Aerosol and Air Quality Research, 14: 33–44, 2014

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2012.07.0189

Urban Atmospheric Ammonia in Santiago City, Chile

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ABSTRACT

To improve the current understanding of the ammonia distribution in the major urban area of Chile, measurements of atmospheric NH_3 were collected in Santiago during three sampling periods (25 April to 27 May, 11 to 26 June and 27 June to 31 July 2008). Additionally, air quality and meteorological data as well as NH_4^+, NO_3^-, $SO_4^=$ and Ca^{+2} concentrations in fine particles were collected during the same period. NH_3 concentrations for the different sites in the three sampling periods varied from 7.7 ± 2.0 µg/m^3 to 19.8 ± 2.1 µg/m^3. The results of one-way ANOVA and cluster analysis suggest that were no significant differences between the three sampling periods, but significant differences in NH_3 concentrations were detected between the sampling sites. Furthermore, two clusters were found with a pronounced difference between sampling sites located in the eastern part of the city and those located in the western part of the city. The results suggest that the distribution of ammonia in the western part of the city is due to the emissions of ammonia by agricultural areas, wetlands and the large sewage treatment plants, while in the eastern part of the city, ammonia emissions are governed by vehicular emissions. Fine particles ($PM_{2.5}$) chemical speciation showed $NH_4^+/SO_4^=$ and $NO_3^-/SO_4^=$ molar-equivalents ratios of 5.7 ± 0.3 and 1.8 ± 0.1, respectively. The results show that during the sampling period, complete neutralisation of H_2SO_4 and HNO_3 occurred in the presence of excess of NH_4^+ and NH_3. Therefore, the atmosphere of Santiago can be considered to be ammonia-rich in the gas phase. Abundant NH_3 was present to neutralise the acid components, such as H_2SO_4 and HNO_3, and to form fine particulate ammonium salts, such as $(NH_4)_2SO_4$, NH_4NO_3 and others. Relatively high humidity and low temperatures in the cold season support the formation of particulate ammonium nitrate.

Keywords: Air quality; Aerosol chemistry; Secondary aerosol; Ammonia aerosol; Santiago; Chile.

INTRODUCTION

Air pollution has become one of the most important concerns of local authorities in Latin-American cities (Molina and Molina, 2004). Urban centres in South America, such as Sao Paulo, Mexico City, Lima, Buenos Aires and Santiago, show significant levels of air pollution; these levels may present a high risk for the population's health; consequently, studies and measurements of atmospheric composition have become critically important for protecting the health of the people and ecosystems.

The city of Santiago (33.5°S, 70.6°W), the capital of Chile, is characterised by high concentrations of fine particles (< 2.5 µm in diameter; $PM_{2.5}$), coarse particles (> 2.5 to < 10 µm in diameter; $PM_{2.5-10}$) and respirable particles (fraction < 10 µm in diameter; PM_{10}). This composition is due to the anthropogenic activities of almost 6.5 million people (approximately 40% of the national population) localised in an abrupt topographical valley on the west side of the Andes mountain range that is also under the influence of the Pacific anticyclone system in autumn and winter (Morales and Leiva, 2006). As a result of these physical conditions, the resulting airborne particulate matter levels have been recognised as a major pollutant, and the Environmental National Commission, today known as the Environmental Ministry, declared the city PM_{10}-saturated in 2004. Additionally, high concentrations of $PM_{2.5}$, over 50% of the total PM_{10}, have been reported (Seguel *et al.*, 2009). This study supports the hypothesis that there is a significant contribution of secondary particulates as important constituents of $PM_{2.5}$ and that there is a critical need to identify these constituents.

Through reactions with acid pollutants to form ammonium nitrate (NH_4NO_3), ammonium sulphates (NH_4HSO_4 and

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$[NH_4]_2SO_4$) and ammonium chloride (NH_4Cl) (Walker *et al.*, 2004; Olszyna *et al.*, 2005; Morales and Leiva, 2006), ammonia (NH_3) is a main contributor to secondary particulate matter. Additionally, those particulates can significantly contribute to visibility impairment and regional haze. A broad air pollution control program for ammonia comparable to the programs for sulphur dioxide (SO_2) and nitrogen oxides (NO_x) has yet to be implemented (Krupa, 2003; Morales and Leiva, 2006; Behera and Sharma, 2010).

The need to reach a better understanding regarding the role of this important air pollutant has been underscored in recent years as ammonia emissions from different sources, such as agricultural activities, animal feedlot operations, wetlands, biomass burning and, to a lesser extent, fossil fuel combustion, have increased. However, the development of cost-effective control strategies for sulphates and nitrates will hinge on a thorough understanding of the relative abundance and distribution of all precursor emissions in an effort to mitigate concerns over health impacts.

Recent studies have found acute and chronic health implications resulting from fine and coarse particulate matter. Most studies to date have determined strong relationships between health impacts and fine particle mass (Leiva *et al.*, 2013). In terms of health impacts related to increasing ammonia concentration, the main concern is the potential for increasing health risks due to a growth in $PM_{2.5}$ associated with ammonium nitrate (Arunachalam *et al.*, 2011). Ammonia gas at the current ambient concentration presents a low impact on human health; however, significant effects have been attributed to fine particles that compose ammonium salts. The extent to which toxicity varies for different aerosol components (i.e., ammonium sulphate versus ammonium nitrate) remains a mostly unanswered question.

The latest emission inventory for Santiago from 2005 (DICTUC, 2007) showed that 7.8% of the total emissions correspond to ammonia (~33×10^3 ton/year). The high level of ammonia in the total emissions can be explained as follows: in the Santiago urban area, there are both anthropogenic emission sources of NH_3, such as industry and sewage treatment plants (the largest in South America), and emissions from several wetland ecosystems, such as the Batuco wetland and the Maipo River and Mapocho River wetlands. These stationary sources and areal sources, such as biomass burning, agriculture, animal feedlot operations and other biogenic sources, are the main sources of the total ammonia emissions (96.8%). Additionally, NH_3 emissions from vehicles were considered negligible until 1990, when vehicles equipped with catalytic converters (an important anthropogenic source of NH_3) were introduced. Santiago accounts for 42% of the motor vehicle fleet in Chile, with 1.4 million vehicles (INE, 2010). There has been a 51% increase in the fleet since 2000, and vehicles equipped with catalytic converters constitute 94% of the gasoline-powered vehicles in Santiago. The net result is that mobile sources correspond to 3.2% of the total emissions of NH_3.

