

Interactive comment on “Chemical composition, microstructure, and hygroscopic properties of aerosol particles at the Zotino Tall Tower Observatory (ZOTTO), Siberia, during a summer campaign” by Mikhailov et al.

We would like to thank Referee #3 for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

Comment

The authors infer much about the chemical and structural information from the single particle images (Section 4.2) that seem outside of the analytical capabilities of the instruments and the figures provided. While a core-shell morphology appears to be present in particles shown in Figures 7d-f, it is not clear that they are solid organic shells since the images provided by Figures 5 and 6 do not match the spatial resolution of the structural variations. Furthermore, it is not stated how many of the observed particles shared this morphology so it is not yet convincing that the observed dehydration experiments of the larger population of particles can be explained by this proposition.

Author Response

In p. 7856, line 26, the following text has been added.

“Limited particle statistics is an inherent difficulty of most single particle techniques. Thus, we applied two different single particle approaches in this study to broaden the statistical basis and to check the consistency of the independent data sets. The total particle number that has been probed with STXM is 150, while the total particle number for TEM analysis is 810. The TEM data allows a classification of the particle ensemble based on morphology, while the STXM data (though more limited in statistics) provide more detailed insights into the chemical composition and therefore complement the TEM data set. The visual TEM analysis of 725 AM and 85 CM aerosol particles has revealed three main morphology types: (i) homogeneous spheres, which can be attributed to terpene- and isoprene-based SOA droplets (Kourtchev et al., 2005; Pöschl et al., 2010), (ii) mixed SOA-inorganic particles with core-shell morphology, and (iii) irregularly shaped primary biological aerosol (PBA) particles, such as plant fragments. In the submicron particle range the balance between uncoated (type i) and coated (type ii) aerosol particles is 32% and 62%, respectively, which agrees with the STXM data. Approximately 5% can be attributed to PBA particles with an organic coating fraction of ~50%. In the coarse particle mode almost all aerosol particles are internally mixed with surface organic coating (~80%). **Among them ~20% have a high-contrast-density outer core (Fig. 7d-f) presumably formed from sparingly soluble organic species due to liquid-liquid phase separation upon particle dehydration (Song et al., 2012).** Approximately 13% are PBA particles. In addition, a minor fraction (<1%) of the fractal-like soot aggregates was found on the TEM images of the AM and CM aerosol particles”.

Additional references

- Song, M., Marcolli, C., Krieger, U. K., Zuend A., and Peter T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, *Atmos. Chem. Phys.*, 12, 2691–2712, 2012; www.atmos-chem-phys.net/12/2691/2012/.
- Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M., and Claeys, M.: Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland, *Atmos. Chem. Phys.*, 5, 2761–2770, 2005.

Further, for clarity just after the phrase (p.7864, lines 8-10):

“Lower values of D_w obtained in our study can be due to solidification and crust formation at the particle surface as can be seen in Fig. 7d–f, which can strongly inhibit the interfacial transport of gas molecules (Pfrang et al., 2011)”

the following sentence has been added.

“As noted in Section 4.2, a significant fraction (~20%) of the coarse mode particles have this type of outer core, most likely formed as a result of liquid-liquid phase separation”.

Comment

The inherent response time of the FDHA measurements to changes in RH is not mentioned, and it seems important in interpreting the timescales for evaporation of water estimated from Figure 10. Relevant

arguments from past publications should be repeated here as the interpretation of evaporation timescales attributed to particle characteristics rests on this detail.

Author Response

The response time of the FDHA system to the water vapor concentration change depends on the measurement cell and detector volumes, as well as on the carrier gas flow rate. Early test experiments showed that this time was 10 ± 3 s, therefore the observed minute time scale of water vapor release (Fig. 10b) appears representative. The observed slow RH change ($\sim 0.4\%$ RH per min) (Fig. 10, red lines) is due to the inertia in the response of the humidification system to a temperature change. Note, the delay of the dehydration peaks was observed at a constant RH (Fig. 10b, marked with green arrows).

Finally in p.7863, line 11 the following sentence has been added.

“This time is much more than the inherent response time of the FDHA system, which is ~ 10 s”.

Comment

Relevant arguments from past publications should be repeated here as the interpretation of evaporation timescales attributed to particle characteristics rests on this detail. Also, the authors attribute observed mass losses of hydration/dehydration to water instead of semivolatile vapors according to repeated cycles (Section 2.3.5); do the hydration/dehydration points in Figure 8 consist of multiple cycles?

