S1 Ion peak area thresholds

The ion peak area threshold describes a certain intensity value in mass spectra that the ion signals have to exceed to be further analyzed. To determine this threshold, we used all ambient single particle mass spectra (in total: 18387) analyzed by the ALABAMA during NETCARE 2014. We further assumed that certain m/z values in single particle mass spectra are likely not occupied by ions produced from atmospheric substances, such as m/z (positive and negative) 2-11 and 245-250. Thus, ion signal intensities from atmospheric substances have to exceed signal intensities at these non-occupied m/z values. Figure 1 presents the cumulative probability of signal intensities belonging to these non-occupied m/z values (black and red lines). At cumulative probabilities between 99 % and 100 % signal intensities reach 10 mV for positive ions and 25 mV for negative ions (vertical red and black lines). These values are defined as ion peak area thresholds in our evaluation.

The cumulative probabilities of the measured ion signals at m/z +59 and +58 (considered as marker peaks for TMA in single particle spectra) are further given in Fig. 1. We can use it to estimate the range of uncertainty of the relative fraction of particulate TMA. For example, by shifting the ion peak area threshold - or + 5 mV, 13 % more or 7 % less spectra with signals at m/z +59 would be analyzed.
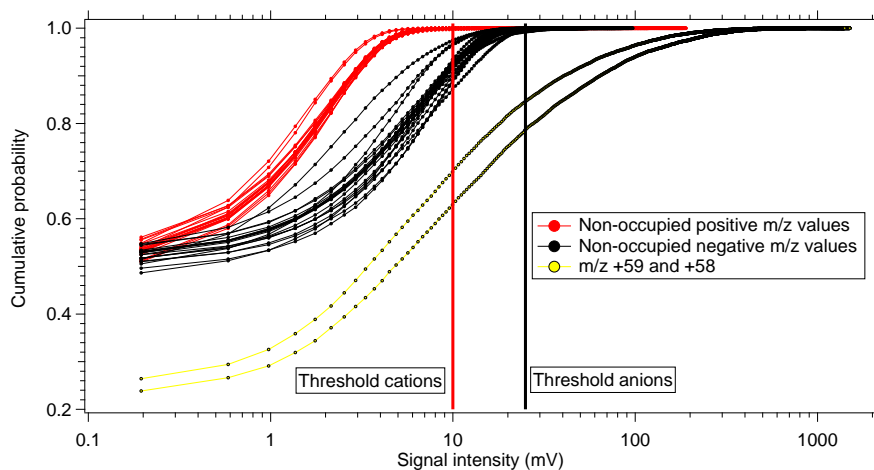
Figure 1. Cumulative probability density functions of signal intensities from different m/z values: m/z +58 and +58 (yellow), m/z -2 to -11 and m/z -245 to -250 (black lines) and m/z +2 to +11 and m/z +245 to +250 (red lines). The vertical red and black lines depict the cation peak area threshold of 10 mV and the anion peak area threshold of 25 mV, respectively.

S2 Potential reasons for missing negative ion signals

In order to describe intensities of anion spectra, we calculated for each spectrum an average value and standard deviation of the 250 negative signal intensities (correponding to 250 m/z values). Small mean values along with small standard deviations indicate the detection of low signal intensities in anion mass spectra.

Regarding the missing sulfate signal mentioned in Sect. 2.5. and 3.3., the absence of signals at m/z -97 and/or m/z -96 correlates well with small values of mean and standard deviation of the negative mass spectra (Fig. 2). We can thus assume that the reason for poor signals from sulfate ions is not primarily that the particles did not contain sulfate, but likely that no negative ions were detected generally or that no negative ions were formed during the ionization process.

