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Summer ammonia measurements in a densely populated Mediterranean city

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Abstract

Real-time measurements of ambient concentrations of gas-phase ammonia were performed in Barcelona (NE Spain) in summer between May and September 2011. Two measurement sites were selected: one in an urban background traffic-influenced area (UB) and the other in the historical city centre (CC). Levels of ammonia were higher at CC (5.6 ± 2.1 µg m^{-3} or 7.5 ± 2.8 ppbv) compared with UB (2.2 ± 1.0 µg m^{-3} or 2.9 ± 1.3 ppbv). This difference is attributed to the contribution from non-traffic sources such as waste containers, sewage systems, humans and open markets more dense in the densely populated historical city centre. Under high temperatures in summer these sources had the potential to increase the ambient levels of ammonia well above the urban-background-traffic-influenced UB measurement station. Measurements were used to assess major local emissions, sinks and diurnal evolution of NH_3. The measured levels of NH_3, especially high in the old city, may contribute to the high mean annual concentrations of secondary sulfate and nitrate measured in Barcelona compared with other cities in Spain affected by high traffic intensity. Ancillary measurements, including PM_{10}, $PM_{2.5}$, PM_1 levels (Particulate Matter with aerodynamic diameter smaller than 10 µm, 2.5 µm, and 1 µm), gases and black carbon concentrations and meteorological data, were performed during the measurement campaign. The analysis of specific periods (3 special cases) during the campaign revealed that road traffic was a significant source of NH_3. However, its effect was more evident at UB compared with CC where it was masked given the high levels of NH_3 from non-traffic sources measured in the old city. The relationship between SO_4^{2-} daily concentrations and gas-fraction ammonia ($NH_3/(NH_3+NH_4^+)$) revealed that the gas-to-phase partitioning (volatilization or ammonium salts formation) also played an important role in the evolution of NH_3 concentration in summer in Barcelona.

1 Introduction

Atmospheric ammonia (NH_3) is among the most abundant nitrogen compounds in the atmosphere and it plays an important role in the neutralization of atmospheric acids to form ammonium salts, preferentially ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bisulfate (NH_4HSO_4) from sulfuric acid. Excess of ammonia is then available to form ammonium nitrate (NH_4NO_3) from nitric acid or ammonium chloride (NH_4Cl) from hydrochloric acid.

The formed ammonium salts are relatively stable particles with a longer lifetime (1–15 days, Sheppard et al., 2011; Aneja et al., 2000) compared with gaseous ammonia which is quickly dry deposited relatively close to the sources (Fowler et al., 1998; Phillips et al., 2004; Clarisse et al., 2009) thus allowing the long range transport of the acidic pollutants to remote areas (Aneja et al., 2000).

One of the main concerns is related with the input of reactive nitrogen species to the terrestrial ecosystems and marine environments by nitrogen (N) deposition leading to possible eutrophication and acidification of the ecosystem with changes in animal and plant populations and degradation of water and habitat quality (Flechard et al., 2011). Deposition of reactive N may be either wet when NH_4^+ particles are washed out in precipitation or dry when NH_3 is directly deposited without chemical transformations (Sheppard et al., 2011; Phillips et al., 2004). High levels of atmospheric ammonia may cause adverse health effects by formation of fine particulate matter (PM_1 and $PM_{2.5}$) (Erisman and Sutton, 2008; Brunekreef and Holgate, 2002; Ellis et al., 2011).

It is widely recognized that the reactive nitrogen available to the ecosystem has increased dramatically over the past 50 yr since humans in the early 20th century started to convert unreactive gaseous N_2 into ammonia as a basis for fertilizers used for food production (Van Der Hoek, 1998; Sutton et al., 1993; Erisman et al., 2007, 2008; Erisman and Sutton, 2008). Overall, more than 80 % of the chemical production of NH_3 is used to produce fertilizer in the forms of ammonium nitrate, urea, and so on (Erisman et al., 2007). As a whole, agriculture is estimated to contribute for 94 % to the total NH_3

emission in Europe with livestock being the largest category in its emission inventory (EEA Report, 2011). As a result, the scale of the environmental effects of ammonia emissions extended over the years from a few hotspots to the whole of Europe (Erisman and Sutton, 2008).

Other sources of NH_3 include animal excreta, biomass burning, industries (mainly manufacture of NH_3 and N containing fertilizers), coal burning, human breath, sweat and smoking, pets, sewage systems, wastes and vehicle emissions (Sutton et al., 2000). Globally these sources form a minor part of the emissions but they might be relevant locally playing the greater role in ammonia emissions. At urban level for example there is a growing concern related with the emissions of ammonia after the introduction of gasoline-powered vehicles equipped with three-way catalytic converters (Cape et al., 2004) and diesel-powered vehicles adopting selective catalytic reduction (SCR) system (Kean et al., 2009). In the first case, ammonia is the product of NO reduction on the catalyst surface which, beyond the formation of molecular N_2, leads to ammonia in motor vehicle exhaust. In the second case ammonia is used as reagent and supplied to the catalyst system by the injection of urea into the exhaust which then undergoes thermal decomposition and hydrolysis into ammonia.

In recent years few studies have been conducted to determine the NH_3 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). Contextually, measurements of ambient ammonia concentrations at urban level have been recently presented in few publications (Nowak et al., 2002; Perrino et al., 2002; Bari et al., 2003; Lin et al., 2006; Edgerton et al., 2007; Saylor et al., 2010; Nowak et al., 2010; Ianiello et al., 2010; Meng et al., 2011; Gong et al., 2011, among others).

These studies agreed with the fact that the concentrations and evolution of ambient NH_3 at urban level were influenced by traffic emissions together with other important factors such as temperature changes (mainly seasonally), wind speed or direction, boundary layer deep and mixing, other local or regional NH_3 emissions, dry deposition, and gas-to-particle partitioning. These factors may mask in some cases the effect of vehicle emissions on the measured NH_3 concentrations. For example Meng et al. (2011) and Gong et al. (2011) measured NH_3 concentrations in the urban areas, respectively of Beijing (annual averages between 18.5–23.5 ppb) and Houston (2.4 ppb in winter and 3.1 ppb in summer) showing that correlations between NH_3 concentrations and traffic tracers, such as CO and/or NO_x, were observed in winter but not in summer thus suggesting that other non-traffic sources became more important during the warm season (i.e. variations in local or regional emission sources, changes in vehicular catalytic converter performance, NH_3 emissions from dew evaporation with increasing temperature in summer or natural release of NH_3 from vegetation and soil through photosynthetic processes). Perrino et al. (2002) also identified vehicles as an important source of ammonia at many traffic sites in Rome (mean NH_3 concentrations between 13.5 $\mu g\,m^{-3}$ and 21.6 $\mu g\,m^{-3}$) with higher NH_3/CO ratio in summer compared with winter as a consequence of the evaporation of ammonia from particulates and from various non-traffic sources present in the selected urban area. Ianiello et al. (2010) compared the concentrations of NH_3 measured in Beijing (5.47 $\mu g\,m^{-3}$ in winter and 25.39 $\mu g\,m^{-3}$ in summer) with NO_x, CO and $PM_{2.5}$ and concluded that traffic was an important source of NH_3. Nevertheless, the mean NH_3 concentration was around five times higher in summer than in winter likely due to agricultural emissions enhanced under higher atmospheric temperatures (Ianniello et al., 2010). Saylor et al. (2010) analyzed the weekday versus weekend differences in composite hourly mean diurnal profiles of NH_3 at an urban site (Atlanta) during July–December 2007 (mean NH_3 at urban site: 1.3 ppb) and concluded that mobile sources had a measurable but relatively small impact on NH_3 indicating the interaction of local NH_3 emissions and dry deposition with the evolution of the diurnal and nocturnal boundary layer as concomitant important phenomenon affecting the concentrations of NH_3.

Concomitance of different NH_3 sources was also presented by Nowak et al. (2006) which showed that the diurnal cycles of NH_3 measured at an urban site in Atlanta (from

0.4 to 13 ppb NH_3) in summer presented a morning peak related with the rush hours and an afternoon peak related with non-traffic sources such as NH_3 emissions from soil or NH_3 release from secondary nitrate particle volatilization. Similarly, Lin et al. (2006) and Bari et al. (2003) associated the summer increase in the concentrations of NH_3 measured at urban sites in Central Taiwan (annual mean 8.5 µg NH_3 m^{-3}) and New York (3–5 µg NH_3 m^{-3}), respectively, with the higher volatility of NH_4NO_3 particulate under typical summer temperatures. Some of these studies also reported significant positive differences in NH_3 levels between traffic and urban background stations (Perrino et al., 2002) or between urban and rural stations (Meng et al., 2011; Edgerton et al., 2007; Perrino et al., 2002) thus confirming traffic and human activities as potentially important sources of NH_3 at urban levels.

Maybe as a consequence of the difficulties in distinguishing between the different NH_3 sources, ammonia emissions from engines and vehicles are not yet regulated, but NH_3 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). This national decree establishes 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. The critical level for NH_3 has been established in 8 µg m^{-3} as an annual mean (air quality guidelines for Europe) although recent studies reported important effects on vegetation when ammonia levels are above 3 µg m^{-3} (Cape et al., 2009).

