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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#2 for his useful comments.

GENERAL COMMENTS:

A)"The analysis presented is not very detailed. It mainly compares. . .. .and particles composition measurements at both sites"

1)Figure 5 was splitted into two Figures: Figure 5 to compare the common measurements at both sites, and Figure 6 with the additional measurements at the UB site. Captions and text were opportunely changed.

2)As also suggested by the Referee#1, the following text was added:

Pag. 10392, Line 12:

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

Table 2: Coefficients of determination (R2) at UB measurement site.

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

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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)."

B)"Results Section 3.1. . . . .and the 1 min time resolution is brought

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up in section 2.2.1."

1)Figure 2 was changed and 1-minute data were compared. Figure caption and text were accordingly changed.

C)"Results Section 3.2. How was the traffic density. . . . . .on Fig.1, it should be removed and CC site used instead."

1) Traffic density is measured in Barcelona by means of induction loops embedded in the road pavement. Data of traffic density are not available in a digital database form. Data have to be requested to the Traffic Department of Barcelona. The data of traffic density presented in the manuscript were collected concurrently with the measurement campaign, taking the closest induction loops to the two measurement sites as reference.

The following sentence was added to the manuscript:

Pag.10390, Line 27:

"Traffic density data were collected concurrently to the measurement campaign by means of induction loops embedded in the road pavement and the closest induction loops to the measurement sites were used as reference."

2) "Raval area" was removed and replaced with "CC site".

D)"Results Section 3.3 From what sector. . . . .to understand Fig.5 c and f."

Pag. 10393, Lines 11-14:

The following sentence: "As reported in the Figures 5c, f the sea breeze at CC over the period 13 May–28 June developed around 07:00 GMT while at UB (6 May–7 September) it developed at around 08:00 GMT.",

was replaced with:

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"As reported in Figure 5c during the period 13 May – 28 June the sea breeze at CC developed on average around 07:00 GMT with winds blowing from the sector 130 – 180 degrees. At UB (6 May – 7 September) the sea breeze developed later around 08:00 GMT with the winds blowing approximately from the same sector."

E)"Results Section 3.3.1 The first paragraph (page 10394, line 4). . . . . .is also increasing at these time periods."

Pag. 10394, Lines 3-4:

The following sentence: "Thus traffic was more effective in increasing the levels of BC above the values measured at night rather than those of NH3.",

was replaced with:

"Despite the fact that BC is mainly emitted by diesel vehicles (60% of the fleet in Barcelona), whereas NH3 is emitted by diesel and gasoline vehicles, the vehicle emissions were more effective in increasing the levels of BC above the values measured at night rather than those of NH3. The observed increase in BC concentrations was consistent with the increase of traffic density at these time periods (Figure 3)."

F)"The last paragraph on page 10394 claims that. . . . . ., there does not seem to be enough data to support this hypothesis"

1) We agree with the Referee#2. The following sentence on Pag. 10394, Lines 17-29:

"The concentrations of ammonia reached their minimum mean value (4.1 μgm$-$3) at 18:00 GMT with fairly constant mean concentrations around 4–4.5 μgm$-$3 observed between 13:00 and 18:00 GMT. The lowest BC mean concentrations (between 590 and 640 ngm$-$3) were instead observed around 15:00–16:00 GMT when the sea breeze was fully developed. Then, the concentrations of BC increased again starting from 16:00 GMT reflecting the decreasing trend of wind velocities and consequent accumulation of BC emissions from traffic which was still high at 16:00 GMT (Fig. 4). The reason for the longer tile toward decreasing NH3 values (from 07:00 to 18:00 GMT)

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compared with BC (from 07:00 to 16:00 GMT) was likely due to the depletion of NH3 in favor of the formation of ammonium salts during the whole afternoon. Starting from 19:00 GMT the concentrations of NH3 accumulated again with time as wind velocity decreased reflecting the tendency toward the stagnant atmospheric conditions observed at night.";

Was replaced with the following sentence:

"The concentrations of ammonia reached their minimum mean value (4.1 μgm$-$3) at 18:00 GMT with fairly constant mean concentrations around 4–4.5 μgm$-$3 observed between 13:00 and 18:00 GMT. Starting from 19:00 GMT the concentrations of NH3 accumulated again with time as wind velocity decreased reflecting the tendency toward the stagnant atmospheric conditions observed at night. The lowest BC mean concentrations (between 590 and 640 ngm$-$3) were instead observed around 15:00–16:00 GMT when the sea breeze was fully developed. Then, the concentrations of BC increased again starting from 16:00 GMT reflecting the decreasing trend of wind velocities and consequent accumulation of BC emissions from traffic which was still high at 16:00 GMT (Fig. 3)."