It is important to understand that despite the importance of NH_3 to the chemistry of particulates in Santiago's atmosphere, the ammonium aerosol is not routinely measured and, in fact, only a few data sets are available concerning the ammonia concentration in the urban area of Santiago during the last two decades. These reported values were generally approximately 10 µg/m^3 and not higher than 30 µg/m^3 (Koutrakis, 1998). Unfortunately, these measurements are scarce and were randomly collected due to difficulties with the chemical adsorption of NH_3 onto surfaces and measurement artefacts from the volatilisation of some ammonium salts. This study is designed to rectify these shortcomings and lead to a better understanding of the mechanisms at play in the complicated Santiago air basin.

This work presents the results of three sampling periods and includes measurements of ammonia with Ogawa passive samplers at nine different sites in Santiago. The measurements have allowed for a better understanding of concentration variability across the basin in which the city is located. During the first period, we simultaneously collected $PM_{2.5}$ at two sites to evaluate the concentration of nitrate and sulphate salts of ammonium on the filters. The results allowed us to assess which areas of the city were most affected by the formation of secondary inorganic aerosols.

MATERIALS AND METHODS

Measurements Sites

Santiago (33.5°S, 70.6°W) is located in a valley in the central zone of Chile, between the Maipo and Mapocho rivers, covering a surface area of approximately 1400 km^2. The city is 500 m above sea level and is surrounded by the Andes and Coastal mountains (Fig. 1) (Rutllant and Garreaud, 1995; Morales and Leiva, 2006). The weather in Santiago is classified as Mediterranean. While the regional wind patterns are complex due to topography and urban surface roughness, the winds in Santiago can be characterised by a very persistent valley-mountain breeze system, with a predominant low speed (frequently lower than 2.0 m/s) wind from the southwest in autumn and winter. In addition, the prevailing anticyclonic meteorological conditions throughout the year lead to a permanent subsidence and thermal inversion layer between 400 and 1000 m above the city, thus providing a very stable atmospheric gradient that reduces the dispersion of air pollutants.

Ammonia Gas Sampling and Analysis

Ammonia samples were collected using Ogawa passive samplers (OPS, Ogawa & Co. USA, Inc., FL, USA) (Roadman *et al.*, 2003). The efficacy of passive samplers in measuring atmospheric ammonia has been shown in previous studies (Sather *et al.*, 2007; Siefert and Scudlark, 2008). Passive samplers were deployed in the nine city sites for three sampling periods (See Fig. 1 and Table 1). The periods, designated as Periods 1, 2 and 3, were in autumn (25 April to 27 May 2008 and 11 to 26 June 2008) and winter (27 June to 31 July 2008). The exposure time for each period corresponded to 730 ± 11 and 354 ± 12 hours during the autumn sampling and 775 ± 15 hours during the winter sampling.

In OPS, ammonia is absorbed on two replicate cellulose pads coated with citric acid, forming ammonium citrate (Roadman *et al.*, 2003). Filters were placed in vials containing

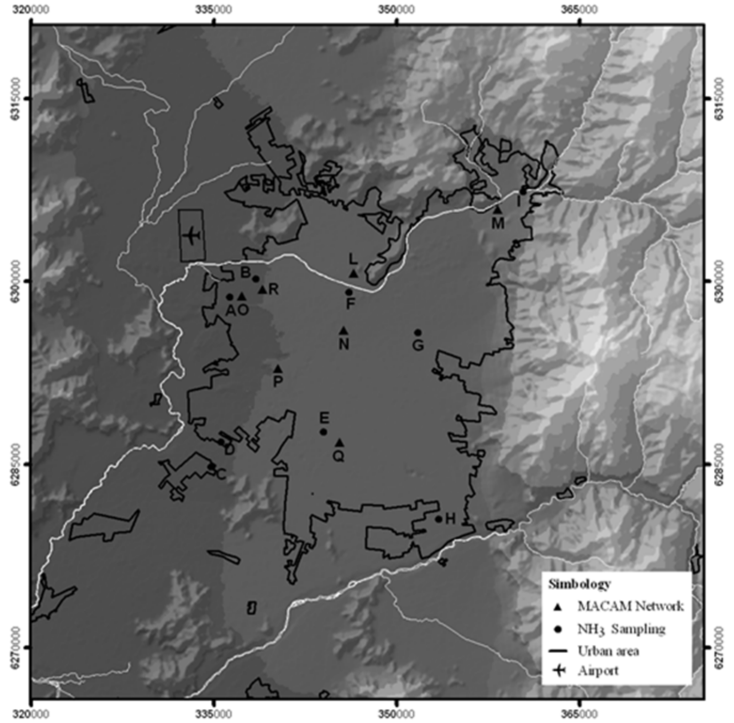

Fig. 1. Regional topography of Santiago, Chile. The black line represents the urban area, and the white lines represent the rivers and streams. Round dots are the ammonia sampling sites using passive samplers, and triangular dots designate the air quality-monitoring network (see Table 1).

Table 1. Sampling sites in the Santiago Metropolitan Area. Map projection and coordinate system: UTM, Zone 19 South, Datum WGS 1984.

Ammonia Sampling Sites				
Label	Site name	UTM coordinates X	UTM coordinates Y	Altitude (m)
A	Pudahuel	336317	6298632	492
B	Cerro Navia	338438	6300107	496
C	Maipú 1	334780	6284751	480
D	Maipú 2	335594	6286757	485
E	La Cisterna	344002	6287610	563
F	Santiago centro	346083	6299046	565
G	Ñuñoa	351749	6295709	586
H	Puente Alto	353470	6280436	692
I	Lo Barnechea	360377	6307274	832
Air Quality Monitoring network				
Label	Site name	UTM coordinates X	UTM coordinates Y	Altitude (m)
L	Independencia	346480	6300625	561
M	Las Condes	358281	6305827	793
N	Parque O´Higgins	345661	6295961	540
O	Pudahuel	337311	6298745	492
P	Cerrillos	340259	6292826	510
Q	El Bosque	345306	6286758	580
R	Cerro Navia	338979	6299299	500

8 mL of ultrapure H_2O and shaken for 15 min on a wrist-action laboratory shaker. The ammonium concentration in the filter extracts was determined colorimetrically using the phenol-hypochlorite method (Solorzano, 1969). The absorption spectra were measured on a Perkin Elmer Lambda 11 UV/Vis spectrophotometer at room temperature in a 10 mm optical path quartz cell. The analytical precision for all ions was better than 5%. The detection limits were

80 µg/L in the liquid phase. All reactants were of the highest commercial quality available and were purchased from Aldrich Co. and Merck.

