Ammonia Levels In Different Kinds Of Sampling Sites In The Central Iberian Peninsula

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Abstract — Ammonia is the Secondary Inorganic Aerosol (SIC) gaseous precursor which has been studied to a lesser extent in the Madrid Metropolitan Area up to date. A study conducted in the city of Madrid with the aim of characterizing levels of ammonia took place in 2011. These campaigns formed part of a larger study conducted in 6 Spanish cities. A time series of weekly integrated ammonia measurements available at an EMEP rural site (Campisábalos) has been used to obtain information on the ammonia rural background in the region. The results point to traffic and waste treatment plants as the main ammonia sources in Madrid. Relevant seasonal differences have not been observed in the Metropolitan Area. The explanation can be related to the fall in the rural background levels during July 2011, which might conceal urban summer emission increases observed in other cities.

Keywords — ammonia, traffic, urban waste, rural background

1 INTRODUCTION

Ammonia is the SIC gaseous precursor which has been studied to a lesser extent in the Madrid Metropolitan Area up to date. Air Quality objectives have not been established yet in Spain, but the main role of this gas in the formation of secondary particles raises the interest in its study. In general terms, it is recognised that the main source of ambient ammonia is livestock waste, followed by vegetation and agriculture. However, the source contribution to ammonia in urban areas is not yet fully characterised. These sources would include traffic, human and pets´ excretions, landfill, garbage, household products and sewage treatment plants.

In 2002, Perrino et al studied the relationship between gaseous ammonia and traffic in the urban area of Rome. The authors found at traffic sampling sites a high correspondence between the hourly time evolution of a primary gas emitted by traffic, carbon monoxide, and NH_3. This study also corroborated results from other researchers who found that in the USA the petrol-engine vehicles equipped with three-way catalytic converters generated gaseous ammonia [1]. Most recent observations also suggest that the NH_3 emissions from the traffic exhaust could be a major source of the ambient NH_3 in other urban areas such as New York [2] Manchester [8] or Beijing [3].

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2 METHODOLOGY

A study conducted in the city of Madrid with the aim of characterizing levels of ammonia in the urban ambient air took place in 2011 [6]. Two 10-11 days sampling campaigs were performed in two periods - winter and summer, and allowed to make a first estimation of the spatial distribution pointing at the main contributing sources. Passive samplers were used, obtaining a measurement integrated over the exposure time period. Madrid campaigns formed part of a larger study conducted in 6 Spanish cities: Barcelona, A Coruña, Valencia, Huelva and Santa Cruz de Tenerife. The results obtained in Barcelona were presented by Reche et al [5].

High sensitivity passive samplers (CEH ALPHA: Adapted Low-cost High Absorption) designed at the Centre for Ecology and Hydrology of Edinburgh [7]. were used. Samplers are made up of a polyethylene vial with one open end. An internal ridge supports a filter, which is coated with a solution of phosphorous acid in methanol, which serves to capture the ammonium ion. The ambient air ammonia concentrations were calculated according to the principle of diffusion of gases from the atmosphere along a sampler of defined dimensions onto an absorbing medium, governed by Fick’s law.

In the winter period, 64 passive samplers were deployed all over the Metropolitan Area of Madrid with the objective of identifying ammonia sources and also obtaining the highest possible spatial coverage. 29 samplers were placed in traffic sites, 28 in urban background sites, 6 close to sewage treatment plants and 1 close to a solid waste treatment plant. Some of the samplers had a duplicate separated around 10m to study the reproducibility of the procedure, taking into account shielding effects and the proximity to point sources (sewers). In the summer campaign the number of sites was smaller due to sampler availability. (See Appendix I)

Ancillary data were used to obtain information on the ammonia rural background in the region. A time series of weekly integrated ammonia measurements is available at a rural site in the Central Iberian Peninsula (Campisábalos, 41.27° N, 3.14° W, 1360 m asl.) provided by the EMEP network. These samples are analysed using visible spectrophotometry.

3 RESULTS

3.1 Madrid Metropolitan Area

Two sampling campaigns covering more than 50 sites in the Metropolitan Area of Madrid were performed with the objective of estimating the levels of this pollutant and its seasonal variability, and at the same time identifying the sources which contribute most to ammonia concentrations in the city. The results obtained in the campaigns are presented below according to the type of site.

Sites close to sewage and solid waste treatment plants registered the highest concentrations. The traffic sites showed significantly higher than the urban background sites in both seasons. No significant differences between winter and summer were registered for any kind of sampling site in the Madrid Metropolitan Area.