In this study we present the results of a measurement campaign performed in Barcelona (NE Spain) between May and September 2011 and mainly aimed: (a) to study the differences in the concentrations and dynamics of ambient ammonia at two urban sites with different characteristics in term of NH3 emission sources; (b) to asses major sources and sinks affecting the daily evolution of NH_3 concentrations; (c) to understand the reasons for the high concentrations of secondary sulfate particles usually observed in Barcelona in summer compared with other urban and industrial sites across Spain (Querol et al., 2008). With this aim, the differences in NH_3 concentrations and daily evolutions at the two selected sites in Barcelona (one in the historical city centre and one in a traffic-influenced urban background area) will be presented and discussed.

2 Methods

2.1 Sampling sites

The measurements of ammonia and ancillary data were performed at two measurement sites in the city of Barcelona (NE Spain) (Fig. 1). The first site (UB; 41°23′24.01″ N 02°06′58.06″ E; 68 m a.s.l., 1 m a.g.l.) is a urban background site influenced by vehicular emissions from one of the main avenues of the city (Diagonal Avenue) located at a distance of around 300 m with a traffic density of 132 000 vehicles per day (around 60 % diesel in vehicle fleet; Council of Barcelona, Serveis de Mobilitat, 2009). The second measurement site (CC; 41°22′58.18″ N 02°10′08.59″ E; 30 m a.s.l.) is placed on the roof of a 20 m height building in the densely populated historic city centre of Barcelona, less influenced by traffic emissions but dense with commercial activities (markets, restaurants, pubs and so on) and people wandering around the old city and mainly in summer when tourism is high. The two measurement sites were around 4.7 km far.

2.2 Measurements

The measurements of NH_3 were implemented with a set of ancillary hourly measurements as gaseous pollutants (NO_2, NO, O_3, SO_2), particulate matter (PM_x) and black carbon (BC) concentrations, meteorological data (wind speed and direction, temperature, humidity, solar radiation and pressure) and daily mean concentrations of secondary inorganic aerosols (NH_4^+, SO_4^{2-} and NO_3^-). Measurements were performed at UB from 6 May 2011 to 7 September 2011 and at CC from 13 May up to 28 June

2011. Not all the parameters were monitored at both sites, thus the concentrations of NH_3, BC and meteorological data were determined for both measurement sites while the concentrations of PM_x (PM_{10}, $PM_{2.5}$, PM_1) and gaseous pollutants were measured only at UB site.

2.2.1 Ammonia measurements

On-line measurements of gas-phase ammonia (NH_3) on 1-min base were performed by means of two gas-phase-ammonia-measuring instruments (AiRRmonia; http://www.mechatronics.nl) (Erisman et al., 2001; Wyers et al., 1993). The instrument has the potential to detect NH_3 concentrations from 0.1 $\mu g\,m^{-3}$ up to 100 $\mu g\,m^{-3}$ in real time and has shown good performances during a field inter-comparison campaign in Scotland (von Bobrutzki et al., 2010).

The instrument uses a gas-permeable PTFE (polytetrafluoroethylene) membrane to selectively permeate the ammonia from the air flow ($1\,l\,min^{-1}$) into the stripping solution where NH_3 is converted to NH_4^+. Otjes and Erisman (1999) showed that the ammonium contained in ammonium nitrate and sulfate particles is not retained by the sampling membrane and less than 1 % and 3 % of $(NH_4)_2SO_4$ and NH_4NO_3, respectively are captured. The pH of the stripping solution is raised by addition of sodium hydroxide (NaOH) to form molecular NH_3 which is transferred through a second PTFE membrane in the detector block into a stream of pure deionised water where the NH_3 is reverted to NH_4^+. The NH_4^+ concentrations are then determined by a conductivity measurement of the water and calibration is made using aqueous NH_4^+ standard solutions. During the measurement campaign both AiRRmonias were calibrated approximately once per week.

2.2.2 Ancillary measurements

Hourly levels of PM_{10}, $PM_{2.5}$ and PM_1 at UB were continuously measured by means of a laser-spectrometer dust monitor (Grimm Labortechnik GmbH & Co. KG; model

180). Then the levels of PM were corrected by means of standard 24 h PM gravimetric measurements performed twice per week with high volume samplers (DIGITEL and MCV at 30 $m^3 h^{-1}$) with appropriate (PM_{10}, $PM_{2.5}$ and PM_1) cut-off inlets.

The measurements of the ambient concentrations of black carbon (BC) were performed at UB by means of a MAAP instrument (Multi Angle Absorption Photometer, model 5012, Thermo) and at CC by using an aethalometer (microAeth Model AE51, Magee Scientific). With the MAAP the content of BC were continuously determined by simultaneously measuring the optical absorption and scattering of light by the particles collected on the filter tape (Müller et al., 2011). The Magee aethalometer is a small and portable monitor with a Teflon coated borosilicate glass fibre filter where particles were captured. The aethalometer detects changes in the optical absorption of the light transmitted through the filter and calculates the BC load. Filter inside the aethalometer was replaced every day in order to prevent saturation.

Finally, conventional analyzers were used for measurements of levels of gaseous pollutants at UB (Thermo Scientific, Model 42i for NO_x and MCV S.A., model 48AUX for O_3) and meteorological data were collected at both UB and CC by means of meteorological stations.

3 Results

3.1 AiRRmonia intercomparison

The two AiRRmonia instruments deployed at UB and CC sites were intercompared before the measurement campaign in order to assure the quality of the intercomparison between the NH_3 concentrations measured at both measurement sites. Figure 2 shows the results of the intercomparison performed between 6 May and 11 May at UB site based on hourly data.

As reported in the Fig. 2 the correlation between the two instruments was very good with a coefficient of determination R^2 of 0.99 and a small bias of around 4 %.

3.2 General features

Figure 3 shows the time series of NH_3, BC, PM_1, $PM_{2.5-10}$ and gaseous pollutant concentrations and meteorological data available at CC and UB measurement stations. The black dashed boxes named sc1–sc3 highlight periods considered as special cases and discussed in detail in the following paragraphs.

As reported in Fig. 3 some measurements were sporadically not available because of technical problems. This is the case of NH_3 at UB from 19 May to 9 June and from 12 August to 15 August, BC at UB after 20 August, gases concentrations and meteorological data at UB from 22 June to 27 June and from 20 June to 5 July, respectively.

Table 1 shows the statistics for the measurements performed at both sites reporting sampling periods, percentage of available measurements on hourly base, means, standard deviations, 25th, 50th (i.e. medians) and 75th percentiles, minimum and maximum values. Table 1 also reports the statistics for the UB station averaged over the CC sampling period, i.e. from 13 May to 28 June.

On average the levels of NH_3 at CC station were higher compared with UB. Mean NH_3 levels of $5.6 \pm 2.1\,\mu g\,m^{-3}$ (7.5 ± 2.8 ppbv) and $2.2 \pm 1.0\,\mu g\,m^{-3}$ (2.9 ± 1.3 ppbv) were measured at CC and UB, respectively. Over the same CC sampling period (13 May–28 June) the mean NH_3 concentration at UB was $2.6 \pm 1.1\,\mu g\,m^{-3}$, close to the mean value obtained by averaging all the NH_3 data available for UB station. The minimum and maximum NH_3 concentrations at CC station on hourly base were $1.8\,\mu g\,m^{-3}$ (2.4 ppbv) and $16.2\,\mu g\,m^{-3}$ (21.6 ppbv), respectively, while $0.2\,\mu g\,m^{-3}$ (0.27 ppbv) (or $0.5\,\mu g\,m^{-3}$ over the CC sampling period; Table 1) and $10.6\,\mu g\,m^{-3}$ (14.1 ppbv) were, respectively measured at UB site. The Black Carbon (BC) concentration at UB ($1665 \pm 1158\,ng\,m^{-3}$ over the same CC sampling period) was higher compared with the mean BC concentration registered at CC ($1190 \pm 1059\,ng\,m^{-3}$) where higher NH_3 concentrations were observed. Higher BC concentrations at UB were consistent with the higher number of vehicles registered on average at UB site compared with CC (Fig. 4). Figure 4 shows that the mean number of vehicles traveling the Diagonal Avenue (close to the UB site) and the main avenue (Parallel Ave.) close to the Raval area (CC site; Fig. 1) was high from around 05:00 GMT to 19:00 GMT at both sites. However, the mean number of vehicles at UB was almost twice compared with CC. Thus, by comparing the CC and UB measurement sites in terms of number of vehicles and BC concentrations it can be deduced that an important contribution to the higher NH_3 concentrations measured at CC came from other sources than traffic. A measurement campaign with passive NH_3 samplers performed at different sites in Barcelona (Reche et al., 2012) showed that humans, waste containers and sewage systems were potential important sources of NH_3 in the historical city centre. These sources are especially dense in the old city where the population density is also high. Under high temperatures in summer these sources have the potential to increase the ambient levels of ammonia at CC well above the urban-background-traffic-influenced UB measurement station. Moreover, the urban design of the old city of Barcelona with narrow streets also favored the accumulation of NH_3 preventing the dispersion of air pollutants. Finally, the fact that the lowest hourly NH_3 concentration at CC was 1.8 $\mu g\,m^{-3}$ also demonstrates the presence of a relatively high background of ammonia in the old city. The difference between the NH_3 concentrations between both sites was around 3 $\mu g\,m^{-3}$ (4 ppbv) which can be seen as the minimum mean contribution from non-traffic sources affecting CC site.