The air concentration of NH_3 was calculated using Eq. (1):

$$C_{NH_3} = m_{NH_3} V \alpha^{-1} t^{-1} \quad (1)$$

where C_{NH3} is the ambient concentration of the sampled ammonia in units of µg/m^3, m_{NH3} is the concentration of NH_3 in the extract in units of µg/mL, V is the volume extracted from the filter in mL, t is the time of exposure in minutes, and α is the mass transfer coefficient, which is dependent on the geometry of the sampler's diffusive pathways and the molecular diffusivity of NH_3. At 25°C, α is 1.55×10^{-5} m^3/min for NH_3 for each side of the Ogawa sampler (Roadman *et al.*, 2003; Leiva *et al.*, 2013).

PM$_{2.5}$ Sampling and Analysis

Measurements of ammonia (NH_4^+), nitrate (NO_3^-) and sulphate ($SO_4^=$) were performed at the Pudahuel and Ñuñoa sampling sites (sites A and G in Fig. 1 and Table 1). Twenty-four hour particle samples were collected daily during the sampling period of 10 to 18 May 2008. Eight valid $PM_{2.5}$ samples were collected during this period using Dichotomous Samplers (Sierra Instruments Model 244) and IMPROVE (Interagency Monitoring of PROtected Visual Environments) samplers (Crocker Nuclear Laboratory, University of California Davis, CA, USA) also placed at the Pudahuel and Ñuñoa sites. Particle samples were collected on PTFE membranes (W/PMP Ring 2.0 µm from Pall Corporation).

Prior to particle sampling, the filters for both instruments were conditioned for 24 hr. and then weighed in a controlled-environment chamber maintained at a relative humidity of 30 ± 2% and a temperature of 20 ± 2°C. After exposure, the filters were stored in sealed containers under refrigeration. Exposed filters were typically weighed within a day or two of collection, which involved returning the filters to the controlled-environment chamber, conditioning the filters for 24 hr., and then weighing the filters to determine the sample weight.

The collected aerosol filters were ultrasonically extracted for 15 min into 5 mL of deionised water (18 MΩ, MilliQ system, Millipore). The extracted solution was then filtered through a syringe (PPE filter pore size 0.25 µm, Orange Scientific). Samples were then placed in the ion chromatograph to measure the charged species. The anion and cation concentrations in the $PM_{2.5}$ samples were determined by ion chromatography (Behera and Sharma, 2010; Leiva *et al.*, 2011) using a Waters 1515 system. Anions were separated using an IC-Pak CM/D column. The mobile phase was 3 mM HNO_3/0.1 mM ethylenediamine-tetraacetic acid. An IC-Pak A/HR column was used for cation separation with a mobile phase of borate/gluconate to 12% acetonitrile.

The ionic species were identified and quantified by interpolation on a calibration curve. Calibration curves were constructed by plotting the peak areas for each ion against the concentration. The quality requirement for the acceptance of a calibration curve was established as a correlation coefficient of $r^2 \geq 0.995$. The analytical precision for all ions was better than 10%. The detection limits ranged between 0.07 mg/L for ammonium and 0.32 mg/L for sulphate. All experiments were performed at room temperature and lasted approximately 20 min for each injected sample. All reactants were of the highest commercial quality available and were purchased from Aldrich Co. and Merck.

Some studies suggest that losses due to volatilisation may occur during storage, especially for NO_3^- and SO_4^- (Behera and Sharma, 2010; Leiva *et al.*, 2012). This loss may introduce biases into the measurements, which also depend on the sampling device used, the particle size fraction, the composition of aerosol, the chemical form of the reactive species during sample storage and the analytical technique used. However, bias can be minimised by removing the samples soon after sampling and storing them in sealed containers under refrigeration, keeping them in coolers for transport between the sampling site and laboratory and maintaining proper storage techniques in the laboratory.

Air Pollutants and Meteorological Measurements

In 1997, the Santiago Metropolitan Government established an Air Quality Pollution Watch Program, managed by the Ministry of Health. Eight monitoring stations distributed throughout the city are currently measuring the concentrations of pollutant gases and atmospheric aerosols, as well as meteorological data (SINCA, 2011). All these stations are part of the MACAM-2 network, which is the base of the Air Quality Monitoring Program in the Santiago Metropolitan Area (Fig. 1 and Table 1).

Average daily profiles for $PM_{2.5–10}$, $PM_{2.5}$, $PM_{10}/PM_{2.5}$ and meteorological parameters (wind speed, wind direction, temperature, and relative humidity) were obtained from the MACAM-2 network, coinciding with each ammonia sampling period for the air quality monitoring stations at Pudahuel (site O), Parque O′Higgins (site N) and Las Condes (site M). Pudahuel is located in the western part of Santiago in a small park near a medical clinic. Around this station, there are two major roads with commercial activity occurring in small retail stores. The remainder of the surrounding area is mainly residential. Generally, the west side of the city includes agricultural areas, the international airport, wetlands and the largest sewage treatment plants. The Parque O'Higgins sampling site is located in a large park approximately 2 km south of the downtown and 1 km west of a major highway. The area has a mixture of houses, retail and light industry (machine shops, auto repair shops, furniture manufacturing shops, etc.). The Las Condes sampling site is located on the northeast side of Santiago in a small park. The area is primarily residential with some commercial portions.

Statistical Analysis

Statistical analyses of the differences in NH_3 concentrations between sites and sampling periods were conducted by one-way analysis of variance (ANOVA) using MS Excel© 2010 (Microsoft Corporation, Redmond, WA, USA) to determine whether the NH_3 concentration differences between the sampling periods and sampling sites were significant. Comparison of means between sites and collection periods were carried out using the Tukey-Kramer adjustment method. A confidence interval of 99% (α = 0.01 level of significance) was used for analysis of significant difference.

The clustering of data was conducted using IDL© version 6.1 from RSI (Research Systems Inc., Boulder, CO, USA) using a short script that defined the arrays of data and CLUST_WTS. This function uses a matrix of n-columns and m-rows that points to variables and samples, respectively. The method uses k-means clustering, whereby k random clusters are formed and then items are iteratively moved between them, minimising variability within each cluster while maximising variability between them. This method is appropriate to show correlations between variables. We characterised the relationships between air ammonia levels and sampling sites utilising these tools.

RESULTS AND DISCUSSION

Ammonia Concentration Levels

Variations in ammonia concentrations (including pertinent statistical results) over the three sampling periods for the nine city sites are shown in Table 2.

The NH_3 concentrations ranged from 7.73 ± 1.95 µg/m^3 (Lo Barnechea site, eastern part of the city) to 19.8 ± 2.1 µg/m^3 (Pudahuel site, western part of the city). The average ammonia concentrations were similar in the three sampling periods and ranged between 14.8 ± 5.2 and 16.2 ± 2.8 µg/m^3. The result of the one-way ANOVA presented in Table 3 suggests that there were no significant differences between the three sampling periods, but significant differences in NH_3 concentrations were detected between sampling sites.

