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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.

Anonymous Referee #1

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The manuscript by Pandolfi et al. reports on on-line gas phase ammonia measurements carried out by automated ammonia analyzer (AiRRmonia) at two sampling sites in Barcelona during a summer period. Meteorological parameters and relevant concentrations of other important pollutants have been considered in data analysis. The data analysis focuses mainly on the measured concentrations and daily evolutions of ammonia. The paper has scientific merit and presents novel data, however, there are some gaps and shortcomings which need to be addressed to make the paper more robust and scientifically rounded before publication in ACP.

General comments: The introduction section is fulfilling, however, I lack some background/information on the natural sources (soils, oceans, vegetation, living organisms) of ammonia and on environmental effects of fine ammonium aerosols (atmospheric

visibility, radiation budgets). There are plenty of publications discussing NH3 emission factors from power generation and mobile sources that has not been cited and seems not to have been reviewed (e.g. Heeb et al., 2006 and 2008). Similarly, different sources of ammonia are discussed in the manuscript but the impact of long-rang air transport on NH3 levels is not thoroughly analyzed and would be discussed in the introduction section. Ianniello et al. (2010 and 2011) discussed and analyzed the sources and temporal and diurnal patterns of gaseous ammonia and inorganic particulate ammonium salts, particularly ammonium nitrate and sulphate. These studies provide insight into the contributions of local and regional sources to observed urban pollution (such as high levels of ammonia, nitric acid, sulphur dioxide and ammonium salts) during a winter and summer periods.

A more detailed discussion and analysis should be carried out about ammonia measurements in the section of methods, including the determination of response linearity, detection limits, precision, reproducibility, response time, stability, loading capacity of analytical and sampling system, calibration procedures, the temperature and relative humidity influences.

A detailed map of the domain within which the measurements have taken place, locating the measurement sites, surrounding regions and, thus, the potential strong sources of NH3 (agricultural fields/farms, major roads/highways, power plants etc.), and overlaying the wind roses of averaged NH3 concentrations, would be essential to underpin the assumptions and conclusions given in the manuscript.

While the wind roses provide insight into the distribution of local emission sources around the measurement sites, trajectory analysis are further used to identify the impact of long-range air transport on the surface air pollutants levels. Therefore, to interpret further in general terms the source regions affecting the sampled ammonia and, thus, to identify the origin and transport pathway of large-scale air masses, backward trajectories arriving at the measurement sites should be calculated for the sampling periods. Where are major sources (source groups) located in relation to the measurement

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sites and with regard to wind direction/speed and distance from the source? Could the authors tell us about agricultural activity in the sampling areas and surrounding areas? Where and what type?

I do believe that with minimal effort the analysis could be strengthened. A more detailed analysis should be carried out. For example, correlations (R2) between various gases (especially NH3, NOx, CO) and between gases and particles should be discussed and presented in a table. Correlations are alluded in the manuscript but not specifically given. In addition, correlation analysis between anions and cations can indicate the possible form in which the aerosols existed and correlation analysis between inorganic components and gases can give some indication of the transformation velocity and formation mechanism from gases to particles. The analysis of the ratios of NO3-, SO42- and NH4+ can identify the neutralisation of aerosols and reactivity of NO3-, SO42- and NH4+. Fine particulate (NH4)2SO4 and NH4NO3 formations depend on the quantities of NH3, acid precursors (i.e., SO2 and NOx) present, and the meteorological conditions. Thus, in the systems related to NH3, H2SO4, HNO3, and water droplets, the composition of aerosols in the atmosphere may be influenced by the characteristics of the experimental sites. Using the data measured, the constituents of aerosols can be analyzed in a meaningful manner by examining the equivalent ratios of NH3/NH4+, NH4+/SO42-, NH4+/NO3- and NH4+/(SO42- + NO3- + Cl-). Equivalent NH4+/SO42- ratios are expected to range from 0.5 to 1 (i.e., the molar NH4+/SO42- ratios are expected to range from 1 to 2), corresponding to a composition intermediate between NH4HSO4 and (NH4)2SO4. Larger observed equivalent NH4+/SO42- ratios suggest that the site is located in the predominant NH3-rich environment. This excess NH4+ must be assigned to the presence of HNO3 and HCl, which also binds some NH3. What are the relationships between the inorganic components, sulfate, nitrate, and ammonium? Was the fine aerosol neutralised or acidic? What is the importance ammonium nitrate compared with the ammonium sulphate? Can current information provide insights into the formation processes of sulfate and nitrate? It is important that the authors show fine particulate species. It would be highly informative to investigate

