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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Summer ammonia measurements in a densely populated Mediterranean city" *by* M. Pandolfi et al.

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We would like to gratefully thank the Referee#1 for his useful comments.

GENERAL COMMENTS:

A) "The introduction section is fulfilling, however. . . . .high levels of ammonia, nitric acid, sulphur dioxide and ammonium salts) during winter and summer periods".

1) Pag.: 10383, Line 21:

The following sentence was added: "Moreover, fine ammonium aerosols have strong environmental impacts being very effective in scattering visible light thus affecting visi-

bility and radiation budget of the Earth-atmosphere system (e.g. Barthelmie and Pryor, 1998; Langridge et al., 2012). "

2) Pag.: 10383, Line 12:

The following sentence was added: "For example, Ianniello et al., (2011) related the high concentrations of fine ammonium aerosols observed in Beijing to the impact of regional sources from areas with high concentrations of primary precursors (such as NH3, SO2, and NOx)."

3) Pag.: 10384, Lines 5-8:

The sentence: "Other sources of NH3 include animal excreta, biomass burning, industries (mainly manufacture of NH3 and N containing fertilizers), coal burning, human breath, sweat and smoking, pets, sewage systems, wastes and vehicle emissions (Sutton et al., 2000).",

was replaced with: "Other sources of NH3 include natural sources such as soil, oceans, vegetation, animal excreta, biomass burning, or anthropogenic sources such as industries (mainly manufacture of NH3 and N containing fertilizers), coal burning, power generation, sewage systems, wastes, human breath, sweat and smoking, and vehicle emissions (Sutton et al., 2000; Zhao et al., 2012)."

4) Pag.: 10384, Lines 12:

The following reference was added: "; Heeb et al., 2006)"

5) Pag.: 10384, Lines 18-22:

The sentence: "In recent years few studies have been conducted to determine the NH3 emission factors from vehicles by means of tunnel or dynamometer experiments showing the increased ammonia emissions from catalyzed vehicles (Moeckli et al., 1996; Fraser and Cass, 1998; Kean and Harley, 2000; Durbin et al., 2004; Burgard et al., 2006; Kean et al., 2009).",

was replaced with: “Many studies have been carried out to determine the NH3 emission factors from vehicles under different driving conditions by means of tunnel or dynamometer experiments showing the increased NH3 emissions from catalyzed vehicles (e.g. Moeckli et al., 1996; Fraser and Cass, 1998; Kean and Harley, 2000; Durbin et al., 2004; Burgard et al., 2006; Heeb et al., 2008; Kean et al., 2009).

B) “A more detailed discussion and analysis should be carried out. . .., the temperature and relative humidity influence”.

1) Pag.: 10388, Line 11:

The following sentence was added: “Detection limit, precision and accuracy of the instruments were around 0.05 ug/m3, 0.04 ug/m3 and $\pm$ 3%, respectively. The precision of the AiRRmonia ranged from 0.5% to 1.0% RSD (relative standard deviation), with an average precision of 0.7%. Rise response times ranged between 20 to 12 minutes for changes in NH3 concentrations between 300 – 600 ppb and 1500 – 2000 ppb, respectively. The fall response time was around 18 minutes for the 2000 – 0 ppb NH3 change.”

Concerning details on AiRRmonia calibration by means of standard NH4+ solution the following reference was added:

“Slanina, J., ten Brink, H. M., Otjes, R. P., Even, A., Jongejan, P., Khlystov, A., Waijers-Ijpelaan, A., and Hu, M.: The continuous analysis of nitrate and ammonium in aerosols by the steam jet aerosol collector (SJAC): extension and validation of the methodology, Atmos. Environ., 35, 2319–2330, 2001.

C) “A detailed map of the domain within which the measurements. . . .assumption and conclusions given in the manuscript”

1)Figure 1 was replaced with a new Figure 1 where the potential strong sources of NH3 were located.