The levels of PM_{10}, $PM_{2.5}$ and PM_1 measured at UB were $25.2 \pm 8.2\,\mu g\,m^{-3}$, $19.1 \pm 7.1\,\mu g\,m^{-3}$ and $13.6 \pm 5.1\,\mu g\,m^{-3}$, respectively during the period 6 May–7 September. Amato et al. (2009) reported concentrations of PM_{10}, $PM_{2.5}$ and PM_1 of 40.3 $\mu g\,m^{-3}$, 27.7 $\mu g\,m^{-3}$ and 17.3 $\mu g\,m^{-3}$ during the period 2003–2007 in Barcelona. The relatively low PM concentrations reported in this study were due to the atmospheric conditions typically observed in summer in the Western Mediterranean Basin (WMB) characterized by higher dispersion of pollutants in the atmosphere at a local scale due to higher planetary boundary layer heights and higher recirculation of air masses over the WMB (Jorba et al., 2011; Pey et al., 2008) thus leading to lower mean levels of PM in summer in Barcelona compared with the whole year.

The mean concentrations of NO, NO_2, O_3 and SO_2 during the UB measurement period (6 May–7 September) were around 5, 24, 63, 2 $\mu g\,m^{-3}$, respectively and the mean T, RH, precipitation, solar radiation and wind speed were similar at both sites (Table 1). Relatively high mean temperatures around 22–24 °C were measured during the measurement campaign with relative humidity (RH) around 73 % and 65 % at UB and CC, respectively (the RH mean value at UB over the CC sampling period was 70 %). A slightly higher wind speed at CC (2.1 $m\,s^{-1}$) was observed compared with UB (1.9 $m\,s^{-1}$). Differences in meteorological data between UB and CC were mainly due to the distance between the measurement sites (Fig. 1). The measurement period was on average sunny with sporadic rain events resulting in a total of 47 h (1.6 %) at UB and 60 h (5.5 %) at CC with mm of rain per hour ranging from 0.1 to around 14 (highest value registered at CC).

3.3 Daily cycles

Figure 5 shows the mean daily cycles of NH_3 and ancillary data measured at CC and UB measurement sites and averaged over the whole measurement periods available at both stations. Thus, Fig. 5a–c show the daily cycles of NH_3 and BC concentrations, and wind speed and direction at CC averaged over the 13 May–28 June period, while Fig. 5d–n show the mean daily cycles at UB averaged over the 6 May–7 September period. In Fig. 5a the daily cycle of NH_3 concentrations measured at UB (black lines) over both the UB and CC measurement periods were presented with a different scale (right-hand y-axes in Fig. 5a) for better comparing the dynamic of NH_3 at both stations. The daily cycles of relative humidity (Fig. 5k), temperature (Fig. 5m) and solar radiation (Fig. 5n) measured at UB were used as reference for both sites while wind data were reported separately for the two sites.

We will refer to the Fig. 5 in order to not only separately describe the characteristics of ammonia at UB and CC but also to study the differences in the daily evolution of NH_3 between the two measurement stations.

In general, comparisons between different measurement sites should be done approximately over the same measurement period in order to avoid any bias due to possible changes in meteorological conditions or sources characteristics. However, as reported in Table 1, the differences between the concentrations of NH_3 and ancillary data collected at UB and averaged over the whole UB period (6 May–7 September) or over the CC period (13 May–28 June) were relatively small thus allowing the comparison between the two sites over different measurement periods. The feasibility of this approach is further demonstrated in the Supplement S1 showing that the differences between the concentrations and daily cycles of data collected at UB and averaged over the two different measurement periods were relatively small. Differences were observed mainly for wind speed and direction. As reported in the Fig. 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. As reported in the Supplement S1 this difference was due to the different measurement periods thus the sea breeze at UB also developed at around 07:00 GMT after averaging the UB wind data over the CC measurement period. Consequently, wind data were reported separately for both stations.

3.3.1 NH_3 levels at the old city (CC site)

The levels of NH_3 at CC site (Fig. 5a, red dots) showed a daily cycle driven mainly by the direction and velocity of the wind. The lowest wind velocities were measured between 00:00 and 06:00 GMT with scalar and vectorial means lower than $1.6\,\mathrm{m\,s^{-1}}$ and $0.2\,\mathrm{m\,s^{-1}}$, respectively. The vectorial means, which are weighted by the directions of the wind, reflected general stagnant conditions at night/early morning with winds blowing mainly from N–NE (black triangles in Fig. 5c) with low and rather constant velocities within a shallow nocturnal boundary layer. Under low dispersion conditions the ambient concentrations of NH_3 and BC measured at CC accumulated with time reaching their highest mean values of more than $7.5\,\mu\mathrm{g\,m^{-3}}$ and $2000\,\mathrm{ng\,m^{-3}}$, respectively around 05:00–06:00 GMT. The median concentrations of BC emitted by passing vehicles increased by around 200 % between 01:00 GMT and 06:00 GMT (from 550 and 1640 ng m^{-3}) while the medians NH_3 concentrations increased by less than 20 % (from 5.9 µg m^{-3} to 7.1 µg m^{-3}). Thus traffic was more effective in increasing the levels of BC above the values measured at night rather than those of NH_3.

Starting from 07:00 GMT the increasing solar radiation (Fig. 5n) and temperature (Fig. 5m) activated the sea breeze characterized by winds blowing, with increasing velocities, from the S–SE direction (from the Sea) reaching relatively constant values of more than 3 m s^{-1} (scalar) and 2 m s^{-1} (vectorial) between 11:00 and 15:00 GMT. The cleansing effect of the sea breeze led to the observed gradual reduction in the concentrations of NH_3 and BC observed in the morning. The NH_3 and BC median concentrations reduced from 6.5 µg m^{-3}to 4.4 µg m^{-3} (~ 30 %) and from around 1500 ng m^{-3} to 700 ng m^{-3} (~ 50 %) from 07:00 to 12:00 GMT, respectively. The lower relative reduction of NH_3 median concentrations compared with BC was likely due to the increasing evaporation of NH_3 from other fugitive urban sources which contrasted the cleansing effect of the breeze and the possible depletion of NH_3 due to the formation of ammonium salts.

The concentrations of ammonia reached their minimum mean value (4.1 µg m^{-3}) at 18:00 GMT with fairly constant mean concentrations around 4–4.5 µg m^{-3} observed between 13:00 and 18:00 GMT. The lowest BC mean concentrations (between 590 and 640 ng m^{-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 NH_3values (from 07:00 to 18:00 GMT) compared with BC (from 07:00 to 16:00 GMT) was likely due to the depletion of NH_3 in favor of the formation of ammonium salts during the whole afternoon. Starting from 19:00 GMT the concentrations of NH_3 accumulated again with time as wind velocity decreased reflecting the tendency toward the stagnant atmospheric conditions observed at night.

On average during the measurement campaign at CC site low correlation was observed between the hourly concentrations of NH_3 and BC (Fig. 6a; $R^2 = 0.21$). Low R^2 (0.26) was also observed by correlating the hourly concentrations of NH_3 and BC between 03:00 and 06:00 GMT (around 170 points, not shown) when traffic intensity (Fig. 4) and vehicle emissions increased under stagnant conditions at night. The observed poor correlation was a consequence of the higher number of sources and sinks affecting the ambient concentrations of ammonia compared with BC. Poor correlation between the hourly concentrations of NH_3 and BC was observed also at UB (Fig. 6b) while BC correlated well ($R^2 > 0.9$) with NO_2, being both components emitted mostly by passing vehicles (Fig. 6c).

A further evidence of the fact that non-traffic sources dominated the levels of ammonia at CC is given from Fig. 5a,b. The BC concentrations showed the typical bimodal diurnal cycle driven by increasing (morning) or decreasing (night) emissions from traffic coupled with meteorological conditions favoring the accumulation (low wind and shallow planetary boundary layer (PBL) at night) or dispersion (sea breeze and higher PBLs during the day) of pollutants. The NH_3 concentrations also showed the same peak in the early morning due to the start of the sea breeze after the stagnant nocturnal conditions. However, at night the NH_3 concentrations increased monotonically from 19:00 to 06:00 GMT without showing the second peak around 20:00 GMT. The constant nocturnal NH_3 increase observed at CC was not detected at UB where the NH_3 levels were rather constant at night with a slight but detectable increase around 20:00 GMT due to traffic emissions (Fig. 5d). The lack of equilibrium between the concentrations of NH_3 and all possible sources and sinks at CC, under relatively stable nocturnal conditions with fairly constant temperature and humidity, suggested the presence of active non-traffic sources of ammonia at CC at night likely related with the night life in the historical city centre of Barcelona in summer. A certain degree of equilibrium for the concentrations of NH_3 with time was instead observed when the sea breeze was fully developed blowing with high and relatively constant velocities (Fig. 5c). Mean NH_3 concentrations of 4.5 $\mu g\,m^{-3}$ with relatively low standard deviation of 1.0 $\mu g\,m^{-3}$ were measured based on the 120 hourly data available between 12:00 and 14:00 GMT. The NH_3 equilibrium conditions at these times are better represented in Fig. 7 showing the relationship between the frequency distribution of scalar wind velocities and the concentrations of NH_3 (Fig. 7a) and BC (Fig. 7b). Given the low occurrence for wind velocities higher than 4.5 $m\,s^{-1}$ the frequency distribution of hourly wind velocities in Fig. 7 was calculated for values between 0 $m\,s^{-1}$ and 4.5 $m\,s^{-1}$ (99.3 % of occurrence). Figure 7 shows that the highest BC and NH_3 concentrations were on average measured under low wind speeds and viceversa. Moreover, for wind speed higher than around 2.5 $m\,s^{-1}$ the concentrations of NH_3 were on average constant (horizontal dashed black line in Fig. 7), while BC decreased almost monotonically ($R^2 > 0.8$). This demonstrates that besides meteorology different sources and processes were affecting the concentrations and evolution of NH_3 at CC during the measurement campaign.