G)"The use of equilibrium in the last paragraph of section 3.3.1. . . . . Here 'equilibrium seems to be used in unique context that needs further explanation"

1) We agree with the Referee#2. The word "equilibrium" was used here in a general form making less clear the sentence. Consequently, the following sentence (Pag. 10395, Lines 22-23):

"The lack of equilibrium between the concentrations of NH3 and all possible sources and sinks at CC",

was replaced with:

"The observed monotonic increase of NH3 concentrations at CC".

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2) The following sentence (Pag. 10395, Lines 26-27):

“A certain degree of equilibrium for the concentrations of NH3 with time was instead observed”,

was replaced with:

"Relatively constant NH3 concentrations with time were instead observed"

3) The following sentence (Pag. 10396, Lines 1-2):

“The NH3 equilibrium conditions at these times”,

was replaced with:

"The observed constant NH3 concentrations at these times"

H)“Specific Cases, Section 4.1. . . . . refer to Barcelona and not all cities in general”

1)The sentence Pag. 10400, Lines 20-20, was replaced with the following sentence:

"Thus, the traffic-driven bimodal diurnal cycles of NH3 can be expected to be more frequent in winter than in summer in Barcelona."

I)“What do the negative values for the BC minimum mean?”

Zero and negative BC values may appear in MAAP data due to statistical variations at very low concentrations.

J)“Figure 2. The axis labels are confusing. . . . . ’AiRRmonia Instrument #2 NH3 [ug/m3]”’

Done. Axis labels in Figure 2 were changed.

K)“Figure 3. Figure 3 is difficult to read due to. . . . . I suggest moving this figure to the supplemental material”

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Figure 3 was moved to the supplemental material.

L)“Figure5. This figure is not organized very well. . . . . would also simplify the figure legled”

Figure 5 was splitted in two Figures. Please, see also comment A).

M)“Figure6. Axis font are different for the panels. . . . . since their meaningis not clear withouth adequate discussion”

1) Axis font in Figure was changed.

2) Equations were removed.

Minor Comments and Technical Corrections

N)“In certain sections of the paper. . . . . In some Figure captions the 3 in NH3 is not in subscript format.”

1) Ammonia was replaced with NH3 through the manuscript.

2) All 3 in NH3 are now in subscript format.

O)“Abstract, p10382 line23. Insert particle into ‘gas-to-particle phase partitioning”

Done.

P)“Introduction, p10383 line 5. Remofe of after excess.”

Done.

Q)“Introduction, p. 10384, lines 18-26. This paragraph. . . . . NH3 to the analysis of these observations.”

The sentence Pag. 10384, Lines 18-26, was replaced with the following one:

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"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). Contextually, measurements of ambient ammonia concentrations at urban level have been recently presented in many publications (Nowak et al., 2002; Perrino et al., 2002; Bari et al., 2003; Lin et al., 2006; Edgerton et al., 2007; Saylor 25 et al., 2010; Nowak et al., 2010; Ianniello et al., 2010; Meng et al., 2011; Gong et al., 2011, among others)."

R)"Introduction, p. 10386, lines 12-21. The first sentence in this paragraph is awkward and confusing"

The sentence Pag. 10386, Lines 12-21, was replaced with the following one:

"As consequence of the difficulties in distinguishing between the different NH3 sources, NH3 emissions from engines and vehicles are not yet regulated. Neverthless, NH3 is listed as a toxic air pollutant by the EU and emission ceilings are defined for each member state (EC, 2001). In Spain, a new regulation has been implemented on 28 January 2011 (Royal Decree 102/2011) establishing the requirement to measure ammonia levels at five rural background stations covering the country and in one traffic site in cities with more than 500 000 inhabitants. At European level the critical level for NH3 has been established in 8 μgm$-$3 as an annual mean (air quality guide lines for Europe) although recent studies reported important effects on vegetation when ammonia levels are above 3 μgm$-$3 (Cape et al., 2009)."

S)"Methods, p 10386, line 16. Recommend 'The two measurement sites were 4.7 km apart'"

"far" was replaced with "apart".

T)"Methods, p 10387, line 19. Recommend 'The measurement of NH3 were supple-

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mented with a set of ancillary hourly measurements of. . .."

Done. The sentence was accordingly changed.

U)"Methods, p 10388, line 1. Recommend 'Not all the . . .. .while PM. . ."

Done. The sentence was accordingly changed.

V)"Methods, p 10388, line 6. Insert 'a' before 1-min"

Done.

W)"Methods, p 10389, line 12. Insert 'The' before filter."

Done.

X)"Results, p. 10394, line 24. I do not understand the use of the word 'tile' in this sentence."

Solved. Please, refer to the point F).

Y)"Results, p. 10396, line 8. Vice versa is two words"

Changed.

Z)"Results, p. 10397, line 7. There is no panel o in Figure 5."

Changed.

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