Fig. 2 depicts a dendrogram derived from the average linkage clustering of seven sampling sites based on NH_3 concentrations. Two sites, Cerro Navia (site B) and Lo Barnechea (Site H), were discarded due to the lack of data for the May and July sampling periods, respectively, resulting in cluster analysis of only 7 sites. Comparison between the sampling sites indicates that two distinct clusters were obtained; the first cluster includes sampling sites A, C, D and E, and the second cluster includes sampling sites F, G and I. The cluster analysis also provides evidence of variations in the NH_3 concentrations. For all three sampling periods, a significant difference between the western and eastern parts of the city was found.

It is a well-known fact that gaseous ammonia concentrations can vary from place to place in relation to the emission sources. Gaseous ammonia could be emitted from ammonia-containing fertilisers, wetlands, wastewaters, water treatment plants, industrial activities, and vehicular and residential emissions (Anderson *et al.* 2003; Walker *et al.*, 2004). Consequently, in some areas of Santiago, it is possible to find more relevant emission sources than in other parts of the city. In fact, in the western part of Santiago city, important ammonia sources such as agricultural areas, wetlands and the largest sewage treatment plant in South America can be found in suburban areas. On the other hand, the eastern part of the city is a residential and commercial area and the emission sources of the ammonia result predominantly from vehicular traffic and residential emissions. These characteristic patterns of emission sources and differences between the western and eastern parts of the city could be used to explain the results of the cluster analysis. In fact, the results showed two clusters, grouping sampling sites based on their location in either the western or eastern parts of Santiago city.

Ammonia emissions from animal manure, natural and fertilised soils, and vegetation are elevated by higher temperatures; the atmospheric NH_3 concentration may be indirectly affected by air temperature (Robarge *et al.*, 2002; Shen *et al.*, 2011). An approach to the determination of the weight of traffic emissions in determining the NH_3 urban concentration is to compare the ammonia trend with the trend of a primary non-reactive pollutant mainly emitted by motor-vehicle exhausts, such as carbon monoxide (Perrino *et al.*, 2002). Fig. 3 shows the relationship between the measured ammonia at six sampling sites placed close to six monitoring stations of the local air quality network, which include temperature (T) and carbon monoxide (CO) measurements. Ammonia measurements were compared with the average values of T and CO during the same sampling periods. The first letter of each label indicates the ammonia sampling site, while the second letter indicates the nearest station in the network of air quality monitoring stations in Santiago. Sites C, G and H are not located near a station of the air quality monitoring network, so they are not included in this correlation.

Table 2. Ammonia concentration levels (µg/m^3) in the Santiago Metropolitan Area (± SD).

Site	Label	Period 1	Period 2	Period 3	Average
Pudahuel	A	22.1 ± 0.9	17.5 ± 0.9	19.9 ± 0.1	19.8 ± 2.1
Cerro Navia	B	-	17.4 ± 0.5	17.2 ± 0.1	17.3 ± 0.3
Maipú 1	C	17.0 ± 1.2	16.3 ± 1.3	14.0 ± 0.3	15.7 ± 1.6
Maipú 2	D	20.6 ± 0.7	14.8 ± 1.0	19.4 ± 0.8	18.2 ± 2.8
La Cisterna	E	15.8 ± 0.6	17.9 ± 2.1	18.1 ± 0.3	17.2 ± 1.5
Santiago Centro	F	13.9 ± 1.2	15.0 ± 1.5	13.6 ± 0.8	14.2 ± 1.2
Ñuñoa	G	11.3 ± 0.9	12.4 ± 1.4	14.5 ± 0.1	12.8 ± 1.6
Puente Alto	H	11.7 ± 0.2	10.7 ± 1.7	12.8 ± 1.0	11.7 ± 1.3
Lo Barnechea	I	6.2 ± 0.9	9.2 ± 1.4	-	7.7 ± 2.0
Average		14.8 ± 5.2	14.6 ± 3.1	16.2 ± 2.8	15.4 ± 3.8

Table 3. P values of ANOVA between sites and sampling periods related to ammonia concentrations.

		Ammonia	
Between Periods		0.657	(> 0.05)
Between sites			
	Period 1	2.00E-07	(< 0.01)
	Period 2	2.97E-03	(< 0.01)
	Period 3	1.70E-08	(< 0.01)

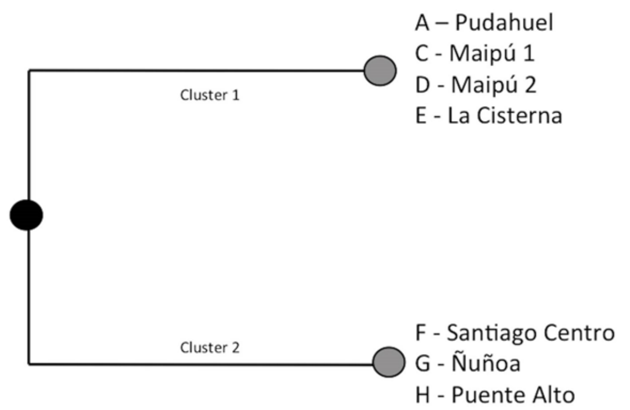

Fig. 2. Dendrogram resulting from the k-means clustering analysis of the seven sampling sites with NH_3 measurements during the three field sampling periods.

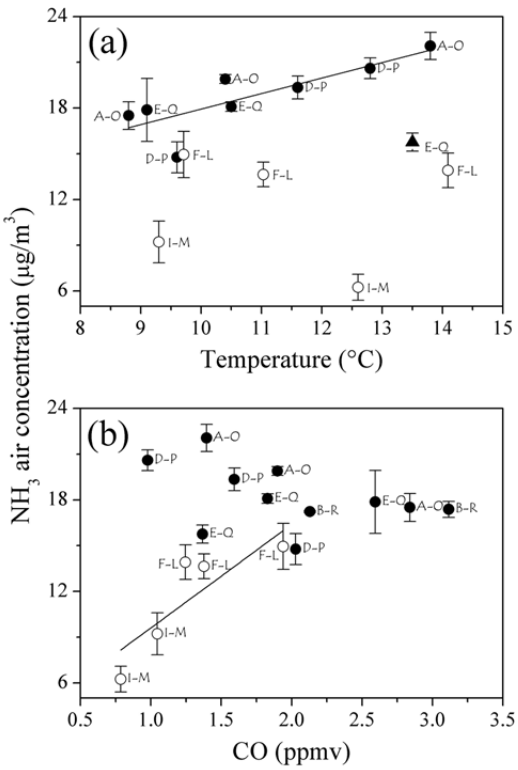

Fig. 3. Relationship between and linear correlation of (a) atmospheric ammonia vs. temperature and (b) atmospheric ammonia vs. carbon monoxide. Black and white dots are the sampling sites located in the western and eastern parts of the city, respectively. The black triangle is an outlier.