3.3.2 NH_3 levels at the urban background (UB site)

As for the CC site the concentrations of aerosol components and gaseous pollutants measured at UB showed daily cycles driven mainly by meteorology. The concentrations of NO_2 (Fig. 5h) and BC (Fig. 5e) which as already noted were highly correlated at UB (Fig. 6c), increased in the early morning up to around 08:00 GMT with a peak around 05:00–06:00 GMT mirroring the rush hours in the Diagonal Avenue. Then, the levels of traffic related pollutants decreased with time, as the velocity of the wind increased under the sea breeze circulation (Fig. 5f), reaching their minimum value around 13:00 GMT when the sea breeze was fully developed. Subsequently, traffic emissions accumulated again as wind velocity decreased and the concentrations of BC and NH3 showed a second peak at around 20:00 GMT. Thus the daily cycles of BC at UB and CC were fairly similar reflecting the similarities in the daily evolution of vehicles number and meteorology at both sites.

The concentrations of ammonia at UB increased in the morning from 06:00 GMT up to the development of the sea breeze which caused the observed reduction of NH_3

levels at UB. As reported in Fig. 5 the concentrations of NH_3 presented a relatively large peak in the morning compared with the concentrations of NH_3 at CC (Fig. 5a) with relatively constant values from 07:00 to 10:00 GMT. The NH_3 increase in the early morning at UB was likely due to the concomitance of different factors: traffic emissions, volatilization of secondary particles formed during the night under stagnant and cooler atmospheric conditions with the beginning of the solar activity around 06:00 GMT (Fig. 5o), transport of background NH_3 from the old city and the Diagonal Avenue when sea breeze developed, or natural release of NH_3 from vegetation and soil may have account for the observed morning increase in NH_3 concentrations at UB. All these factors increased the levels of ammonia from around 2.1 $\mu g\,m^{-3}$ (or 2.4 $\mu g\,m^{-3}$ over the CC site sampling period) at 05:00 GMT up to 2.7 $\mu g\,m^{-3}$ (or 3.5 $\mu g\,m^{-3}$) at 09:00 GMT. Thus, an increase with respect to the values measured at night was clearly detectable at UB but it may have been masked at CC where the concentrations of ammonia were continuously increasing at night-early morning for the aforementioned reasons. Moreover, at CC a sudden entrance of clean air was guaranteed with the beginning of the sea breeze at 07:00 GMT given the proximity of the CC station to the sea causing the fast reduction of pollutants concentrations observed at CC.

Traffic emissions from the close Diagonal Avenue were in part responsible for the observed increase in NH_3 levels in the morning and in the evening at UB. We will show in the next paragraph that the concentrations of NH_3 at UB showed a clear bimodal diurnal cycle as BC (or NO_2) under specific atmospheric conditions favoring the accumulation of pollutants but that these conditions were not dominating during the summer measurement campaign.

Figure 5j shows that the daily cycles of NH_3 and PM_1 were anticorrelated in the early morning with PM_1 concentrations decreasing from 06:00 GMT (before the development of the sea breeze) despite the increase in the concentrations of traffic tracers (BC, NO, NO_2) likely due to particle volatilization. Thus, volatilization of ammonium particles was also responsible, at least in part, for the observed NH_3 morning increase.

Moreover, the transport of elevated background NH_3 concentrations from the historical city centre and of NH_3 emitted from the vehicle crossing the Diagonal Avenue downwind the measurement station, may occur at the beginning of the sea breeze when wind direction changed from 0 degrees at 07:00 GMT to around 120 degrees at 09:00–10:00 GMT. A prolonged morning peak at UB similar to that observed for ammonia was observed for the coarse PM mode ($PM_{2.5-10}$, Fig. 5l). The $PM_{2.5-10}$ fraction in Barcelona is mainly composed by crustal material (wind blown and traffic resuspended dust) and marine aerosols (Amato et al., 2009, 2010). The increase in $PM_{2.5-10}$ in the early morning (under stagnant conditions) was due to traffic-resuspended road dust from vehicles crossing the Diagonal Avenue. However, with the development of the sea breeze the transport of coarse aerosols from wind blown and traffic resuspended dust (also from construction works) from the historical city centre and marine aerosols from the sea may have contributed to the relatively constant values observed for the coarse aerosol mode between 06:00–10:00 GMT. The second peak at 15:00 GMT for $PM_{2.5-10}$ concentrations was mainly due to coarse marine aerosols when sea breeze was fully developed (Amato et al., 2010). Thus, the similarities in the diurnal cycles of NH_3 and $PM_{2.5-10}$ in the morning suggest the transport of NH_3 from the old city as concomitant effect affecting the concentrations of ammonia at UB station.

A common characteristic of NH_3 diurnal cycles at UB and CC sites was the delay observed in NH_3 concentrations in reaching their minimum values compared with BC. Thus, at UB the minimum mean values for NH_3 and BC were reached at 18:00 and 13:00 GMT, respectively. As for CC site, this delay was probably due to the continuous reduction in NH_3 levels due to gas-to-particle partitioning in the afternoon. Conversely, at night from around 20:00 to 04:00 GMT the concentrations of NH_3 at UB were rather constant with mean value of $2\,\mu g\,m^{-3}$ and relatively low standard deviation of $0.7\,\mu g\,m^{-3}$ on hourly base. This equilibrium condition for the NH_3 concentrations at UB site was favored by the virtual absence at night of the continuously emitting non-traffic NH_3 sources observed at CC site. The different behavior of NH_3 and BC at UB is further shown in Fig. 8 where relationship between BC concentrations and wind speed was clearly observed ($R^2 = 0.78$) while a low correlation was observed for NH_3.

Thus, the differences observed between the concentrations and evolutions of NH_3 at UB and CC were mainly due to the differences in the sources affecting both sites which determined the degree of equilibrium of ambient concentrations of NH_3 under different atmospheric condition during the 24 h.

4 Specific cases

As reported in the previous paragraphs different factors contributed to the measured concentrations and daily evolutions of NH_3 in Barcelona in summer. We present and discuss in this section three cases observed during the campaign with levels and daily evolutions of NH_3 dominated by specific sources or processes such as traffic emissions or gas-to-particle partitioning. Data from UB site were used with this aim given the larger dataset collected at this station compared with CC.

4.1 SC1: traffic dominated scenario

A closer analysis of each day of measurements performed at UB station revealed that a clear traffic-driven bimodal NH_3 diurnal cycle, similar to that of NO_2, was observed on 12 days (only weekdays) out of 90 days with simultaneous NH_3 and NO_2 measurements. Five out of these 12 days were consecutively observed between 9 and 13 May and the mean diurnal cycles of the measurements available at UB during this period (named SC1) are reported in Fig. 9 and compared with the mean diurnal cycles during the whole campaign.

As shown in Fig. 9 the beginning of the campaign was characterized by atmospheric conditions favoring the accumulation of pollutants. The mean concentrations of NH_3, PM_1, $PM_{2.5-10}$, NO_2, BC and SO_2 during SC1 were higher compared with the whole campaign by around 32 %, 65 %, 10 %, 112 %, 53 % and 70 %, respectively. The lower increase was observed for the coarse PM mode ($PM_{2.5-10}$) indicating that these atmospheric conditions favored the accumulation mainly of fine particles. In fact, the mean concentration of PM_1 under SC1, around 22.7 µg m^{-3}, was higher than the mean value of 13.6 µg m^{-3} reported by Amato et al. (2009) for the 2003–2007 period. The opposite was observed for ozone which was around 37 % lower than the mean. The SC1 period was characterize by low temperatures and wind speeds, less breeze and higher solar radiation and pressure. The analysis of the backtrajectories (not shown) indicated the lack of strong synoptic winds during these days with air masses coming mainly from the Mediterranean Sea thus explaining the reduction in temperature despite the slightly higher solar radiation. A certain degree of local recirculation of air masses was also observed thus explaining the accumulation of pollutants. Under these atmospheric conditions the NH_3 emitted by passing vehicles were easily accumulated with ammonia showing the typical bimodal diurnal cycle, in parallel with NO_2 and BC, clearly related with traffic emissions during rush hours in the morning and in the evening when the sea breeze was not active.

