Urban Atmospheric Ammonia in Santiago City, Chile

Richard A. Toro¹, Mauricio Canales¹, Robert G. Flocchini², Raúl G.E. Morales¹, Manuel A. Leiva G.¹*

¹ Centro de Ciencias Ambientales and Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile
² Deparment of Land, Air and Water Resources, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA

ABSTRACT

To improve the current understanding of the ammonia distribution in the major urban area of Chile, measurements of atmospheric NH₃ 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 NH₄⁺, NO₃⁻, SO₄²⁻ and Ca²⁺ concentrations in fine particles were collected during the same period. NH₃ concentrations for the different sites in the three sampling periods varied from 7.7 ± 2.0 µg/m³ to 19.8 ± 2.1 µg/m³. The results of one-way ANOVA and cluster analysis suggest that there were no significant differences between the three sampling periods, but significant differences in NH₃ 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 (PM₂.₅) chemical speciation showed NH₄⁺/SO₄²⁻ and NO₃⁻/SO₄²⁻ 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 H₂SO₄ and HNO₃ occurred in the presence of excess of NH₄⁺ and NH₃. Therefore, the atmosphere of Santiago can be considered to be ammonia-rich in the gas phase. Abundant NH₃ was present to neutralise the acid components, such as H₂SO₄ and HNO₃, and to form fine particulate ammonium salts, such as (NH₄)₂SO₄, NH₄NO₃ 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; PM₂.₅), coarse particles (> 2.5 to < 10 μm in diameter; PM₁₀₀) and respirable particles (fraction < 10 μm in diameter; PM₁₀). 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 PM₁₀₀-saturated in 2004. Additionally, high concentrations of PM₂.₅, over 50% of the total PM₁₀₀ 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 PM₂.₅ and that there is a critical need to identify these constituents.

Through reactions with acid pollutants to form ammonium nitrate (NH₄NO₃), ammonium sulphates (NH₄HSO₄ and
ammonium chloride (NH4Cl) (Walker et al., 2004; Olszyna et al., 2005; Morales and Leiva, 2006), ammonia (NH3) 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 (SO2) and nitrogen oxides (NOx) 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 PM2.5 associated with ammonium nitrate (Arunchalam 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 NH3 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, NH3 emissions from vehicles were considered negligible until 1990, when vehicles equipped with catalytic converters (an important anthropogenic source of NH3) 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 NH3.

It is important to understand that despite the importance of NH3 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/m³ and not higher than 30 µg/m³ (Koutrakis, 1998). Unfortunately, these measurements are scarce and were randomly collected due to difficulties with the chemical adsorption of NH3 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 PM2.5 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 km². 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.

| Label | Site name      | X   | 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 | 6287610 | 586          |
| H     | Puente Alto    | 353470 | 6280436 | 692          |
| I     | Lo Barnechea   | 360377 | 6307274 | 832          |

| Label | Site name      | X   | 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 | 580          |

8 mL of ultrapure H$_2$O 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 NH₃ was calculated using Eq. (1):

\[ C_{NH_3} = \frac{m_{NH_3} V \alpha \cdot t}{t} \]  

where \( C_{NH_3} \) is the ambient concentration of the sampled ammonia in units of μg/m³, \( m_{NH_3} \) is the concentration of NH₃ 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 \( \alpha \) is the mass transfer coefficient, which is dependent on the geometry of the sampler’s diffusive pathways and the molecular diffusivity of NH₃. At 25°C, \( \alpha \) is 1.55 × 10⁻⁵ m²/min for NH₃ for each side of the Ogawa sampler (Roadman et al., 2003; Leiva et al., 2013).