Figure 1 shows the mean NH_3 concentrations calculated for the traffic sites in the winter and summer campaigns. The mean values were very similar in both seasons (2.7± 0.5 $\mu g \cdot m^{-3}$ in winter and 2.6±0.4 $\mu g \cdot m^{-3}$ in summer). In winter, three of the four samplers placed very close to bus stops registered concentrations above the mean. In P15 and E16 very high concentrations were measured in both seasons. These sites were nearby the very busy streets Alcalá and Arturo Soria (yearly average 47812 and 29087 vehicles$\cdot$ day^{-1})

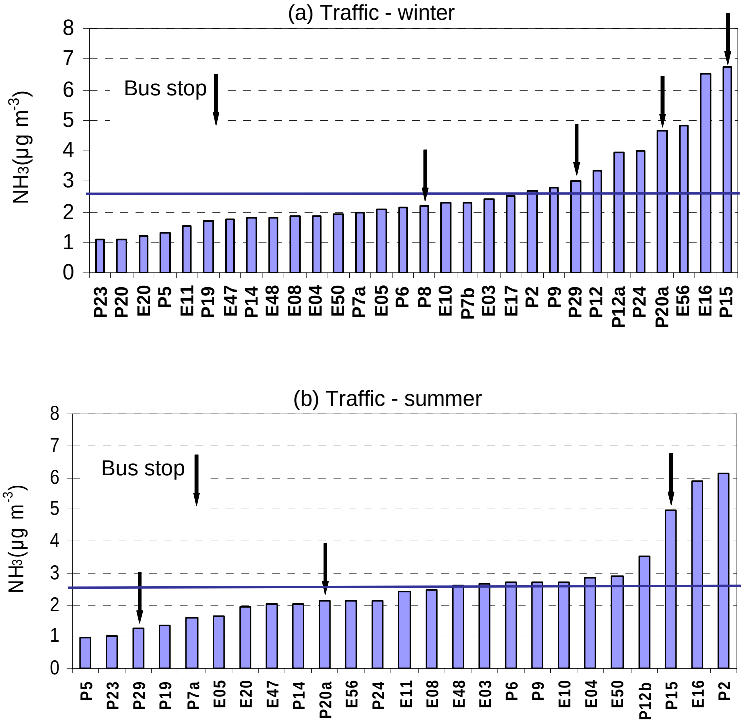

Figure 1. Mean NH3 concentrations in the traffic sites in (a) winter and (b) summer. Horizontal lines represent the average of all measurements. Black arrows indicate bus stops.

Urban background sites also registered very similar mean NH_3 concentrations in both seasons (1.6±0.3 $\mu g \cdot m^{-3}$ and 1.5±0.3 $\mu g \cdot m^{-3}$). RV (Retiro Viveros) showed very high concentrations both in winter and summer. The sampler was placed in a big urban park, close to the park's nursery. The lowest values were registered at Casa de Campo (E24), a big forested area located on the western part of the city.

Figure 2 shows the mean NH_3 concentrations calculated for the sewage treatment plants and the solid waste treatment plant (so-called

"Valdemingómez incinerator") sites in winter and summer. The Rejas sewage treatment plant registered concentrations more than two times higher in summer, being the highest value obtained (~4 µg·m^{-3} winter; ~10 µg·m^{-3} summer) in the study. The rest of the plants showed values in the range 2-5 µg·m^{-3} in both seasons.