The specific case under study demonstrated that traffic was an important source of NH_3 at UB. On the base of previous publications in the area under study we know that the most intense stagnant atmospheric conditions leading to accumulation of pollutants were usually observed in winter (Jorba et al., 2011; Pandolfi et al., 2011; Pey et al., 2010). Thus, the traffic-driven bimodal diurnal cycles of NH_3 can be expected to be more frequent in winter than in summer. Similar findings were reported for example by Meng et al. (2011) and Gong et al. (2011).

4.2 SC2: regional recirculation scenario

Figure 3 shows that the measurement campaign at UB can be divided in two main periods: one from the beginning of the campaign up to around the first half of July with mean NH_3 and PM_1 levels of 2.7 ± 1.0 µg m^{-3} and 15.8 ± 6.7 µg m^{-3}, respectively, and the other one from 15 July up to the end of the campaign with considerably lower mean concentrations of NH_3 (1.6 ± 0.7 µg m^{-3}) and PM_1 (11.8 ± 4.9 µg m^{-3}). The observed reduction in both NH_3 and PM_1 concentrations was due to the typical summer recirculation/dispersion conditions enhanced during the second half of the campaign. The period 1–5 August (SC2; Monday–Friday), reported in Fig. 10, was characterized by these typical summer atmospheric conditions with sea breeze circulation and relatively high wind speed. Solar radiation and pressure were close to the mean values observed during the whole campaign while the temperatures registered under SC2 were considerably higher than the mean.

During SC2 the levels of PM_1 and NH_3 at UB were 14.8 $\mu g\,m^{-3}$ and 1.0 $\mu g\,m^{-3}$, respectively higher and lower than the corresponding means calculated over the second part of the campaign. Consequently, as reported in Fig. 10 the levels of PM_1 under SC2 were similar to the levels measured during the whole campaign while the concentrations of NH_3 were among the lowest on average measured. Figure 10 also show the lack of the clear bimodal diurnal profile of ammonia observed in Fig. 9 under more stagnant conditions. Our interpretation is that the enhanced formation of secondary sulfate during the days under study may cause the relative difference observed between the concentrations of NH_3 and PM_1 with respect to the mean values observed during the whole campaign. The influence of gas-particle partitioning on ammonia during the day with depletion of NH_3 in favor of the formation of high concentrations of sulfates was recently presented by e.g. Ellis et al. (2011) in an agricultural area in Canada. Moreover, Reche et al. (2011) showed that in Barcelona in summer nucleation episodes involving NH_4HSO_4 particles formation are commonly observed at midday causing high levels of ultrafine particles.

Figure 11 shows the relationship between the 24 h-averaged gas fraction of ammonia (gas fraction = $NH_3/(NH_3+NH_4^+)$) and sulfate concentrations from off-line analysis of 24 h filters collected during the campaign. Twenty-two filters collected from 10 May to 5 August were available for this analysis. Details on experimental procedures used for the determination of SO_4^{2-}, NO_3^- and NH_4^+ from filters are given in Querol et al. (2001). Figure 11 shows that low ambient concentrations of ammonia in its gas fraction were available when the concentrations of sulfate were high as expected from to the gas-to-particle conversion which in summer involved mainly the formation of secondary sulfates (mean value (22 filters) = 3.3 µg m^{-3}) rather than nitrates (mean value = 0.3 µg m^{-3}). Only one filter collected between 4 and 5 August was available during SC2 (highlighted in Fig. 11) and it was used as reference for the whole SC2 period. On the other end, the conditions during the selected 5 days were very stable and the mean diurnal cycles calculated on 4 and 5 August separately did not differ very much from the mean diurnal cycles calculated over the whole SC2 period (mainly showing low NH_3, relatively high PM_1 and temperatures).

Thus, during the specific case under study (SC2) the general atmospheric conditions, including higher mean temperatures, led to the formation of high concentrations of sulfate particles with consequent reduction in the concentrations of gas-phase ammonia. Thus, the gas-to-particle conversion also played an important role during the campaign in the variation of NH_3 concentrations.

4.3 SC3: high NH_3 episode

The last specific case described in this section was the episode (one day, 13 July 2011) with the highest mean daily NH_3 concentrations (4.9 µg m^{-3}) registered during the whole campaign at UB. The mean diurnal cycle for 13 July was reported in Fig. 12.

The 13 July started with some rain at night around 03:00–05:00 GMT causing the drastic reduction in the concentrations of the atmospheric components reported in Fig. 12 (NH_3, BC, NO_2, PM_1 and $PM_{2.5-10}$) scavenged by raindrops. High NH_3concentrations were instead observed before the rain event. This day was characterized by strong wind velocities and the virtual absence of sea breeze circulation, with winds blowing from the NW direction from 00:00 to 13:00 GMT. The high NH_3 concentrations observed at night, before the rain, were likely due to the transport of ammonia from the rural areas located NW the city. High solar radiation and temperature were recorded at midday in concomitance with a reduction in RH. The NH_3 increase after the rain was likely due to the increased microbial processes in soil and vegetation that can release ammonia (e.g., Ellis et al., 2011) or from dew evaporation in the morning.

5 Final considerations

We have shown that the levels of ammonia in summer in Barcelona were regulated by different chemical and physical atmospheric processes. In the old city (CC measurement station) traffic did not dominate the measured concentrations of ammonia ($5.6 \pm 2.1\,\mu g\,m^{-3}$ or 7.5 ± 2.8 ppbv) which were higher compared with those simultaneously measured at the traffic-influenced urban background station (UB) ($2.2 \pm 1.0\,\mu g\,m^{-3}$ or 2.9 ± 1.3 ppbv) where higher BC concentrations and number of vehicles were observed compared with CC. Thus, other non-traffic fugitive NH_3 sources such as waste containers, sewage systems, humans and open markets strongly contributed to the measured levels of ammonia in the densely populated old city of Barcelona.

In summer, under high atmospheric temperatures, these fugitive emissions had the potential to increase the concentrations of NH_3 well above the levels measured at the traffic-influenced urban background UB site. Moreover, the urban design of the old city of Barcelona with narrow streets also favored the accumulation of NH_3 preventing the dispersion of air pollutants.

At UB the lower contribution from non-traffic NH_3 sources compared with CC led to a more marked effect of traffic emissions which contributed to the NH_3 increase observed in the morning and in the evening during the rush hours. Conversely, at night-early morning, when traffic intensity was low, the NH_3 concentrations at UB were constant indicating that equilibrium between the NH_3 sources and sinks was reached under relatively stagnant atmospheric conditions at night.

The typical bimodal-traffic-driven NH_3 diurnal cycle at UB was especially marked at the beginning of the campaign when the lack of synoptic winds favored the accumulation of pollutants. This bimodal diurnal cycle was not observed at CC site where the NH_3 concentrations showed a monotonic increasing tendency at night-early morning (from 19:00 GMT to 05:00 GMT) before the development of the sea breeze as a consequence of the emissions from non-traffic NH_3 sources in the old city which were active also during the night.

From the off-line analysis of the 24 h filters collected during this summer measurement campaign resulted that lower ambient concentrations of ammonia in its gas fraction were available when the concentrations of sulfate were high as expected from to the gas-to-particle conversion which in summer involved mainly the formation of secondary sulfates (mean value = 3.3 $\mu g\,m^{-3}$) rather than nitrates (mean value = 0.3 $\mu g\,m^{-3}$). Thus, the gas-to-particle conversion also played an important role during the campaign in the variation of NH_3 concentrations.

The levels of NH_3 measured in Barcelona, especially high in the old city, may contribute to the high mean annual concentrations of secondary sulfate and nitrate measured in Barcelona compared with other cities in Spain affected by high traffic intensity. In Madrid (around 3 millions inhabitants) for example considerably lower concentrations of NH_3 have been observed (not shown) compared with Barcelona. These high NH_3 concentrations in Barcelona may also explain the increase of around 4 $\mu g\,m^{-3}$ in the mean annual concentrations of fine PM ($PM_{2.5}$) measured in Barcelona compared with Madrid. Finally, the concentrations of ammonia measured in Barcelona may also be the reason for the nucleation episodes involving NH_4HSO_4 formation which have been observed in Barcelona and which caused high levels of ultrafine particles (Reche et al., 2011). Consequently, we conclude that it is important to take specific measures in order to reduce the emissions of NH_3 in the city of Barcelona and mainly in the old city.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/10381/2012/acpd-12-10381-2012-supplement.pdf.