Author Response

Yes, they do. The different hydration/dehydration points in Figure 8 consist of multiple cycles on the same sample. This was mentioned on p.7849, line 27, p.7850, lines 1-5.

On p.7857, line 6, the following clarification has been added “The different symbols represent repetitive measurements on the same sample, indicating a good reproducibility of the water uptake/release results and negligibly small effect of particle evaporation due to semivolatile organics (Sect. 2.3.5)”.

Comment

That mineral dust is not present in large quantities is argued by their absence from STXM analysis (Section 4.1) even while nss-potassium that is not due to burning and calcium. The detection limit for each element should vary according to the photon flux, sample response, and detector response at wavelengths corresponding to their ionization energies, so it is difficult to interpret this information directly from comparison of images across elements. The authors may wish to refer to absorption cross sections provided by CXRO for various elements (as the authors used to estimate N/O ratios) to justify part of the observed differences between calcium and O, N, and C.

Author Response

Both types of single particle analysis consistently show that mineral dust-like particles only account for a minor fraction of the particle ensemble. In STXM analysis, mineral dust particles typically are a rather noticeable phenomenon due to their comparably large size, irregular-shaped morphology, and strong absorption (particularly in the carbon pre-edge range and also at the oxygen edge due to Al, Si, and Fe oxides). The dominant particle type on the samples is sulfate salts with variable amounts of organics (often as particle coating). In other words, the footprint of the inorganic constituents in most particles equals the footprint of the nitrogen and oxygen absorption, suggesting that ammoniated sulfate salts account for most of the inorganic fraction. Moreover, the morphology of most particles has a droplet-like appearance in contrast to the irregular shape of mineral dust particles. The potassium traces observed are typically associated with the sulfate cores, suggesting that potassium acts besides ammonium as a cation for sulfate. Few particles show absorption at the iron absorption edge, indicating that there is only a small fraction of dust-like particles. The absorption cross section of iron is of the same order of magnitude as the cross sections for C, N, and O, indicating that the technique is sensitive enough for Fe detection (Henke et al. 1993). We suggest that the combination of these different observations regarding size, morphology, and

absorption properties is strong enough to support our statement that mineral dust accounts only for a minor fraction of the particle burden.

The following modifications have been implemented in the text to clarify this aspect:

On page 7853, l. 15-17, the sentence:

“Mineral dust was not considered in the mass closure since the STXM-NEXAFS results indicate the absence of significant dust-like components in the samples (Fig. S2.2).

has been replaced by:

“Mineral dust was not considered in the mass closure, since the STXM-NEXAFS results indicate the absence of significant dust-like components in the samples (Fig. S2.2). In STXM analysis, mineral dust particles are typically a rather noticeable phenomenon due to their comparably large size, irregular-shaped morphology, and strong absorption (i.e., at carbon pre-edge and also at the oxygen edge due to Al, Si, and Fe oxides). Most of the observed particles differ strongly from dust-like particles in morphology and absorption properties.”

Moreover, the caption of Fig. S2.2 has been modified slightly to clarify our statements:

“STXM overview images and maps for various elements showing a characteristic region on an aerosol sample taken on 15 June. (A and F) show carbon and oxygen post-edge images with all particles in the field of view. (B-E and G-J) show elemental maps for various elements. Overview maps show that the clear majority of particles is strongly absorbing at the characteristic energies of N as well as O and shows moderate absorption for C. Few particles also absorb at the K and/or Ca edges. Faint x-ray absorption has been found for iron (Fe) and aluminum (Al), which are typical components of mineral dust particles. The absence of irregular shaped particles (except irregular shaped PBA particles with obvious biological appearance) further emphasizes that mineral dust does not play a significant role in the sampling period of this study. Axes display image dimensions in μm . Optical density is unified for all STXM images (black-white code; OD range 0-1.7) and unified for all elemental maps (color code; OD range 0-0.7). The red box in (A) marks a particle with beam damage (horizontal line) due to refocussing.”

Reference

Henke, B. L., Gullikson, E. M., and Davis, J. C.: X-ray interactions - photoabsorption, scattering, transmission, and reflection at $E=50\text{-}30,000$ eV, $Z=1\text{-}92$, Atomic Data and Nuclear Data Tables, 54, 181-342, 10.1006/adnd.1993.1013, 1993.