Fig. 3 shows the relationships between (a) atmospheric ammonia and temperature and (b) atmospheric ammonia and carbon monoxide. The results of the linear regression analysis between the ambient temperature and NH_3 showed a good correlation (R^2 = 0.60) for data from the western urban area (cluster 1, black circles in Fig. 3). This trend is likely related to the increase of evaporative emissions from sources present in the western urban areas (agricultural areas, wetlands and sewage treatment plants). One exception to this behaviour was found and corresponds to the La Cisterna site in sampling period 1 (black triangle in Fig. 3). In contrast, the data from eastern sites (cluster 2, white circles in Fig. 3) do not correlate well with ambient temperature because it is not an important factor in NH_3 emissions. Moreover, CO and NH_3 correlate fairly well (R^2 = 0.66) only at monitoring sites located in the eastern part of the city (cluster 2).

Traffic exhaust can act as an important source of ammonia in urban areas. In fact, Perrino *et al.* (2002) showed a linear relationship between the CO and NH_3 concentrations in urban locations. Kean *et al.* (2000) showed that the use of three-way catalytic converters has contributed to decreases in NO_x and CO emissions. However, their use was likely the cause of ammonia emissions from motor vehicles. Our findings support the hypothesis that the main cause of NH_3 air concentrations in the eastern part of the city, which is without question the most urbanised part of Santiago, is emissions from motor vehicles (CO).

The average ammonia concentrations for the three sampling periods studied are comparable with studies (Koutrakis, 1998) conducted ten years ago (see Table 4). Koutrakis collected data during two one-week periods (29 October to 13 November 1998) at twenty-five sampling sites (both urban and rural) throughout Santiago. The sampling, which utilised Ogawa samplers, showed a range of ammonia concentrations from 2.3 µg/m^3 to 29.0 µg/m^3. On average, the ammonia concentrations in Santiago showed a small increase over the ten-year period from 1998 to 2008, from 11.1 ± 4.4 (Koutrakis, 1998) to 15.4 ± 3.8 µg/m^3 (this study). If we consider the standard deviations, the differences of the absolute values between the 1998 and 2008 results would not be considered significant. However, the results could be affected by the different locations of the passive samplers between the present study and the Koutrakis study.

Furthermore, Table 4 provides a comparison of worldwide ammonia concentrations. Our ammonia results are similar to levels found in Rome (Perrino *et al.*, 2002), as well as to a swine production facility in eastern North Carolina, USA (Baek *et al.*, 2004). Agricultural (Robarge *et al.*, 2002) and suburban (Hu *et al.*, 2008) areas show slightly lower concentrations, while the Great Smoky Mountains National Park, USA (Olszyna *et al.*, 2005) and the urban area of North Birmingham, USA show concentrations below 2 µg/m^3 (Edgerton *et al.*, 2007). The concentrations of ammonia in Santiago are among the highest, due to the large number and variety of sources (mobile sources, wastewater treatment plants, agricultural activities in the southwestern part of the city, rivers and channels with loads of organic matter, and

Table 4. Ammonia concentration levels in urban, industrial and rural areas.

Denomination	Site	Ammonia Level (μg/m^3) Mean ± STD	Reference
Urban	Santiago, Chile	15.4 ± 3.8	This work, 2008
Urban	Santiago, Chile	11.1 ± 4.4	Koutrakis, 1998
Urban	Rome, Italy	17.2 ± 2.7	Perrino *et al.*, 2002
Urban	North Birmingham, AL, USA	1.9 ± 1.3	Edgerton *et al.*, 2007
Urban	Manhattan, NY, USA	3.8 ± 2.0	Bari *et al.*, 2003
Industrial	Swine production facility in eastern North Carolina, USA	15.7 ± 11.3	Baek *et al.*, 2004
Sub-urban	Pearl River Delta, Guangdong Province, China	7.3	Hu *et al.*, 2008
Agricultural	Clinton Horticultural Crops Research Station, NC, USA	5.6 ± 5.4	Robarge *et al.*, 2002
Park	Great Smoky Mountains National Park, USA	1.6 ± 1.1	Olszyna *et al.*, 2005

wetlands) and adverse geographical and meteorological conditions for dispersion of gases and particles. The latter are especially adverse in cold months (April to August) due to atmospheric stability and a reduced mixing volume as a result of thermal inversions.

Particulate Matter during Ammonia Sampling

Fig. 4 shows the daily profile of $PM_{2.5}$, $PM_{2.5–10}$ and the $PM_{2.5}/PM_{10}$ ratio during the same ammonia sampling periods for the Pudahuel (site O, western part of the city), Parque O´Higgins (site N, central part of the city) and Las Condes (site M, eastern part of the city) monitoring stations (see Fig. 1 and Table 1). The daily profiles of $PM_{2.5}$ and $PM_{2.5–10}$, in general, indicate that vehicular emissions have a strong influence on $PM_{2.5–10}$ and $PM_{2.5}$ only in the morning (7:00–11:00 hrs.). In the afternoon (12:00–18:00 hrs.), there was a decrease in the concentration of both fractions of PM due to an increase in the wind speed and clean air coming from the west. The highest concentrations were observed at night (20:00–24:00 hrs.) due to an increase in atmospheric stability. Wind speed decreases at night, and because of large temperature differences between day and night, a radiative thermal inversion layer is generated.

In general, the average $PM_{2.5}$ concentrations for all the sites during the study period were highest at the Pudahuel station and lowest at the Las Condes station. The maximum and minimum $PM_{2.5}$ concentrations at Pudahuel, Parque O´Higgins and Las Condes were 79 ± 37 and 51 ± 14 μg/m^3; 69 ± 18 and 44 ± 8 μg/m^3; and 33 ± 11 and 30 ± 9 μg/m^3, respectively. The highest $PM_{2.5}$ concentrations were observed during the second sampling period, and the lowest were observed during the first sampling period. The high concentrations of fine particle masses found at Pudahuel may be due to contributions from gas emission aerosol precursors and favourable meteorological conditions present in the western part of the city.

The arithmetic averages of $PM_{2.5–10}$ were observed to increase east to west from Las Condes to Parque O´Higgins and, finally, to Pudahuel. The maximum and minimum $PM_{2.5–10}$ concentrations in Las Condes, Parque O´Higgins and Pudahuel were 34 ± 16 and 29 ± 13 μg/m^3; 51 ± 20 and 41 ± 17 μg/m^3; and 53 ± 21 and 41 ± 14 μg/m^3, respectively. In general, the highest $PM_{2.5–10}$ concentrations were observed during the second sampling period and the lowest concentrations were observed during the first sampling period.