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Table 1. Statistics on available measurements performed at the urban background (UB) and historical city centre (CC) measurement stations. Statistics at UB were also reported for the same sampling period of CC station (13 May–28 June).

station UB (6 May–7 Sep) 2967 h	Unit	Availability	Mean	SD	25th perc.	50th perc.	75th perc.	min	max
NH_3	µg m^{-3}	2157 h (73 %)	2.2	1.0	1.4	1.9	2.6	0.2	10.6
NO	µg m^{-3}	2791 h (94 %)	5.1	10.4	1.5	3.0	5.0	1.0	211.0
NO_2	µg m^{-3}	2791 h (94 %)	23.9	16.2	13.0	19.5	30.0	1.0	138.5
O_3	µg m^{-3}	2773 h (93 %)	62.7	25.6	46.0	63.5	79.5	1.0	194.5
SO_2	µg m^{-3}	2791 h (94 %)	2.2	1.9	1.0	1.5	2.5	1.0	27.5
BC	ng m^{-3}	2394 h (81 %)	1554	1158	870	1231	1870	−22	11 153
PM_{10}	µg m^{-3}	2853 h (96 %)	25.2	8.2	19.2	23.9	29.8	10.8	97.9
$PM_{2.5}$	µg m^{-3}	2853 h (96 %)	19.1	7.1	13.7	17.7	22.8	7.4	63.5
PM_1	µg m^{-3}	2853 h (96 %)	13.6	5.9	9.1	12.5	16.7	4.2	44.6
T	°C	2611 h (88 %)	23.7	3.1	21.7	23.7	25.9	14.1	34.4
RH	%	2611 h (88 %)	73.4	12.6	65.7	75.0	83.2	34.0	100.0
Prec	mm	2611 h (88 %)	0.01	0.1	0.00	0.00	0.00	0.00	3.43
Wind speed	m s^{-1}	2611 h (88 %)	1.9	1.1	1.0	1.7	2.5	0.2	6.8
Sol Rad	W m^{-2}	2611 h (88 %)	252.9	314.8	0	75	488	0	1035
CC (13 May–28 Jun) 1100 h									
NH_3	µg m^{-3}	978 h (89 %)	5.6	2.1	4.2	5.2	6.5	1.8	16.2
BC	ng m^{-3}	899 h (82 %)	1190	1059	524	867	1552	−20	7383
T	°C	1100 h (100 %)	21.6	3.2	19.2	21.5	23.8	14.3	30.9
RH	%	1100 h (100 %)	65.1	13.9	56.0	66.0	76.0	26.0	94.0
Prec	mm	1100 h (100 %)	0.1	0.8	0.0	0.0	0.0	0.0	14.4
Wind speed	m s^{-1}	1100 h (100 %)	2.1	1.0	1.3	2.0	2.8	0.1	5.1
Solar rad.	W m^{-2}	1100 h (100 %)	284	335	0	101	602	0	964
UB (13 May–28 Jun) 1100 h									
NH_3	µg m^{-3}	526 h (48 %)	2.6	1.1	1.8	2.3	3.2	0.5	10.6
NO	µg m^{-3}	930 h (85 %)	4.9	11.4	1.0	2.0	4.5	1.0	211.0
NO_2	µg m^{-3}	930 h (85 %)	25.6	17.6	13.5	21.5	33.0	1.0	138.5
O_3	µg m^{-3}	930 h (85 %)	66.9	25.4	51.5	68.0	83.0	6.0	132.0
SO_2	µg m^{-3}	930 h (85 %)	2.9	2.1	1.5	2	3.5	1	17.5
BC	ng m^{-3}	1047 h (95 %)	1665	1283	904	1293	2010	−22	11 153
PM_{10}	µg m^{-3}	1100 h (100 %)	23.4	6.4	18.6	22.6	27.0	12.0	54.1
$PM_{2.5}$	µg m^{-3}	1100 h (100 %)	18.3	6.0	13.8	17.1	21.4	9.1	48.7
PM_1	µg m^{-3}	1100 h (100 %)	13.4	5.3	9.4	12.2	16.3	6.0	40.9
T	°C	907 h (83 %)	20.6	3.2	18.1	20.4	22.5	14.1	30.3
RH	%	907 h (83 %)	69.9	15.2	59.2	71.8	81.1	27.0	98.5
Prec	mm	907 h (83 %)	0.0	0.1	0.0	0.0	0.0	0.0	3.3
Wind speed	m s^{-1}	907 h (83 %)	1.9	1.2	1.0	1.7	2.4	0.2	6.7
Sol Rad	W m^{-2}	907 h (83 %)	266.7	328.7	0.0	75.8	490.8	0.0	1034.7

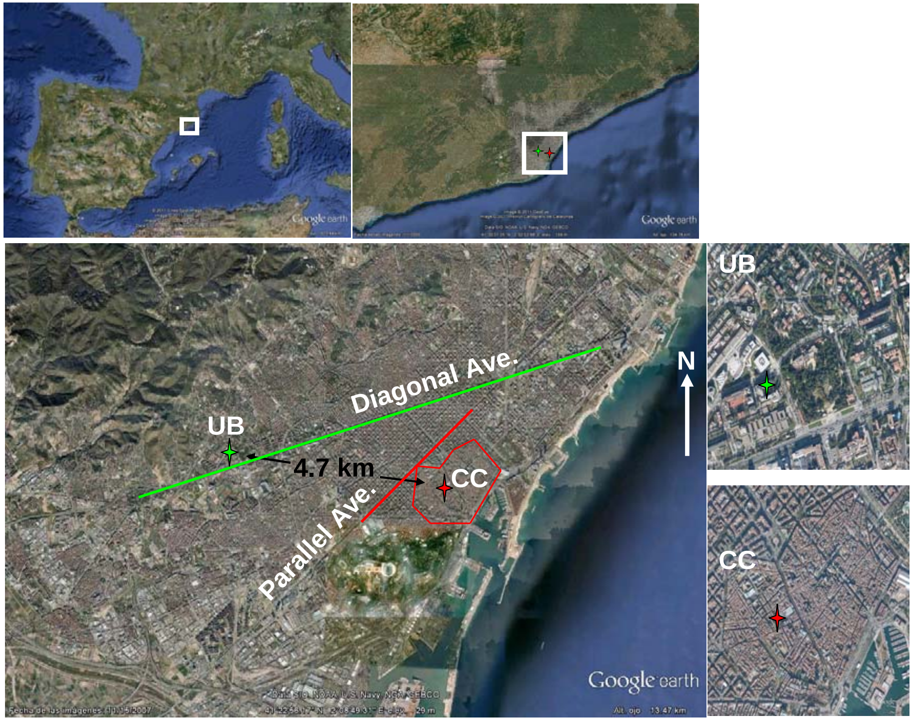

Fig. 1. Location of the two measurements sites in Barcelona (NE Spain): UB (traffic-influenced urban background) and CC (historical city center).

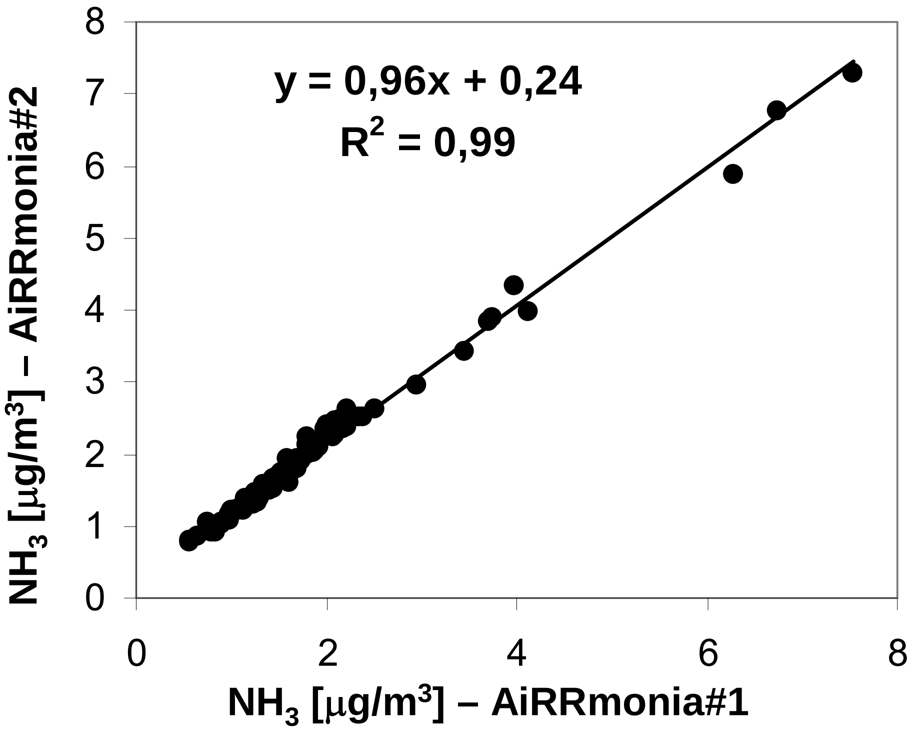

Fig. 2. Intercomparison between the two AiRRmonia instruments deployed during the measurement campaign. Site used for the intercomparison: UB.