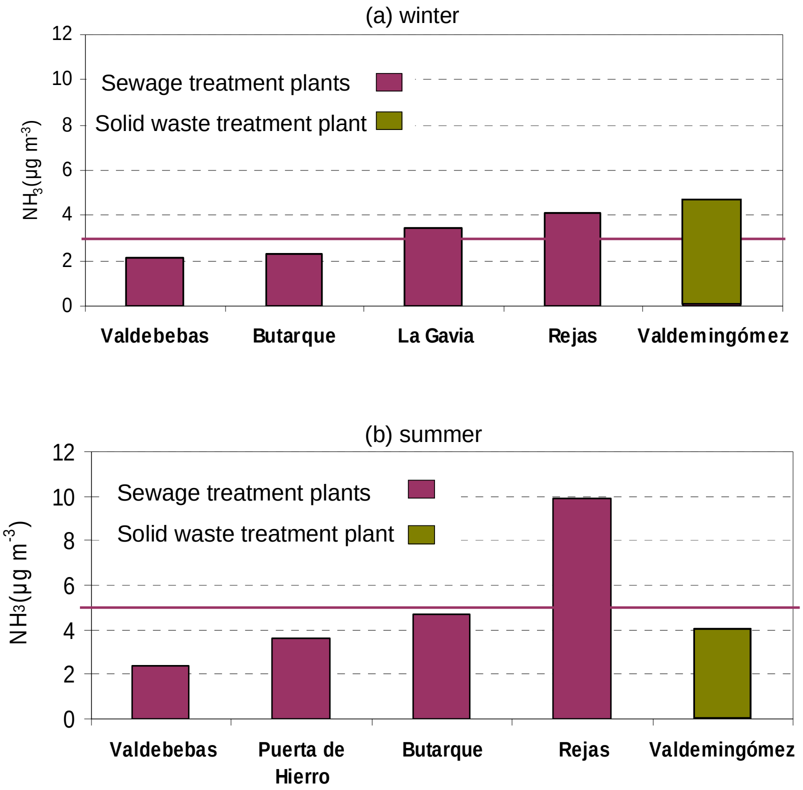

Figure 2. Mean NH3 concentrations in the sewage treatment plants and the incinerator in (a) winter and (b) summer. Horizontal lines represent the average of the sewage treatment plants.

Table 1 shows the results obtained in the sites adjacent to sewers and the duplicates, separated >10 m. The sampler closer to the sewer showed slightly higher ammonia concentrations at P7 and P12 (traffic sites) and P21 (urban background). However, P20a, located on a bus stop, showed a much higher ammonia concentration than P20b. Thus, the proximity to sewers might influence ambient ammonia levels locally, but the results obtained are not conclusive.

Table 1. Mean NH_3 concentrations (µg·m^{-3}) in sites adjacent to sewers and duplicates. *bus stop

Site	Sewer adjacent	NH_3	Sewer >10m	NH_3
Traffic	P7b	2.3	P7a	2.0
	P20b	1.1	P20a*	4.7
	P12a	4.0	P12b	3.4
Urban bg	P21a	1.1	P21b	1.0

Comparing the mean values calculated in traffic and urban background sites we can see there is a statistically significant difference in both seasons, with higher mean concentrations in the traffic sites. In contrast, the sewage treatment plants and incinerator showed the highest NH_3 levels, but the difference with the mean ammonia levels registered in the traffic sites was not significant. This result is in agreement with the studies in other cities which had pointed to traffic emissions as a major source of ammonia in urban areas. No significant differences between winter and summer were registered for any kind of sampling site.

3.2 Rural background: Campisábalos

Weekly integrated ammonia measurements have been obtained at Campisábalos since August 2004 (see Figure 3). Monthly mean concentrations are in the range 0-2.5 µg·m^{-3} and a seasonal pattern with summer maxima is observed most of the years being less pronounced in 2007 and 2011. Nevertheless, a drop in the middle of the summer is clearly observed in 4 out of the 8 years

sampled, very pronounced in 2011. The explanation may be due to the extreme dryness of the countryside during the summer months, which inhibits the decomposition of soil organic matter, responsible for a large part of the emissions of NH_3 at rural areas.
Trend analysis has been performed by the Theil-Sen method using deseasonalised data. The analysis does not show any tendency (see upper-right corner of Figure 3), i.e., annual mean concentrations remained constant at this site in the period Aug-2004 to Dec-2012.

In winter the mean concentrations registered at the urban background sites in the Madrid Metropolitan Area were slightly higher than the monthly mean in March 2011 at Campisábalos (~1 μg·m^{-3}). However, in July 2011 mean NH_3 at Campisábalos were extremely low. This fall in summer ammonia rural background can be related to the constant ammonia concentrations observed in the urban area of Madrid, inhibiting possible summer increases observed in other cities such as Barcelona [5].

