On the enigma of new particle formation in the atmosphere

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It is still an enigma of atmospheric science how aerosol particles are formed at the molecular level although scientists have peeled away layer after layer of this mystery by developing new techniques to observe smaller and smaller particles (Andreae, 2013; Kulmala *et al.,* 2013). It is interesting that in the Amazon rainforest new particle formation (NPF) almost never occurs (Pöhlker *et al.,* 2012). Can it be related to potential role of high humidity, besides the effects of the molecules, such as acids, amines and organics? Also, the mystery of the chemical processes that lead from volatile organic gases to organic aerosols in the atmosphere should be unravelled (Andreae, 2013).

We use an advanced method to investigate the formation of aerosol particles starting from gas phase reactions including trace gases and ions in the laboratory conditions (Luts *et al.,* 2011, Parts *et al.,* 2012). Particularly, we study the effect of enhanced humidity. We produce new air ions by a radioactive ^{241}Am and trace their evolution within the age interval from few tenths of a second (young ions) up to few ten seconds (old ions). The changes in size and mass distributions of ions are investigated concurrently by means of two instruments: 1) air ion spectrometer (AIS, Airel Ltd) and 2) mass spectrometer (MS, Sciex API-300).

The behaviour of the air ions obviously depends on the particular chemical composition of the air.

Mass spectra of negative air ions show that the enhanced concentration of water has no effect on the set of the abundant MS peaks, but changes their relative intensity. This effect is especially noticeable in the case of young negative ions. Old ions undergo insignificant modification of the mass spectra (Luts *et al.,* 2011). In several cases, we observed *m/z* at 89, 125, 179, and 269, which are in a good correspondence with the masses of water clusters $OH^-(H_2O)_4$, $OH^-(H_2O)_6$, $OH^-(H_2O)_9$, $OH^-(H_2O)_{14}$. Even though the existence of such clusters remains questionable and needs to be proved.

The AIS spectra of negative ions demonstrate that variations in the concentration of water vapour have effect both upon young and old negative ions. More water vapour induces more large young ions, but less large old ions, when to compare with the background spectra of young and old ions, respectively. This can be interpreted as smaller clusters are more stable and the size distribution of negative ions depends on the age and water vapour concentration. The AIS spectra of positive ions is also affected by changes in water concentration, but the modifications are weaker.

Mass spectra of positive air ion consist of a large number of peaks (Fig. 1). Positively charged clusters are larger than dominant negative clusters. Contrary to negative ions, high water vapour concentration altered the set of abundant MS peaks what complicates the interpretation of results. The observed at *m/z* 378(379), 408 and 436 peaks could be related to known stable water clusters $(H_2O)_{21}$, but this proposal should be proved later.

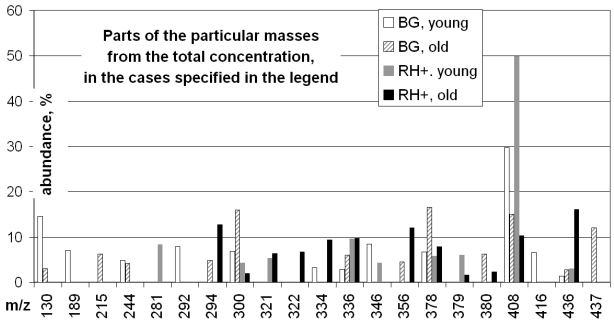

Figure 1. Positive air ions mass distribution at different relative humidity (BG – background ions, RH – relative humidity).

In the Amazon rainforest (Pöhlker *et al*., 2012), the concentration of water vapour is high. Polar oxidized volatile organic compounds (VOCs) and other biogenic emission can react with water and lead to secondary organic aerosol particles. Water should play an important role in these processes and could be a reason why NPF is not observed. Unravelling the enigma of water properties (*eg* clusters formation and stability) could be a key to understand new particle formation in the atmosphere.

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