PM₂.₅ Sampling and Analysis

Measurements of ammonia (NH₄⁺), nitrate (NO₃⁻) and sulphate (SO₄²⁻) 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 PM₂.₅ 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 PM₂.₅ 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 HNO₃/0.1 mM ethylenediaminetetraacetic acid. An IC-Pak A/HR column was used for cation separation with a mobile phase of borate/glucinolate 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 NO₃⁻ and SO₄²⁻ (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 PM₂.₅, PM₁₀, PM₁₀/PM₂.₅ 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 NH₃ 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 NH₃ 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.

| 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 2. Ammonia concentration levels (µg/m³) in the Santiago Metropolitan Area (± SD).

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 NH₃ 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 NH₃ 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 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 NH₃ measurements during the three field sampling periods.

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 NH₃ 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 NH₃ emissions. Moreover, CO and NH₃ 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 NH₃ concentrations in urban locations. Kean *et al.* (2000) showed that the use of three-way catalytic converters has contributed to decreases in NOₓ 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 NH₃ 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/m³ to 29.0 µg/m³. 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/m³ (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/m³ (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/m³) | 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 |

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$_4^{2-}$ (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$_4^{2-}$ 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$_4^{2-}$ 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$_2$SO$_4$) 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$_2$SO$_4$ 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$_4$)$_2$SO$_4$, 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$_4^{2-}$ is 2 µeq/m$^3$ (Krupa, 2003), which indicates the complete neutralisation of H$_2$SO$_4$ and a predominance of (NH$_4$)$_2$SO$_4$ 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$_4^{2-}$ (µeq/m$^3$) is 4.52 ± 0.14, which indicates the complete neutralisation of H$_2$SO$_4$ and a predominance of (NH$_4$)$_2$SO$_4$ aerosol during the sampling periods. The NO$_3^-$ and SO$_4^{2-}$ 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$_4$NO$_3$ 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$_4^{2-}$ 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$_4^{2-}$ (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).

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 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. 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$_2$SO$_4$ and HNO$_3$, which are the base of the fine particulate ammonium salts, such as (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, 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.

REFERENCES

Anderson, N., Strader, R. and Davidson, C. (2003). Airborne Reduced Nitrogen: Ammonia Emissions from Agriculture and Other Sources. Environ. Int. 29: 277–286.

Arunachalam, S., Wang, B.Y., Davis, N., Baek, B.H. and Levy, J.I. (2011). Effect of Chemistry-transport Model Scale and Resolution on Population Exposure to PM_{2.5} from Aircraft Emissions during Landing and Takeoff. Atmos. Environ. 45: 3294–3300.

Baek, B.H., Aneja, V.P. and Tong, Q.S. (2004). Chemical Coupling between Ammonia, Acid Gases, and Fine Particles. Environ. Pollut. 129: 89–98.

Bari, A., Dutkiewicz, V.A., Judd, C.D., Wilson, L.R., Luttinger, D. and Husain, L. (2003a). Regional Sources of Particulate Sulfate, SO_{2}, PM_{2.5}, HCl, and HNO_{3}, in New York, NY. Atmos. Environ. 37: 2837–2844.

Bari, A., Ferraro, V., Wilson, L.R., Luttinger, D. and Husain, L. (2003b). Measurements of Gaseous HONO, HNO_{3}, SO_{2}, HCl, NH_{3}, Particulate Sulfate and PM_{2.5} in New York, NY. Atmos. Environ. 37: 2825–2835.

Behera, S.N. and Sharma, M. (2010). Investigating the Potential Role of Ammonia in Ion Chemistry of Fine Particulate Matter Formation for an Urban Environment. Sci. Total Environ. 408: 3569–3575.

DICTUC (2007). Actualización del Inventario de Emisiones de Contaminantes Atmosféricos en la Región Metropolitana de Santiago del 2005, CONAMA RM.

Edgerton, E.S., Saylor, R.D., Hartse, B.E., Jansen, J.J. and Hansen, D.A. (2007). Ammonia and Ammonium Measurements from the Southeastern United States. Atmos. Environ. 41: 3339–3351.