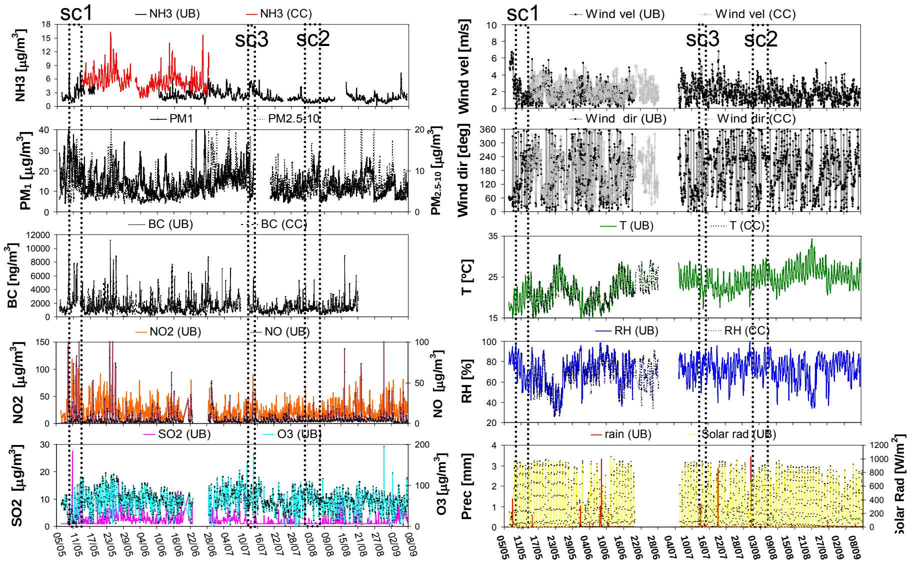

Fig. 3. Temporal series of the NH_3 concentrations and ancillary measurements performed at UB (6 May–7 September 2011) and CC (13 May–28 June 2011). Black dashed boxes sc1–sc3 highlight special cases discussed throughout the text.

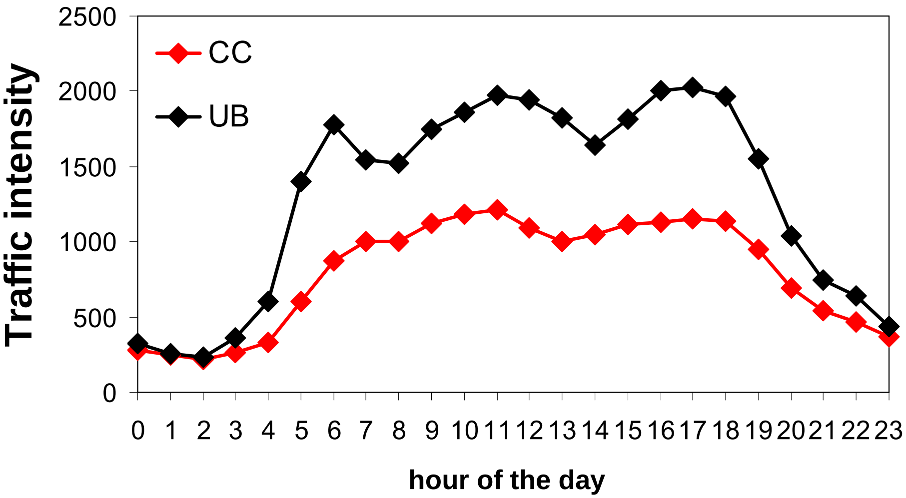

Fig. 4. Mean daily cycles of number of vehicles at UB (Diagonal Ave.) and CC (Parallel Ave.) measurement sites.

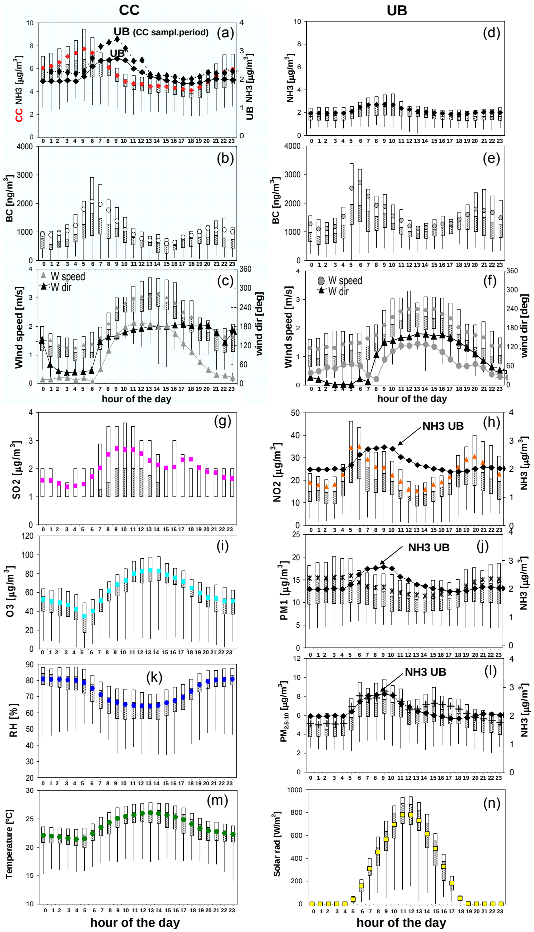

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Fig. 5. Daily cycles of: **(a)** NH_3 concentrations (red dots), **(b)** black carbon concentrations, and **(c)** vectorial (grey triangle in the box-and-whiskers plots) and scalar (grey solid line) wind speed and vectorial direction (black triangles) measured at CC over the period 13 May–28 June. Daily cycles of: **(d)** NH3 concentrations, **(e)** BC concentrations, **(f)** wind speed (scalar and vectorial) and direction (vectorial) measured at UB over the period 6 May–7 September. In Fig. 5a the concentrations of NH3 measured at UB over the periods 6 May-7 September (black solid line) and 13 May-28 June (black dashed line) are also reported. Daily cycles of: **(g)** SO_2 concentrations, **(h)** NO_2 concentrations, **(i)** O_3 concentrations, **(j)** PM_1 concentrations, **(k)** relative humidity (RH), **(l)** $PM_{2.5-10}$ concentrations, **(m)** temperature, and **(n)** solar radiation measured at UB over the period 6 May–7 September. In Fig. 5 **(h, j, l)** the diurnal cycle of NH3 measured at UB over the 6 May–7 September period is also reported. Box-and whiskers plots represent the 25th and 50th percentiles (upper white and lower grey boxes), colored symbols represent the means, the black horizontal bands represent the median (50th percentiles) and lower error bars represent the minimum measured values.

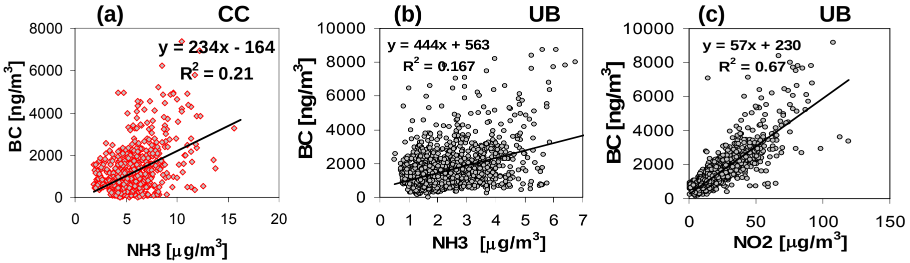

Fig. 6. Correlation between **(a)** NH_3 and BC concentrations at CC, **(b)** NH_3 and BC concentrations at UB, and **(c)** BC and NO_2 at UB.

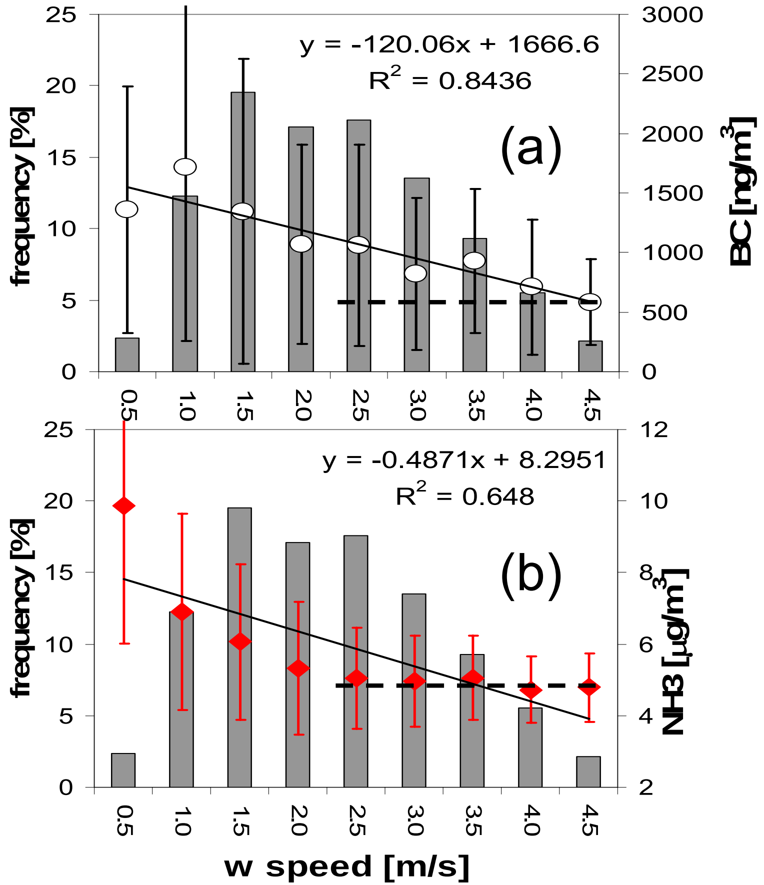

Fig. 7. Correlation between the frequency distribution (%) of scalar wind velocity ($\mathrm{m\,s^{-1}}$) and **(a)** BC concentration and **(b)** NH_3 concentrations at CC.