The $PM_{2.5}/PM_{10}$ ratio for all the air monitoring stations showed little variability and ranged from 0.54 ± 0.15 to 0.62 ± 0.16. In general, the highest ratios were observed at night (20:00–24:00 hrs.) due to an increase in atmospheric stability and favourable meteorological conditions for fine particulate formation. The arithmetic averages of $PM_{2.5}/PM_{10}$ follow inverse trends to those of the $PM_{2.5–10}$ concentrations; therefore, our results verified that Pudahuel is more affected by fine aerosols than Las Condes.

Secondary Ions in $PM_{2.5}$

Fig. 5 depicts the 24-h $PM_{2.5}$ concentration levels of NH_4^+ (Fig. 5(a)), NO_3^- (Fig. 5(b)) and $SO_4^=$ (Fig. 5(c)) at the Pudahuel and Ñuñoa sampling sites for four days (10 to 18 May 2008) during the first period of ammonia sampling. During this sampling period, the PM_{10} concentration exceeded the national air quality standard (150 μg/m^3) at the Pudahuel station.

The average concentrations of $PM_{2.5}$ and ions for the four days of sampling (10 to 18 May 2008) were higher in Pudahuel than Ñuñoa. The exception was the 18 May sampling day, where the ion concentrations were lower in Pudahuel than Ñuñoa. The $PM_{2.5}$, NH_4^+, NO_3^- and $SO_4^=$ concentrations were observed to increase as one moves from 10 to 18 of May. On average, for all samples, the NH_4^+, NO_3^- and $SO_4^=$ concentrations account for 43% and 36% of the $PM_{2.5}$ concentrations in Pudahuel and Ñuñoa, respectively. The Ñuñoa site, as well as the Las Condes site, is characterised by vehicular and residential emission sources. On the other side of the city, the Pudahuel site has vehicular and residential emissions, as well as additional emissions of particulate matter from the airport and all ammonia sources discussed above. This emission source pattern may explain the high concentration of $PM_{2.5}$ with a high ratio of secondary inorganic ions found in the Pudahuel site vs. Ñuñoa site.

In an urban atmosphere, sulphuric acid (H_2SO_4) and nitric acid (HNO_3) compete for the available NH_3 to form ammonium sulphate or ammonium nitrate salts. Because the reaction rate of ammonia with H_2SO_4 is faster than the reaction rate of ammonia with HNO_3 (Baek *et al.*, 2004; Behera and Sharma, 2010), additional ammonia is neutralised by nitric acid. In $(NH_4)_2SO_4$, the molar ratio of NH_4^+ to

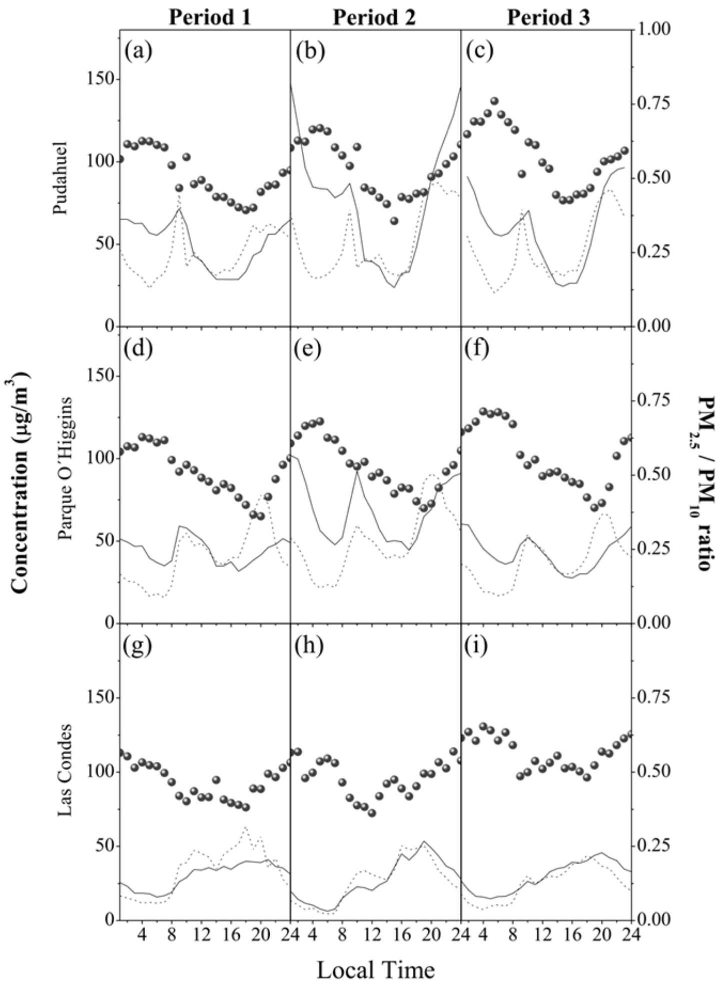

Fig. 4. Particulate matter levels during ammonia sampling periods. Solid line: $PM_{2.5}$; dashed line: $PM_{2.5-10}$; and round dots $PM_{2.5}/PM_{10}$ ratio.

$SO_4^{=}$ is 2 μeq/m^3 (Krupa, 2003), which indicates the complete neutralisation of H_2SO_4 and a predominance of $(NH_4)_2SO_4$ aerosol. If the observed ratio is greater than 2 and a good correlation ($R^2 = 0.93$) exists, the excess NH_4^+ can be combined with NO_3^- or another anion. At the two urban sites, the slope of NH_4^+ (μeq/m^3) vs. $SO_4^{=}$ (μeq/m^3) is 4.52 ± 0.14, which indicates the complete neutralisation of H_2SO_4 and a predominance of $(NH_4)_2SO_4$ aerosol during the sampling periods. The NO_3^- and $SO_4^{=}$ ion concentrations show a good correlation with the ammonium ion concentrations ($R^2 = 0.90$); thus, the slope of 1.39 ± 0.04 indicates an excess of NH_4^+. By extension, we can expect a formation of NH_4NO_3 salt (see Fig. 6).

In fact, the city of Santiago had high concentrations of NH_3 and NH_4^+ during our study period. In general, public policies regarding air quality have focussed on reducing sulphur dioxide emissions from fossil fuels, as evidenced by the concentrations of sulphate in $PM_{2.5}$. However, a reduction in $SO_4^{=}$ precursors promotes large amounts of ammonium nitrate, which became the major ions found in fine particles in the city of Santiago during our study. Therefore, a reduction of NH_3 and NO_x may reduce the production of inorganic secondary aerosols.

