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Atmospheric
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Discussions

Interactive comment on "Seasonal and diurnal characteristics of water soluble inorganic compounds in the gas and aerosol phase in the Zurich area" *by* R. Fisseha et al.

R. Fisseha et al.

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We thank both referees for their helpful comments. Here are our replies.

Referee 1:

The referee mentioned that an influence of carbonate on the nitrate detection was not observed previously. Indeed for only inorganic anion measurements, carbonate does not interfere with nitrate. However, we optimized the method for organic and inorganic anion measurements with a gradient in eluent strength which results in a nitrate interference with carbonate. Further optimization procedures may reduce this interference in the future, however, the performance was considered to be sufficient for the current application. The referee was furthermore astonished to see an overestimation of the SO_2 fluorescence data compared to the WEDD data, and expected the opposite to be true, with a denuder sampling efficiency for SO_2 of about 80-90%. This is indeed contrary to the expectation, but we explain this with the fact that the UV fluorescence has a higher detection limit (1.05μg/m^3 according to the instrument specification) than the WEDD/AC (20ng/m^3). The concentration of SO_2 in some cases was lower than the detection limit of the UV fluorescence. Therefore we believe that the WEDD/AC results are more reliable than the UV fluorescence measurement. In addition we believe that we don't have a major breakthrough of SO2 from the denuder under the environmental conditions since the diurnal variation of the denuder is substantially different from the one of the aerosol collector. The referee indicated that Fig. 1 is unnecessary if the general good agreement is mentioned. We will remove Fig. 1 in the final version, and mention the correlation equation along with the correlation coefficient. We agree that ammonium data would have been beneficial; however, no ammonium measurements were performed for this study. The referee also indicated the assumption that all PM10 nitrate (or TSP nitrate) in Zurich occurs as ammonium nitrate seems to be uncertain and mentioned that according to Hueglin and Gehrig (2000), part of the nitrate is expected to be present in the coarse mode. An excerpt of the data of Hueglin and Gehrig (2000) is now also available as a paper (Hueglin et al., 2005). According to this paper, most of the nitrate was present in the PM2.5 at this site in Zurich in 1989/90, and thus as the fraction of nitrate salts in the coarse mode was negligible. Since 1999, sulfate values have further decreased in Switzerland, further enhancing the chance that particulate nitrate is associated with ammonium. In addition EMEP data indicate that ammonia is generally in excess in Switzerland (see http://www.nilu.no/projects/ccc/emepdata.html). We will change the labeling of the y-axes in Fig. 3 to make it clear that the concentrations of the ammonium salts are presented. Furthermore the difference between Figure 2 (Figure 1 in the new version) and Table 3 are due to the fact that Figure 2 is related to the ammonium salts of nitrate and sulfate while Table 3 relates to the sulfate and nitrate concentrations. The referee

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suggested to add the HCl/Cl^- distribution, however, we decided to skip this because it was not relevant to the topic we discussed. We do not see the significance of adding a time serious of gaseous HNO_3 in Fig. 6, as suggested by the referee, since in March the fraction of gaseous HNO_3 is very low as indicated in the mean diurnal variation of nitric acid in Fig. 4. In addition, the discussion of specific events in Fig. 6 would be speculation and is beyond the scope of this paper. The dates mentioned in the paper indicate only examples which show similar behavior of the model and the measurements. We will add a short summary of the importance of HONO for atmospheric chemistry in the introduction. However, we prefer to keep Fig. 8 in spite of the referee's suggestion to cancel it because it also shows variability of data for different regimes of HONO concentrations. We will add a comparison of the sulfate values for the year 1999 and 2002/2003. However, this is not possible for nitrate values because of the much greater seasonal variation and of the potential artifact involved in the filter nitrate measurements. Furthermore the reviewer mentioned several minor editorial points, which we will be happy to follow in the final version.

Referee 2:

The reviewer suggested that, if ammonium data were available, it would be interesting to see if a similar relationship as Pathak and Chan (2005) could be found between excess ammonium and nitrate in the samples. We did not measure ammonia during this study, and therefore an analysis of excess ammonia following the work of by Pathan and Chan (2005) was not possible. The referee also suggested the presence of sea salt and crustal aerosols that act as a sink of nitrate as a possible reason for the under prediction of nitrate. However, the possibility of nitrate reaction with sea salt is very unlikely in Zurich aerosol as Zurich is situated on the mainland of Europe. The possibility of nitrate binding with crustal aerosol was not completely excluded in our study. However, in an earlier study, Hueglin et al. (2005) showed that more than 85

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5809, 2005.