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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal and diurnal variations of particulate nitrate and organic matter in the Central European atmospheric aerosol" *by* L. Poulain et al.

Anonymous Referee #1

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This review supplements an earlier review which it was not possible to complete because some of the figures were extremely difficult to read in their original size.

The first section of this paper concerning the organic content of the aerosol appears generally sound and presents some interesting results. However, the section concerning particulate nitrate is both extremely difficult to read and highly speculative and requires considerable revision if it is to be published at all.

The authors have provided some clarification of the dissociation constant and deliquescence constant, and as they concede, both should be indicated with a capital letter K rather than the lower case letter currently used. It is nonetheless confusing that the dissociation constant (Kp) is a product of two gas phase concentrations, whereas judging from the units, Kdeliq, appears to be the concentration product of two ions in solution. Consequently, these two constants are very different, one focussing on the gas phase, the other on the aerosol phase. It would have been far more helpful if both expressed the gas phase concentration product with Kdeliq taking account of humidity as well as temperature. The lack of definition and poor explanation of these terms makes it very difficult to follow the arguments. Studies of the ammonium nitrate/ ammonia/nitric acid system are numerous in the literature and generally contain measurements of the gas phase species as well as the aerosol. It is a considerable weakness of this study that the gas phase concentrations are not available and this is one of the reasons that the discussion of the data appears highly speculative.

The implicit assumption made by the authors that equilibrium is obtained instantaneously is incorrect. There are published studies demonstrating marked kinetic constraints. These would be greatest in relation to equilibration of solution droplets (i.e. above the deliquescence humidity) and may well explain some of the apparent lags seen in the data. The authors should also recognise that thermodynamic studies of the ammonium nitrate system nowadays generally take account of internally mixed aerosol whereas their calculations are based purely on an externally-mixed ammonium nitrate particles. Addition of temperature and RH to Figure 4 would be helpful.

There is also an explicit assumption made by the authors that diurnal changes in advected pollutant load are not significant. This is not justified through data and this is again a reason why measurements of ammonia and nitric acid vapour would have been especially useful.

The authors hypothesise that their data demonstrate the formation of nitrous acid vapour and aqueous nitric acid (neither of which was measured) and that photolysis of nitrous acid vapour is occurring leading to an early morning peak in nitric oxide. They presumably also have data for NO2 or NOy which they do not include in Figure 6, and taken together with the lack of HONO and HNO3 data, the picture is highly incomplete. Figure 6 includes a plot of both J(NO2) and J(O1D). They do not provide data for J(HONO) but the diurnal profile of J(HONO) is not very different from that of J(NO2). There is a large rise in nitric oxide occurring almost immediately that J(NO2) begins to rise which persists for about 5 hours. According to Seinfeld and Pandis (p252) the photodissociation lifetime of HONO is about one hour for early morning sun. This rise in NO seems more probably associated with photolysis of NO2, or possibly advection. The reader is unable to assess whether photolysis of NO2 may be a contributor to the peak in NO as the data are not shown. Perhaps most importantly, the diurnal profile of hydroxyl radical parallels that of J(O1D) suggesting that photolysis of HONO is a very small source compared to photolysis of ozone.

Taken together, these points indicate that the interpretation of the nitrate aerosol and associated data is highly speculative and not well supported by the very limited quantity of data. It cannot be recommended for publication.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11611, 2011.