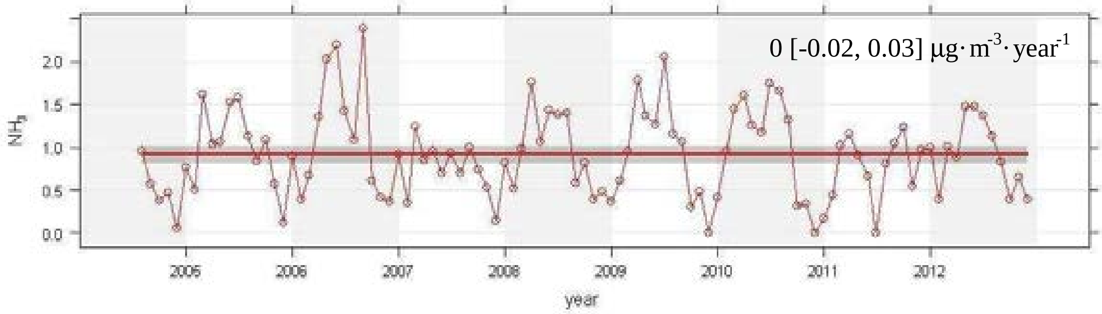

Figure 3. Ammonia monthly evolution at Campisábalos

4 CONCLUSIONS

Ammonia measurement campaigns were performed in 2011 in the Metropolitan Area of Madrid. More than 50 passive samplers were deployed in two seasons: winter and summer.

Sites close to sewage and solid waste treatment plants registered the highest concentrations, followed by the traffic sites. The latter showed significant higher values than the urban background sites in both seasons.

In winter, three of the four samplers placed very close to bus stops registered concentrations above the mean. Sites nearby the very busy streets Alcalá and Arturo Soria registered very high concentrations in both seasons. Traffic emissions could be related to catalytic converters, which have been proved to lead to outstanding reductions in NOx emissions, but also to generate gaseous ammonia, raising controversy on the use of these devices.

The samplers close to sewers showed slightly higher ammonia concentrations than duplicates separated a distance > 10 m. The proximity to sewers might influence ambient ammonia levels locally, but the results obtained are not conclusive.

No significant differences between winter and summer were registered for any kind of sampling site in the Madrid Township, in contrast with the summer maxima observed at the rural EMEP site Campisábalos most of the years. Nevertheless, a drop in the middle of the summer is clearly observed in 4 out of the 8 years sampled, very pronounced in 2011. In winter the mean concentrations registered at the urban background sites were consistent with the monthly mean in March 2011 at Campisábalos, but in summer 2011 the mean NH_3 registered at the rural site was extremely low. This fall in summer ammonia rural background can be related to the constant ammonia concentrations observed in the urban area of Madrid, inhibiting possible summer increases observed in other cities.

5 APPENDIX I

Table A.1 shows the sampling sites selected in the winter NH_3 campaign in Madrid. EXX correspond to stations belonging to the city hall air quality network (Red de Calidad de Aire del Ayuntamiento de Madrid). Sites marked with I and II (samplers D14-D15; D25-D26; D30-D31; D59-D60) were separated a few meters. One of them was adjacent to a sewer. The sampler at Rejas was replicated (D17, D28) to check the reproducibility of the procedure.

The following samplers were not deployed in the summer campaign: D7, D11, D13, D15, D26, D29, D31, D39, D42, D47, D56, D58 and D59. This was due to a lesser availability of samplers.

Table A.1. Sampling sites in the winter NH_3 campaign in Madrid. STP=sewage treatment plant. Urban bg=urban background.

