2500 Th (corresponds to an estimated mobility diameter of 0.2-2.25 nm).

p604, eq 1: the standard expression for mass to charge ratio is m/z. I suggest you use this here and in all subsequent references to this in order to reduce confusion. Eq. 4 can be left as-is, using a capital Z to denote the number of rings+double bonds.

We partly agree with referee that m/z is commonly used, however it is so in the mass spectrometry community. This paper is aimed to aerosol and atmospheric scientists to whom the Q in nominator is commonly used expression for charge. It is also the commonly used symbol in the SI system. We thus prefer to leave symbols for mass – m and for charge – Q

ACTION: none

p605, ln17: the threshold is mentioned here, but nowhere else. It seems to be an important aspect of the analysis worth mentioning. Normally such a threshold is defined as a function of the baseline noise (e.g., three standard deviations of the baseline noise). Please provide some discussion as to its significance in your analysis.

Also the other referee was asking similar question. We have added a new chapter that discusses the noise level and detection limit of the instrument.

Background noise and detection limit

The APi-TOF has a very low background noise level, which makes it possible to accumulate signal over long time periods. The signal quality is limited by counting statistics, but there is a small background noise from scatteres ions and electrons. The instrumental background noise is depicted in figure X1a, where a 60 min average of 15 s spectra has been used. The APi-TOF was sampling from ambient air with an ion filter (50 cm silicone tube) in front of the inlet. The signal has been converted to ions cm^{-3} in the same manner as the samples were. The noise reaches $0.5*10^{-3}$ cm^{-3} below 100 Th and decreases to $0.1*10^{-3}$ cm^{-3} around m/Q 500 Th. Panel B of Figure X1 shows the detection limit of the mass spectrometer (this does not include transmission of the ions) defined as 3 times the standard deviation of the signal during the averaging period. A power law fit has been used to parameterize the relation to m/Q. Ion transmission (Figure 5) has to be taken into account for instrument detection level determination and can be calculated from equation X1.

$$DL_{\frac{m}{Q}} = \frac{c(\frac{m}{Q})^d}{tr_{\frac{m}{Q}}} \qquad \text{Eq. X1}$$

where, $DL_{m/Q}$ is the detection limit for a given m/Q. c and d are empirical parameters that define the detection limit of the mass spectrometer (c=0.008, d=-0.24 based on the power law fit in Fig. X1a) and $tr_{m/Q}$ is the transmission at the chosen m/Q.

We used setting 2 for positive ions (Figure 5) to give an example of the detection limits. In table X1 the detection limits are calculated for the calibration substances using equation X1. It should be noted that the high DL at low and high masses can be drastically improved if the transmission can be optimized.

However, for the range where the transmission is decent, the DL is well below 1 ion/cm^3 for a 60 min average.

Tabel X1. Detection limits (DL) of APi-TOF in ions/cm^3 for a 1 h average with 95% confidence intervals. Settings refer to Figure 5.

Mass/charge	Transmission	DL (ion/cm3)	-95%	+95%	Setting
75	0.0007	4.6	4	5.2	pos 2
80	0.005*	0.6	0.6	0.7	neg*
412	0.0037	0.6	0.5	0.7	pos 2
672	0.0043	0.5	0.4	0.5	pos 2
900	0.0046	0.4	0.3	0.5	pos 2
1392	0.00016	10.7	9.1	12.6	pos 2