Temporally switched off negative high-voltages could explain the absence of signals in anion mass spectra. ALABAMA high-voltages are automatically switched off if the pressure in the mass spectrometer exceeds 5 x 10^{-6} mbar. However, while checking the pressure in the ALABAMA mass spectrometer it appeared that our measurements were always performed above this critical pressure value.
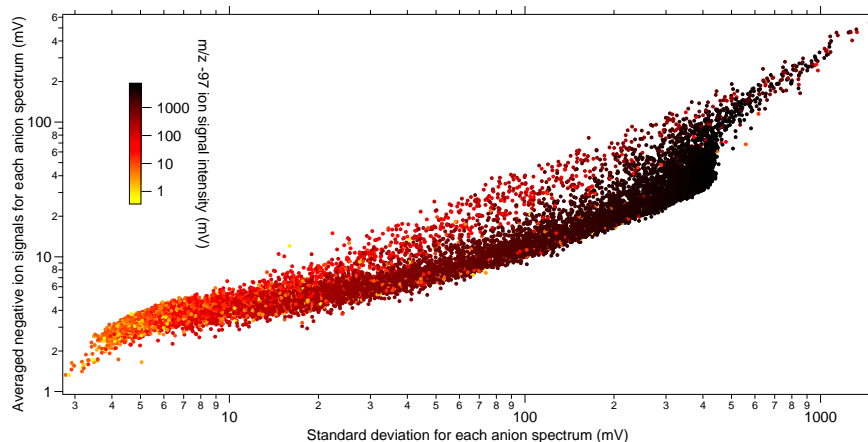
Figure 2. Correlation between average value and standard deviation of the 250 negative ion signal intensities (correponding to 250 m/z values) of each spectrum. The color-code shows the ion signal intensity at m/z -97 (sulfate).
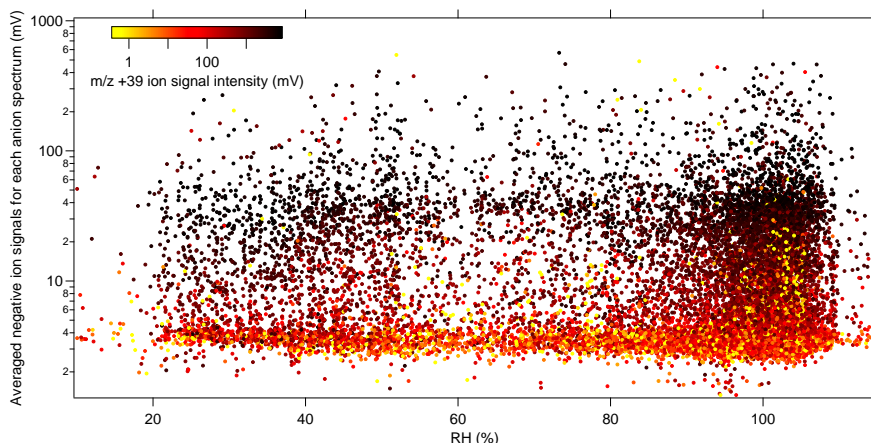
Figure 3. Average value of the 250 negative ion signal intensities (correponding to 250 m/z values) of each spectrum (see Fig. 2) compared with values of relative humidity (RH). The color-code shows ion signal intensities at m/z +39 (potassium).

High values of relative humidity (RH) could also explain poor anion signals as earlier reported by Neubauer et al. (1998). Figure 3 shows the averaged negative ion signal for each spectrum compared to the measured ambient RH and the color-coded ion signal intensity at m/z +39 (potassium). Obviously, averaged negative ion signals at small potassium ion signals (yellow to red colors, Fig. 3) slightly decrease with increasing RH. According to Neubauer et al. (1998), high RH may negatively affect anion mass spectra. Reason for this observation is not known. However, we further observed anion spectra with enhanced averaged ion signals at high RH, but with the concurrent existence of increased potassium ion signals (red to black colors, Fig. 3). This observation indicates that an internal mixing of particles with potassium may positively affect the intensity of anion signals, although RH is high. Thus far, it is not known if matrix effects may favor the formation of negative ions in the laser ablation and ionization process. To conclude, low potassium ion signals combined with high ambient RH may negatively affect our measurements of anion mass spectra. This assumption would further explain the poor anion signal observed in the laboratory mass spectra of TMA-containing particles (even though sulfuric acid was added).

References

Neubauer, K. R., Johnston, M. V., and Wexler, A. S.: Humidity effects on the mass spectra of single aerosol particles, Atmospheric Environment, 32, 2521–2529, 1998.