2) Pag.: 10387, Line 17:

The following sentence was added: “The main possible important sources of NH3 in the area under study included major highways and roads, pig farms, agricultural fields, and power plants. Figure 1 shows that the majority of these sources were located relatively far from Barcelona with the exception of two power plants located at around 5 km south and 10 km north-east the measurement sites and some major roads which surrounded the sites. Main agricultural fields, mainly vegetable groves and orchards, were located 25 km west the measurement stations.”

3) Pag.: 10391, Line 18:

The following sentence was added: “Figure 4 reports the polar plots (source Openair; Carslaw and Ropkins, 2011) of the concentrations of NH3 measured at UB and CC sites. The Figure clearly shows that on average the highest concentrations of NH3 at CC (> 6.0 ug/m3) had a very local origin, being detected under low wind speeds (< 1 m/s), and that important concentrations of NH3 were transported from the north-west toward the CC site when wind speeds were higher (> 2 m/s). Conversely, at UB site the highest concentrations of NH3 (> 2 ug/m3) were detected when winds blew with high velocities from the south, i.e. from major roads and from the city centre, where the highest NH3 concentrations were measured. Thus, Figure 4 shows that the major sources of NH3 in Barcelona were located within the city between the CC and UB sites thus suggesting a more local origin for the measured concentrations of NH3 at both sites. Moreover, the high difference observed for the NH3 concentrations measured at UB and CC also suggested a reduced contribution from regional NH3 sources.”

D) “While the wind rose provide insight into the distribution of local emission sources. . . .Where and what type?”.

1) From the polar plots of NH3 concentrations at CC and UB presented in the new Figure 4, it results that the measured concentrations of NH3 were mainly of local origin. Also, the high difference observed between the concentrations of NH3 at CC and UB suggests a reduced contribution from regional NH3 sources. Backtrajectories analysis

in the manuscript have been performed with the main aim to help the discussion of the special cases presented, by defining the measurement period affected by recirculation of air masses which led to a reduction in the concentrations of the reported atmospheric components.

E)" I do believe. . . . . especially in the coarse mode".

1) Pag. 10392, Line 12:

The following sentence was added:

"Table 2 shows the coefficients of determination (R2) between the atmospheric components and parameters available for UB site where a larger and more complete dataset was collected compared with CC. The R2 higher than 0.6 were highlighted in the Table.

Table 2

As expected high R2 were observed between NO, NO2, NOx, and BC, being these atmospheric components emitted mainly by passing vehicles. Interestingly, SO2 was the only variable which correlated with the direction of the wind due to the transport of SO2 from the port of Barcelona toward the UB site when the sea breeze was active. On average no correlations were observed between NH3 and temperature and/or relative humidity because both variables changed only little during the measurement campaign. Dependences of NH3 with T and RH have been observed mainly by comparing winter and summer months when both atmospheric variables vary considerably (e.g. Reche et al., 2012). Secondary sulfates were strongly correlated with ammonium, PM1 and PM10 but not with the coarse PM mode (PM2.5-10) thus suggesting a finer character of secondary sulfate particles which were present mainly in the form of ammonium sulfates. As previously observed, the chemical reactions processes leading to SIA formation involve precursor gases such as sulphuric acid (H2SO4), nitric acid (HNO3), hydrochloric acid (HCl) and ammonia (NH3). The H2SO4 and HNO3 are oxidation products of gaseous sulphur dioxide (SO2) and nitrogen oxides (NOx),