* average of two settings

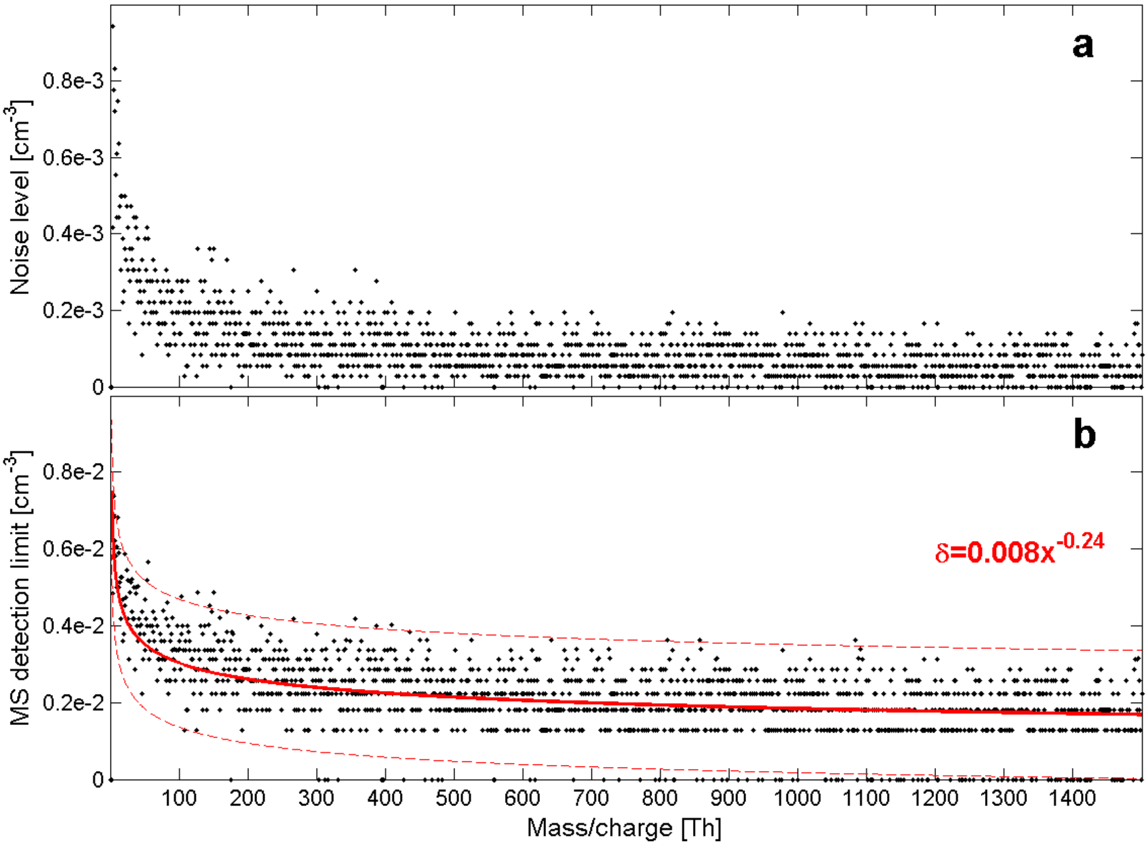

Figure X1. The background noise and mass spectrometer detection limit of the APi-TOF based on a 60 min average of ambient sampling with an ion filter in front of the inlet. In panel a, the black dots are 60 min average integrated signals at 1 Th resolution.In panel b, the black dots are 3 times the standard deviation of the integrated signal, the red solid line is a power law fit to the data, and the red dashed lines are 95% confidence interval levels of the fit.

p606: Some additional discussion of equation 3 may be helpful. The calibration equation (eq. 1) describes the relationship between the flight time and the m/z of the ion.
Given this, the only way that a and b can affect the baseline is if actual ions are in the region defined as "ion free" by the authors, that is, the 0.4 amu area between peaks.
What was the basis for choosing this size for the ion free region? Are there any instances,
when for example working with species with large mass defects like Fe or Si,
in which this criterion may produce erroneous results? If this is a typical procedure for calibrating TOF spectra, can you provide a reference?

The baseline region defined here, is only used for mass calibration, it is not actual baseline. In other words, it is not used to estimate peak heights or anything else. The region of 0.4 Th for baseline region was chosen based on trial and error. If narrower area is used the optimization algorithm has more loose criteria and the result is not as reliable. Imagine that two peaks are 1 Th away from each other and there is 0.5 Th pure baseline in between (peak width is 0.5 Th , not at half height, but at the bottom). Now, if the baseline region used for mass calibration would be 0.1 Th there would be 0.5 Th wide window that gives equal result for baseline minimization calibration (since the baseline is assumed to be flat in this 0.5 Th area). Thus, there are set of mass calibration values that appear to give equal accuracy (same value for baseline average). If again, the baseline region is too wide, let say 0.6 Th, and baseline region is overlapping with rising and falling peak, the baseline average has again set of mass calibration parameters that show no difference. The best value for baseline region in this case would have been 0.5 Th, if mass calibration values are changed in either direction the baseline average value (that is minimized) starts to increase. The 0.4 Th wide region used in this study is found to be optimal over the whole spectrum (<800 Th).

Rest is commented in a separate document "Automatic mass calibration".

ACTION: new chapter will be added

p605, ln 10: add space between 1-D and data

ACTION: done

p607 ln10: please use a consistent notation: suggest Th.

The units used in this paper are Th for mass-to-charge and Da for mass. In this location we refer to mass and that is why the unit is Da. But we agree, if always the charge is 1 to use common unit for mass/charge and mass is tempting.

ACTION: none

p607, ln16: the correct expression for Kendrick Mass and Kendrick Mass Defect (according
to all the papers that this ms references on this subject) are as follows:
Kendrick Mass = Observed Mass - (Nominal mass of CH2) /(Exact mass of CH2)
Kendrick Mass Defect = Nominal Kendrick Mass - Kendrick Mass
The only place I have seen the expression used by the authors is in the Wikipedia entry on the Kendrick Mass. The authors must correct the text in this section, plus the data in Table 1 and Figure 12.

Referee is right; the Kendrick mass defect is defined in references nominal Kendrick mass-Kendrick mass, however we chose to use (and define it in p607 ln16) the Kendrick mass defect so that the resulting values behave similarly with the logic of normal mass defect, eg sulphur has negative mass defect as it weighs less than the integer mass and H has a positive mass defect (in both Dalton and Kelvin scale). Also with figure 12 the species with lower mass defect are plotted below, and species with higher are plotted above. As the sign does not change the conversion to the Kendrick scale and the sign serves no purpose and causes confusion, we chose to use it in the way that is more intuitive and easier for readers.

ACTION: clarifying note will be added to text.

Kendrick (1963) defined the Kendrick Mass Defect as Nominal Kendrick Mass - Kendrick Mass, but this expression produces negative values for masses that are higher than their integer masses. In this work we have chosen to define the Kendrick Mass Defect as Kendrick Mass - Nominal Kendrick Mass as this is more intuitive when the mass defect and Kendrick Mass Defect behave similarly.

p607, ln18: I feel that the authors should emphasize that the compound type (Z, also the number of rings+double bonds) can apply to any species type. The discussion provided here is specific to nitrogen-containing organics and, while it's obvious to those familiar with this analysis that it is generally applicable to CcHhNnOoSsPp: : : it may not be clear to everyone. This is especially important for the study of new particle formation, since sulfur and even halogens such as iodine may be important constituents of observed ambient ions.

Referee is correct. We will add more general expression of compound type to the paper

ACTION:

$C_cH_hN_nO_o$ is changed to $C_cH_hN_nO_oS_sP_p$

p608, ln 7: This paragraph belongs in the section on mass calibration. It only obfuscates the presentation of the Kendrick analysis technique, and does little to explain how exact mass analysis can be used for compound identification.

This paragraph describes the peak fitting routine for Kendrick analysis and exact masses. It is not the same as the one for mass calibration. Thus this paragraph is in correct location.