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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.

Anonymous Referee #1

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The current and future levels of particulate matter, especially in urban areas, are of great concern and air quality standards have been formulated to address impacts on human health as well biosphere. Airborne particulate matter is a complex mixture of pollutants of anthropogenic and biogenic origin and recently it became clear that any impact can't be derived from the particle mass alone. Therefore the authors investigate the chemical composition of aerosols in the urban area of Zurich, although with focus on the watersoluble inorganic fraction and the size range of total suspended matter (TSP). In sampling reactive species or semivolatile compounds (like ammonium nitrate) a separation of the trace gases from their particulate counterparts is recommended

(McMurry, 2000). Among others available wet denuder techniques are major reviewed in Dasgupta (2002). Consequently the authors used a denuder in combination with an aerosol steam jet collector and quasi on-line ion chromatography. This diffusion-based separation, preconcentration and analysis technique the authors adopted from many studies (beside the already mentioned: Neftel et al. (1996), Löflund et al. (2001), Khlystov et al. (1995). Compared to earlier practice the experimental conditions were modified in the right way: higher air flow rate, use of pure deionized water as scrubbing solution, air conditioned operation. From ambient measurements of reactive nitrogen compounds in the gas and aerosol phase at rural as well urban sites in Europe using WEDD/AC and very similar IC equipment it could be seen that often very low concentrations of HNO3/nitrate can occur (e.g., Acker et al., 2004). Any influence of carbonate on the nitrate detection was not observed. 0,2 microgram/m3 should be about 100 times above the detection limit of nitrate. The detection limits for the single anions should be noted, what means in 2.3 “in the rangeĚ”? Figure 1 is unnecessary. The general good agreement should be mentioned. The overestimation of SO2 fluorescence data is unbelievable. The opposite explanation is expected, denuder sampling efficiency for SO2 about 80-90%. Until today WEDD/AC measurements are not routine methods and need special attention throughout the entire use. For the determination of water-soluble cations a second sampling line coupled with cation-IC (or a separation of the solutions containing the scavanged ions before pre-concentration and elution to cation IC) is needed. This is not trivial to do, experiences are known from J.P. Putaud (personal communication). But it seems that all the detailed assumptions concerning ammonium nitrate and ammonium sulfate concentrations based on ammonia data obtained elsewhere. It becomes not clear if ammonium aerosol data are available from the Digitel high volume sampler used in this study. If this is the case, the corresponding averages should be given in Table 3. In Hüglin and Gehrig (2000) the mean chemical composition of PM10 and PM2.5 at Zurich-Kasernenhof is given for 1998/99 and compared with other selected sites. From the annual mean values it could be seen (based on equivalent concentrations), that ammonium compensates about 85 % of the acids (sulfate, nitrate) in the continental influenced aerosol. Whereas all ammonia and sulfate was found in PM2.5, part of the nitrate was present also in coarse particle mode. Results from long-term measurements at the Melpitz site showed a similar nitrate distribution over the particle size (Spindler et al., 2004). The assumption that all PM10 nitrate (or TSP nitrate) in Zurich occurs as ammonium nitrate seems to be uncertain. Moreover the reaction of HNO3 with ammonia starts, if more ammonia is available than needed to neutralize sulfuric acid. Figure 3 shows more or less a correlation of the measured (by AC-IC?) nitrate and sulfate with the PM10 mass, based on daily averages?, what means here in the figure caption “calculated as ammonium sulfate and ammonium nitrate”

If chemical analysis of Digitel filter samples are available (the percentages given in Fig. 2 are tend to be little higher as can be derived from Table 3), the concentrations of both methods should be compared esp. for nitrate. In Fig.5 the time series can not be easely distinguished, axis inscriptions are hardly to see. Although the contribution of chloride to the aerosol mass is expected to be of minor importance, it would be interesting to see the distribution of HCl/Cl from the WEDD/AC measurements. Unfortunately, no time series are shown for gaseous HNO3 in Fig.6. At high relative humidity levels, the liquid water associated with aerosol particles increases rapidly and gaseous HNO3 partitions to the liquid phase due to its high solubility. The partitioning between aerosol nitrate and HNO3 is not only a question of pollution level, it is maily determined by meteorological conditions (photochemistry, mixing processesĚ), too. Fig. 6 should be explained a little bit more. What was happens on evening of 6 March, morning of 10 MarchĚ.. Nitrous acid and nitrite are outsider in the aim of this paper. This chapter should be rewritten. The role of HNO2 in tropospheric chemistry and heterogeneous processes should be mentioned briefly, discussions of sampling artefacts are unnecessary here, because of very different views concerning qualified HNO2 measurements. The observed HNO2 distribution pattern is similar to that generally observed in many atmospheric measurements at other sites (increase during the night, maximum before sunrise followed by a period of low concentrations during the day because of efficient photolysis and atmospheric mixing processes). Despite a rapid photolysis process unexpected high values of HNO2 (100-400 ppt) have been detected during the day in urban but also rural regions (e.g., Febo et al.; 1996; Kleffmann et al.,1998 and 2005; Alicke et al., 2002 and 2003; Zhou et al., 2002; Finlayson-Pitts et al., 2003; Trick, 2004; Stutz et al., 2004; Acker et al., 2005), and found in this study, too. The high fraction of aerosol nitrite found in the urban area of Zurich seems to be an indication of heterogeneous formation on the aerosol surface? Corresponding data may concern this explanation (Kleffmann et al.,1998), possibly intensified under humid conditions (larger surface to volume ratio). Generally higher values are found under winter-time atmospheres compared to summer, because of more PM10, more traffic? Figure 8 should be cancelled, because different meteorological regimes may cause significant differences in the source receptor relationship. It should be mentioned, that the HNO2 concentrations were positively correlated with those of NO2, with r2 = 0.59 if all data (day and night) are used (?). The HNO2 to NO2 ratio varied in a wide range, on average it reached 0.02, higher than observed under very high traffic density conditions. Results from a 3 month program are given. This is a short period for seasonal relevant conclusions (e.g., cold, warm season) with regard to the high variability of meteorological and air pollution parameters. The authors should briefly characterise the selected periods concerning general weather situation compared to long-year observations. Because of the changing emission situation observed now in Europe (for Zurich SO2 shown in Figure 9) it is expected that nitric acid will increasingly bond part of the ammonia. A comparison with possibly available sulfate to nitrate ratio (monthly averaages) from earlier studies (e.g., Hüglin and Gehrig) could be useful.

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