respectively, while NH3 is directly emitted from its sources. Secondary sulphate particles in the atmosphere may exist as sulphuric acid, ammonium sulphate (NH4)2SO4 or ammonium bisulphate (NH4HSO4) and the formation of each depends on the amount of ammonia. If enough ammonia is present, the particulate sulphate will be found as (NH4)2SO4. Ammonium nitrate (NH4NO3) and ammonium chloride (NH4Cl) are formed via reversible phase equilibrium with precursor gases such as NH3, HNO3 and HCl and the thermodynamic equilibrium between gas and particle phase depends on the ambient temperature and relative humidity. Thus, the Formation of NH4NO3 and NH4Cl is favoured under conditions of high relative humidity and low temperature. Given that the affinity of H2SO4 for NH3 is larger than that of HNO3 and HCl the available ammonia is first taken up by sulphuric acid to form ammonium sulphate salts. Any excess available ammonia may then react with nitric and hydrochloric acid to form ammonium nitrate and chloride. During the measurement campaign the chemistry of PM1 (on 24h base) was only available at the UB site and due to technical problems the number of PM1 filters simultaneously sampled with NH3 was reduced down to 24. Mean NH4+, SO42−, NO3-, and Cl- concentrations in PM1 filters at UB site for the campaign period were 0.83 μgm−3, 2.85 μgm−3, 0.10 μgm−3 and 0.22 μgm−3, respectively. As shown in Table 2, NH4+ aerosol was clearly associated with SO42− with a coefficient of determination of 0.8. However, NH4+ was not correlated (R2 <0.1) with NO3- and Cl- (not shown in Table 2). Therefore, and taking into account the relatively low concentrations of NO3- and Cl- with respect to SO42−, the presence of ammonium sulfate salts was evidenced. The average equivalent ratio of NH4+ to SO42− was 0.89 with daily ratios varying from 0.6 to 1.4. A ratio of 1 indicates the presence of (NH4)2SO4, whereas a value of 0.5 suggests the formation of NH4HSO4. The average ratio NH4+ to (SO42−+NO3-+Cl-) was 0.75, with daily ratios varying from 0.5 to 1.4 and the variation of these ratios may indicate differing degrees of aerosol neutralization. On average, the concentrations of NH3 measured at UB were enough for neutralization. This analysis was not possible for CC site given that at CC the concentrations of ammonium salts were not determined. Finally, during the measurement

campaign 100% and 74% of ammonium and sulfates in PM10, respectively, were accumulated in the PM1 fraction. By contrast, during the study period, only 8% of NO3- in PM10 was found in PM1. Therefore, secondary nitrates were characterized by a coarser size distribution and, neutralized by calcium and/or sodium (Pérez et al., 2008; Harrison and Pio, 1983)."

F) "One principal problem of the manuscript is that the interaction of NH3 with HNO3. . .. .for the interpretation about the different sources of NH3":

Unfortunately, the measurements of nitric acid were not available during the measurement campaign given that the main aim of this measurement campaign was to study the different concentrations and evolutions of ammonia at the two selected measurement sites. However, the balance shows that NH4+ particles correlate with SO42- while NO3- was mainly coarse in the form of sodium and/or calcium nitrate.

G) "more detailed discussion. . .. . .should be presented in the paper"

Please, refer to point E).

H) "I would expect clear differences. . .. . .Could you comment this?"

1) Pag.: 10392, Line 12:

The following sentence was added: "Weekdays vs. weekend differences in the concentrations of reported species were studied by means of the non-parametric Kruskal-Wallis test (Kruskal and Wallis, 1952) by using two groups obtained by averaging the available data over the Monday-Friday and Saturday-Sunday periods. The null hypothesis of the Kruskal-Wallis test is that the populations, from which the samples originate, have the same median while the alternative is that the medians are different. In this work a statistically significant result will refer to a significance level of 5% (p-value lower than 0.05). At UB site statistically significant weekdays-weekend differences were observed for traffic related pollutants such as NO2, NO, BC and PM10 ($p<0.0001$) followed by PM2.5 and PM1 for which p values lower than 0.006 and 0.008, respectively

were observed. A slight decrease on weekend was also observed for the concentrations of NH3 ($p=0.04$), while for the remaining parameters no significant difference were observed. Conversely, at CC site no significant differences were observed between weekdays and weekend for NH3 and BC concentrations. The lack of a weekly cycle at CC was related to both the short measurement period available at CC and the peculiar characteristic of the city centre of Barcelona where anthropogenic activities were habitually active also on weekends."

Technical corrections:

1) Ianiello was replaced with Ianniello and suggested References were added to the manuscript.

Added Bibliography:

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10381, 2012.