Sampler	Site name	Latitude	Longitude	Type
D1	Puerta de Hierro	40°27'3"N	3°44'36"W	STP
D2	E05-B° del Pilar	40°28'40"N	3°42'43"W	Traffic
D3	E10-Cuatro Caminos	40°26'43"N	3°42'26"W	Traffic
D4	E11-Ramón y Cajal	40°27'4"N	3°40'39"W	Traffic
D5	E48-Castellana	40°26'22"N	3°41'25"W	Traffic
D6	E50-Plaza de Castilla	40°27'56"N	3°41'20"W	Traffic
D7	E57-San Chinarro	40°29'43"N	3°39'33"W	Urban bg
D8	E58-El Pardo	40°31'6"N	3°46'31"W	Urban bg
D9	E86-Tres Olivos	40°30'1"N	3°41'22"W	Urban bg
D10	P2-Plaza 2 de Mayo	40°25'40"N	3°42'13"W	Traffic
D11	P4-Tetuán	40°27'40"N	3°41'51"W	Traffic
D12	P10-Molins de Rey	40°29'39"N	3°41'34"W	Urban bg
D13	P16-Pinar de Chamartín	40°28'35"N	3°40'22"W	Urban bg
D14	P21a-Antonio Machado I	40°27'55"N	3°43'17"W	Urban bg
D15	P21b-Antonio Machado II	40°27'55"N	3°43'17"W	Urban bg
D16	P22-CIEMAT	40°27'23.25"N	3°43'31.87"W	Urban bg
D17	Rejas	40°27'4.46"N	3°32'7.16"W	STP
D18	Valdebebas	40°29'39.31"N	3°32'54.86"W	STP
D19	E16-Arturo Soria	40°26'24.17"N	3°38'21.24"W	Traffic
D20	E27-Barajas Pueblo	40°28'36.93"N	3°34'48.11"W	Urban bg
D21	E55-Urb. Embajada	40°27'41.02"N	3°34'55.21"W	Urban bg
D22	E59-Juan Carlos I	40°27'54.80"N	3°36'32.70"W	Urban bg
D23	P1-Gran Vía de Hortaleza	40°28'2.21"N	3°39'8.61"W	Urban bg
D24	P3-Silvano	40°27'28.60"N	3°38'38.28"W	Urban bg
D25	P7a-Arcentales I	40°26'4.24"N	3°36'28.70"W	Traffic
D26	P7b-Arcentales II	40°25'59.61"N	3°36'27.94"W	Traffic
D27	P15-Alcalá	40°25'46.26"N	3°39'55.16"W	Traffic
D28	Rejas	40°27'4.46"N	3°32'7.16"W	STP
D29	P18-Sorzano	40°27'7.68"N	3°39'24.61"W	Urban bg
D30	P20a-G. Noblejas I	40°25'55.80"N	3°38'2.40"W	Traffic
D31	P20b-G. Noblejas II	40°25'55.80"N	3°38'2.40"W	Traffic
D32	P26-El Capricho	40°27'16.04"N	3°35'56.22"W	Urban bg
D33	Butarque	40°19'59.5"N	3°39'40.2"W	STP
D34	La Gavia	40°21'8.9"N	3°39'31.7"W	STP
D35	E08-Escuelas Aguirre	40°25'22.1"N	3°40'51.9"W	Traffic
D36	E13-Pte. De Vallecas	40°23'22"N	3°39'1"W	Urban bg
D37	E20-Moratalaz	40°24'32.7"N	3°38'38.4"W	Traffic
D38	E47-Plaza del Amanecer	40°24'0.8"N	3°41'1.7"W	Traffic
D39	E49-Retiro	4025'15.5"N	3°40'44.9"W	Urban bg
D40	Retiro viveros	40°24'40"N	3°41'4.2"W	Urban bg
D41	E54-Pau de Vallecas	40°22'27.0"N	3°36'39.4"W	Urban bg
D42	SODAR-RASS	40°25'22.1"N	3°38'7.1"W	Urban bg
D43	P6-Vicálvaro	40°24'26.2"N	3°36'15.5"W	Traffic
D44	P14-Valdebernardo	40°24'13.8"N	3°37'8.8"W	Traffic
D45	P24-P. Cotos	40°24'6.8"N	3°39'26.6"W	Traffic
D46	P25-G. Dávila	40°22'41.0"N	3°38'17.3"W	Urban bg
D47	P27-S. Alcaraz	40°23'29"N	3°40'0.9"W	Urban bg
D48	P28-Valdemingómez	40°20'10.4"N	3°35'38.3"W	Incinerator
D49	E03-Plaza del Carmen	40°25'07.67"N	3°42'12.91"W	Traffic
D50	E04-Plaza de España	40°25'25.89"N	3°42'45.10"W	Traffic
D51	E17-Villaverde	40°20'51.15"N	3°42'47.95"W	Urban bg
D52	E18-Farolillo	40°23'41.38"N	3°43'55.25"W	Urban bg
D53	E24-Casa de Campo	40°25'06.07"N	3°44'14.19"W	Urban bg
D54	E56-Pza. Fdez. Ladreda	40°23'07.10"N	3°42'59.83"W	Traffic

D55	P5-Aluche A5	40°23'40.58"N	3°46'06.22"W	Traffic
D56	P8-Valle del Oro	40°23'18.58"N	3°43'52.14"W	Traffic
D57	P9-Cava Baja	40°24'43.80"N	3°42'35.00"W	Traffic
D58	P11-Zoo	40°24'28.54"N	3°45'44.54"W	Urban bg
D59	P12a-Lavapies I	40°24'32.64"N	3°42'04.92"W	Traffic
D60	P12b-Lavapies II	40°24'33.26"N	3°42'05.09"W	Traffic
D61	P13-Templo de Debod	40°25'26.59"N	3°43'07.40"W	Urban bg
D62	P19-Carabanchel Alto	40°22'25.92"N	3°45'02.82"W	Traffic
D63	P23-R. Ybarra	40°22'07.86"N	3°42'44.15"W	Traffic
D64	P29-Cuatro Vientos	40°22'39.88"N	3°46'49.59"W	Traffic

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