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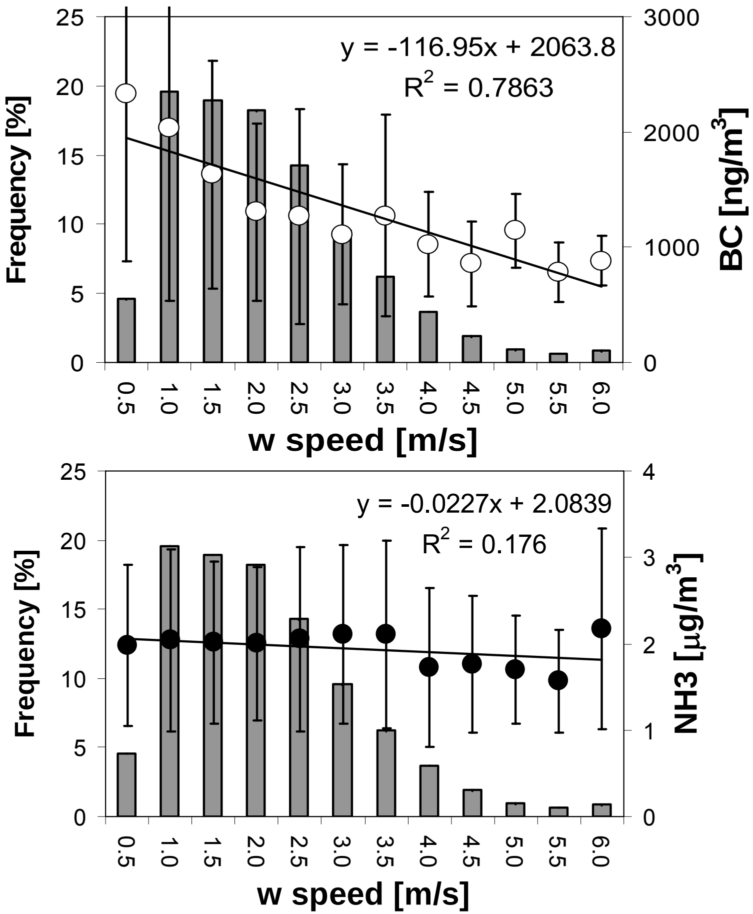

Fig. 8. Correlation between the frequency distribution (%) of scalar wind velocity (m s^{-1}) and **(a)** BC concentration and **(b)** NH_3 concentrations at UB.

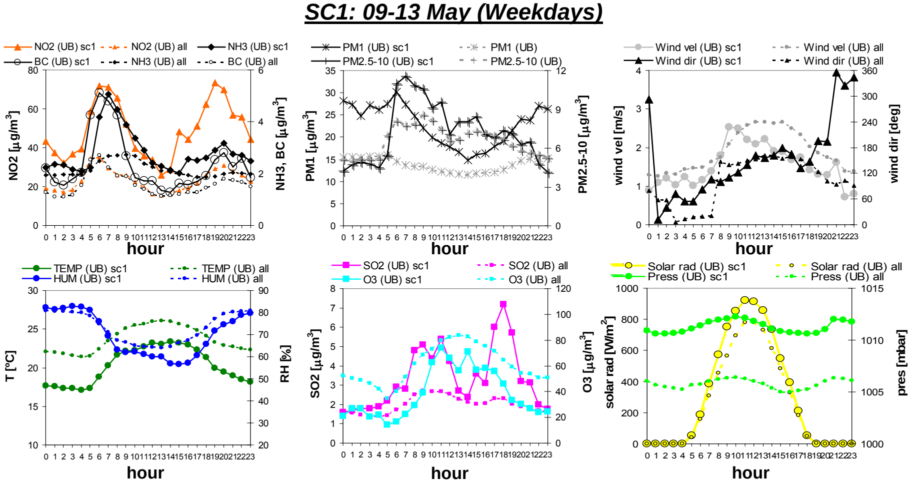

Fig. 9. Mean diurnal cycles of aerosol components and parameters measured at UB station during the period 09–13 May (Special Case 1).

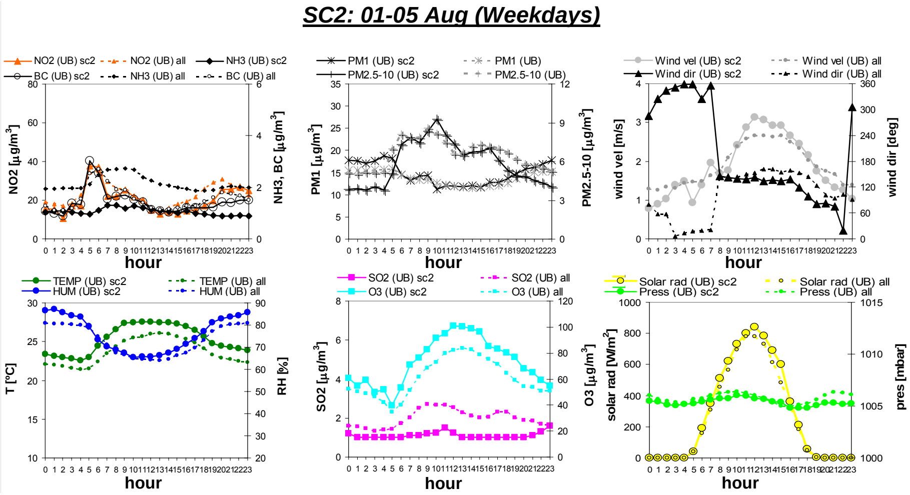
SC2: 01-05 Aug (Weekdays)

Fig. 10. Mean diurnal cycles of aerosol components and parameters measured at UB station during the period 1–5 August (Special Case 2).

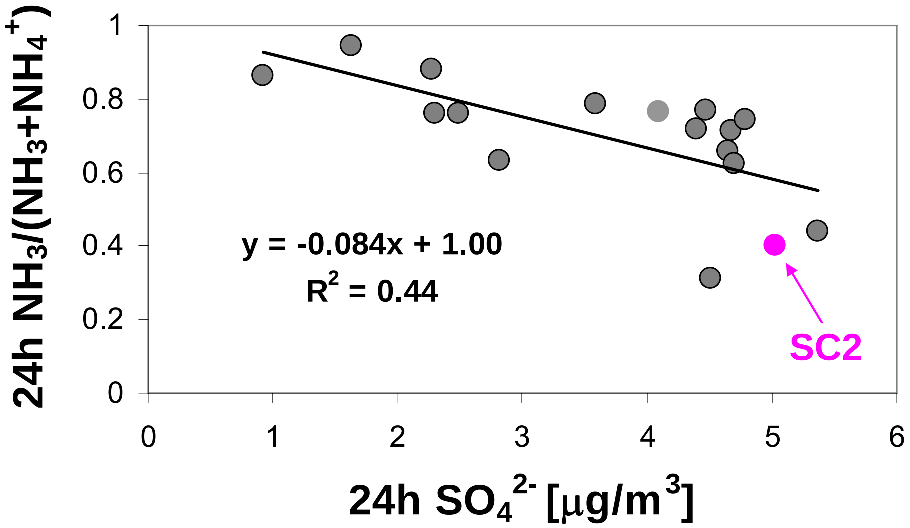

Fig. 11. Relationship between the gas fraction of ammonia ($NH_3/(NH_3+NH_4^+)$) and sulfate (SO_4^{2-}) concentrations from 24 h filters collected over the period 10 May–5 August at UB.

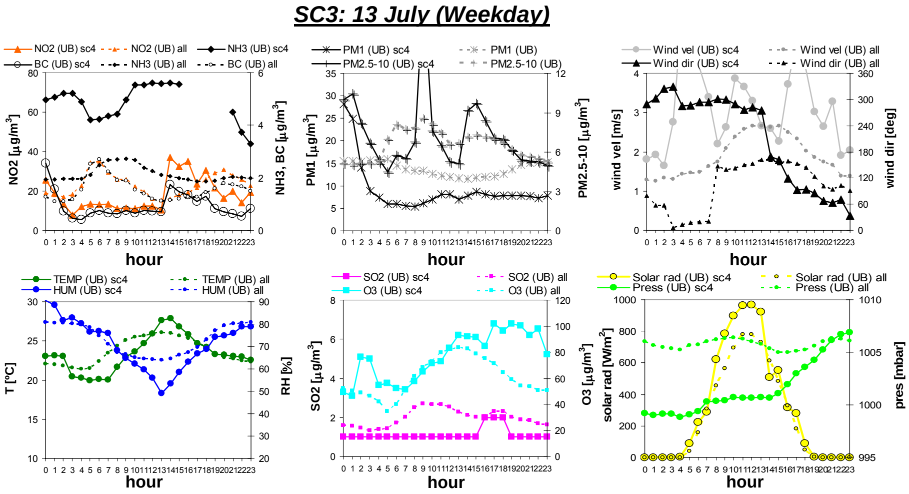

Fig. 12. Mean diurnal cycles of aerosol components and parameters measured at UB station during 13 July (Special Case 3).

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