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to what degree acids were neutralized by ammonia at the sampling sites. Analysis of the PM2.5 filters for sulfate, nitrate and chloride, would allow the authors to comment on whether the NH4+ fully neutralized these species and/or whether excess NH3 is available during the sampling periods as a result. These are unclear in the manuscript.

In addition, SO42- and NH4+ mainly exist in fine particles, NO3- can be found either mainly in fine or in coarse particles, depending on the meteorological conditions. The role of the coarse mode, especially cations, can be very significant where particle nitrate formation is concerned. Calcium, magnesium and sodium nitrate form much more readily than ammonium nitrate (the equilibria for calcium carbonate, magnesium carbonate, and sodium chloride + HNO3 will favour the formation of calcium nitrate, magnesium nitrate and sodium nitrate over ammonium nitrate, even when excess ammonia is available). This in turn will mean that in the presence of coarse mode cations, the formation of ammonium nitrate in the fine mode will be inhibited. In this respect (and if coarse data can be available), it is also important that the authors show particulate matter for total PM10, especially the coarse mode.

One principal problem of the manuscript is that the interaction of NH3 with HNO3 to form NH4NO3 is alluded in the manuscript. A more detailed analysis should be carried out. Because the NH3-HNO3-NH4NO3 equilibrium is highly dynamic it is likely that HNO3 has a strong influence on NH3 concentrations in the gas phase, especially since the measurements indicate the presence of high NH3 episodes during the sampling periods. The comparison between measured and predicted equilibrium gas phase concentration products of NH3 x HNO3 would add some information to the paper. Thus, measurements of nitric acid would be helpful for the interpretation and they should be available in the paper.

Thus, the manuscript would also be strengthened if other data were also available and presented (as said before), including fine and coarse fractions, CO, HNO3, and any other compounds that could helpful for the interpretation about the different sources of NH3.

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More detailed discussion and analysis of the relationships (correlation analysis) of meteorology (relative humidity, temperature, wind speed, wind direction), versus NH3 and meteorology versus fine particulate matter correlations should be presented in the paper.

I would expect clear differences in concentration distributions of all species during weekdays and weekends. However, the authors have not taken this into account. Could you comment this?

Technical corrections: - Page 10384, Lines 25: “Ianiello et al.” should be replaced by “Ianniello et al.” - Page 10385, Lines 16: “Ianiello et al.” should be replaced by “Ianniello et al.” - Page 10385, Lines 5; Page 10388, Lines 16; Page 10391, Lines 20; Page 10392, Lines 2; Page 10393, Lines 28; Page 10401, Lines 9: Add a comma after the word “respectively”.

References Heeb, N. V., Forss, A-M., BrÂÍuhlmann, S., LÂÍuscher, R., Saxer, C. J., and Hug, P.: Three-way catalyst-induced formation of ammonia velocity- and acceleration-dependent emission factors, Atmos. Environ., 40, 5986–5997, 2006.

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Ianniello A., Spataro F., Esposito G., Allegrini I., Hu M., and Zhu T.. Chemical characteristics of inorganic ammonium salts in PM2.5 in the atmosphere of Beijing (China). Atmos. Chem. Phys., 11, 10803–10822, 2011.

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