Meteorological Conditions

Many studies have indicated that the $PM_{2.5}$ concentrations in ambient air are affected by various meteorological factors, such as temperature, wind speed, rainfall, and relative humidity. While ammonium sulphate exists predominantly in the condensed phase under ambient conditions, ammonium nitrate is semi-volatile and exists in equilibrium with gas phase concentrations of nitric acid and ammonia. This equilibrium is strongly influenced by temperature and relative humidity (Stelson and Seinfeld, 1982). The gas phase is highly favoured when ambient temperatures approach or exceed 35 °C, and the equilibrium is highly in favour of the aerosol at temperatures < 15°C. At high relative humidity, both ammonia and nitric acid can dissolve into aerosol droplets. Ammonium nitrate formation is favoured under conditions of high relative humidity and low temperature (Kuhns *et al.*, 2003).

Figs. 7 and 8 show the daily variations of temperature, relative humidity (RH), and wind speed as well as the wind rose averages during the ammonia sampling periods in Pudahuel (site O, western part of the city), Parque O´Higgins (site N, central part of the city) and Las Condes (site M, eastern part of the city). From Fig. 7, it is possible to observe a

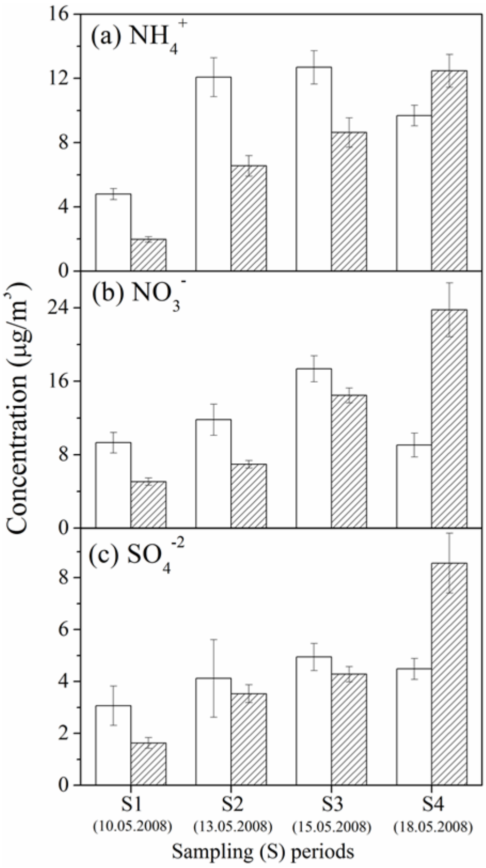

Fig. 5. NH_4^+ (a), NO_3^- (b) and $SO_4^=$ (c) concentrations in $PM_{2.5}$ collected in the eastern and western parts of Santiago. (White box: Pudahuel sampling site; dashed box: Ñuñoa sampling site).

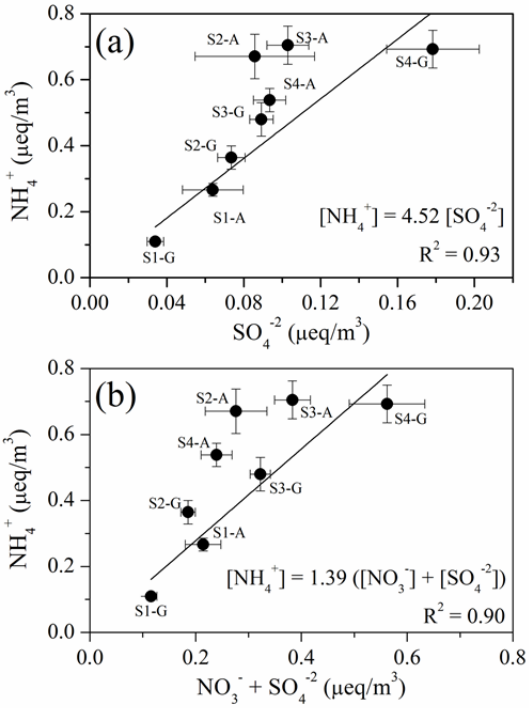

Fig. 6. Linear relationships between the concentrations (μeq/m^3) of NH_4^+ and $SO_4^=$ (a), NO_3^- + $SO_4^=$ (b) and Ca^{+2} - NO_3^- (c) during the $PM_{2.5}$ sampling periods.

diurnal condition with minimum relative humidity (< 60%) and maximum values for temperature and wind speed at approximately 16:00 hrs for the three sites. However, high relative humidity (> 80%), minimum temperatures and a significant decrease in wind speed are observed at night. The increase in the $PM_{2.5}$ concentration at night (Fig. 4) could be associated with thermal inversion events, such as ground cooling (Rutllant and Garreaud, 1995; Morales and Leiva, 2006), a decrease in wind speed or formation of secondary aerosols.

As seen in Fig. 8, the Pudahuel and Parque O´Higgins stations showed a similar pattern of wind speed between 14:00 and 20:00 hrs. However, the Las Condes station showed a more constant wind speed profile throughout the day. The wind speeds and directions are consistent with the mountain-valley breeze pattern observed in Santiago. The influence of the wind speed on the $PM_{2.5}$ concentration is related to a dilution effect (Walker *et al.*, 2004). Because low wind speed inhibits the dilution effect, meteorological conditions observed during the three sampling periods are favourable for the formation of secondary particulate matter. The chemical relationships are all influenced by temperature and relative humidity, as well as by the availability of the chemicals themselves to form secondary aerosols. As already noted, sulphuric acid will readily condense into its particulate form independent of ammonia or nitric acid availability. This gas to particle conversion process is favoured by high relative humidity and a low dilution effect. High relative humidity and cold temperatures induce the formation of ammonium nitrate salts.

CONCLUSIONS AND SUMMARY

The measurement of urban atmospheric ammonia with passive tubes proved to be an efficient, simple and inexpensive methodology to evaluate the spatial distribution levels over a wide area of Santiago, Chile.

These results provide the first evidence concerning the differential distribution of ammonia levels in Santiago. These differences are attributed to the varied emission sources of ammonia in the city. In the western part of the city, the ammonia emissions came from agricultural areas, wetlands and the largest sewage treatment plant in South America. For this side of the city, temperature is the main determining factor of the pattern of atmospheric concentrations of ammonia. In contrast, in the eastern part of the urban area, vehicular emissions become a relevant ammonia source, and a good correlation between ammonia concentration levels and urban carbon monoxide concentrations can be found.

The urban atmosphere of Santiago city can be described as an ammonia-rich, secondary aerosol source. We have detected sufficiently high ammonia concentrations for neutralising the acidic components, such as H_2SO_4 and HNO_3, which are the base of the fine particulate ammonium salts, such as $(NH_4)_2SO_4$, and NH_4NO_3, as well as other derived species. Although ammonium nitrate formation is a

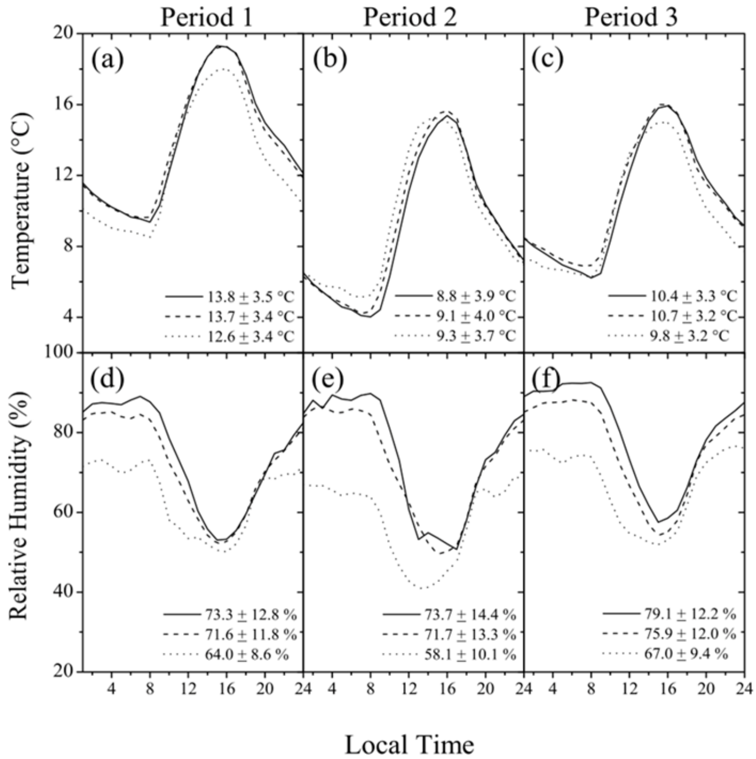

Fig. 7. Daily variations of temperature (a, b and c) and relative humidity (d, e and f) during the three sampling periods. Measurements are presented for three stations: Pudahuel (solid line), Parque O'Higgins (dashed line) and Las Condes (dotted line).

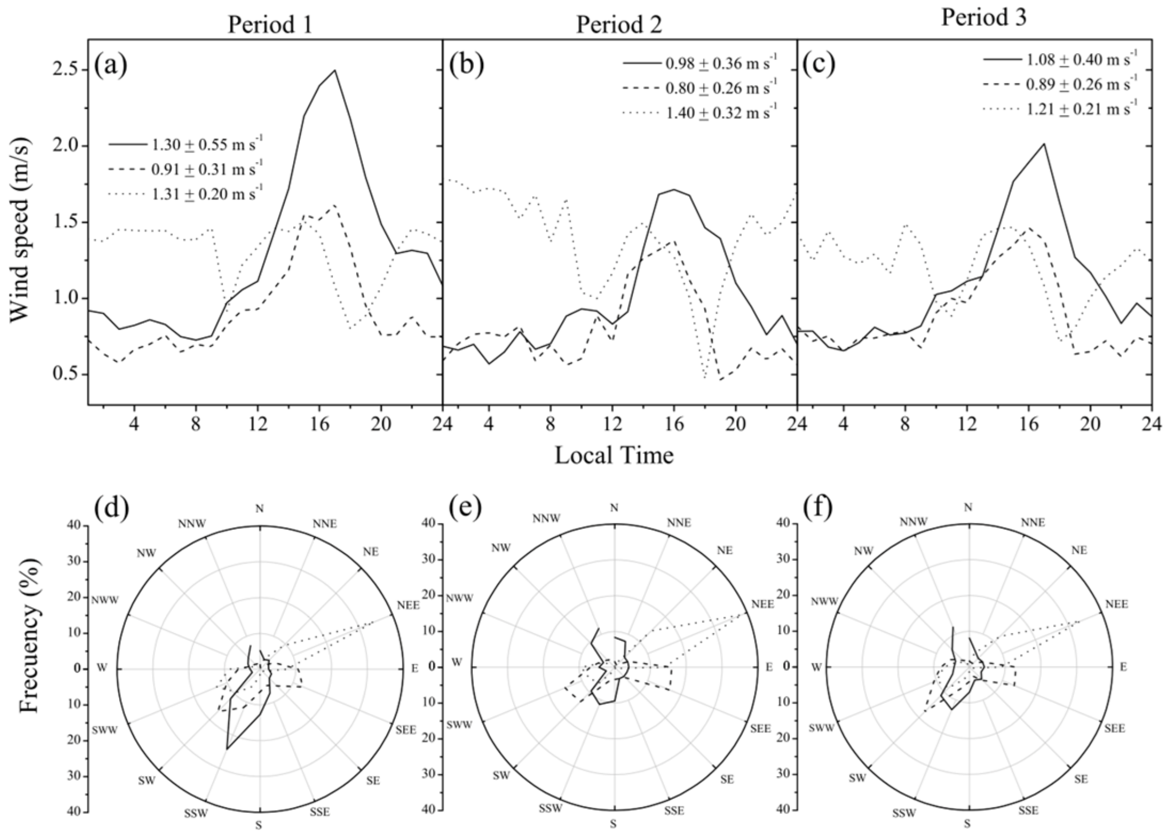

Fig. 8. Daily variations in wind speed (a, b and c) and wind roses (d, e and f). Measurements are presented for three stations: Pudahuel (solid line), Parque O'Higgins (dashed line) and Las Condes (dotted line).

reversible reaction, the equilibrium constant is dependent on temperature and relative humidity, and the physical conditions of the urban atmosphere of the city determine ammonium nitrate formation as particulate matter.

A detailed study and analysis of fine particulate matter formation and annual ammonia concentration distribution would provide crucial information for air quality policy management to develop more specific preventive and control strategies for the critical pollution episodes that frequently occur in Santiago city.

ACKNOWLEDGEMENTS

The authors are grateful to Centro Nacional del Medio Ambiente for conducting the Ogawa passive sampling. The financial support of the Centro de Ciencias Ambientales (CCA) of the Facultad de Ciencias of the Universidad de Chile is gratefully acknowledged. MALG acknowledges CONICYT - BECAS CHILE and Facultad de Ciencias, Universidad de Chile for partial financial support of the Postdoctoral fellowship. The authors wish to thank the anonymous reviewers for their critical and useful recommendations for improving the paper.

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Received for review, *July 18*, *2012*
Accepted, *June 20*, *2013*