Hu, M., Wu, Z.J., Slanina, J., Lin, P., Liu, S. and Zeng, L.M. (2008). Acidic Gases, Ammonia and Water-soluble Ions in PM_{2.5} at a Coastal Site in the Pearl River Delta, China. Atmos. Environ. 42: 6310–6320.

INE (2010). Parque de Vehículos en Circulación 2010 (Vehicular Fleet 2010), Instituto Nacional de Estadísticas, Available Online.

Kean, A.J., Harley, R.A., Littlejohn, D. and Kendall, G.R. (2000). On-road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions. Environ. Sci. Technol. 34: 3535–3539.

Koutrakis (1998). Monitoreo Pasivo de NH_{3} en la RM, Informe Final, CONAMA.

Krupa, S.V. (2003). Effects of Atmospheric Ammonia (NH_{3}) on Terrestrial Vegetation: A Review. Environ. Pollut. 124: 179–221.

Kuhns, H., Bohdan, V., Chow, J.C., Etyemezian, V., Green, M.C., Herlocker, D., Kohl, S., McGown, M., Ramsdell, J., Stockwell, W. R., Toole, M. and Watson, J. (2003). The Treasure Valley Secondary Aerosol Study I: Measurements and Equilibrium Modeling of Inorganic Secondary Aerosols and Precursors for Southwestern Idaho. Atmos. Environ. 37: 511–524.

Leiva, M.A., Araya, M.C., Alvarado, A.M. and Seguel, R.J. (2012). Uncertainty Estimation of Anions and Cations Measured by Ion Chromatography in Fine Urban Ambient Particles (PM_{2.5}). Accredit. Qual. Assur. 17: 53–63.

Leiva, M.A., Gonzales, V., Vargas, D., Toro, R. and Morales, R.G.E. (2013). Uncertainty Estimation of Atmospheric Ammonia Concentration by Passive Samplers. Microchem. J. 110: 340–349.

Leiva, M.A., Santibañez, D.A., Ibarra, S., Matus, P. and Seguel, R. (2013). A Five-Year Study of particulate Matter (PM_{2.5}) and Cerebrovascular Diseases. Environ. Pollut. 181: 1–6.

Molina, M.J. and Molina, L.T. (2004). Megacities and Atmospheric Pollution. J. Air Waste Manage. Assoc. 54: 644–680.

Morales, R.G.E. and Leiva G., M.A. (2006). Distribution and Critical Concentration of PM in the city of Santiago (in Spanish), In Atmospheric Urban Pollution, Morales, R.G.E. (Ed.), Critical Episodes of the Environ. Pollut.in the City of Santiago of Chile (in Spanish), First ed., Editorial Universitaria SA, Santiago, p. 324.

Olszyna, K.J., Bairai, S.T. and Tanner, R.L. (2005). Effect of Ambient NH_{3} levels on PM_{2.5} Composition in the Great Smoky Mountains National Park. Atmos. Environ. 39: 4593–4606.

Perrino, C., Catrambone, M., Di Buccianico, A.D.M. and Allegrini, I. (2002). Gaseous Ammonia in the Urban Area of Rome, Italy and Its Relationship with Traffic Emissions. Atmos. Environ. 36: 5385–5394.

Roadman, M.J., Scudlark, J.R., Meisinger, J.J. and Ullman, W.J. (2003). Validation of Ogawa Passive Samplers for the Determination of Gaseous Ammonia Concentrations in Agricultural Settings. Atmos. Environ. 37: 2317–2325.

Robarge, W.P., Walker, J.T., McCulloch, R.B. and Murray, G. (2002). Atmospheric Concentrations of Ammonia and Ammonium at an Agricultural Site in the Southeast United States. Atmos. Environ. 36: 1661–1674.
Rutllant, J. and Garreaud, R. (1995). Meteorological Air-Pollution Potential for Santiago, Chile - Towards an Objective Episode Forecasting. *Environ. Monit. Assess.* 34: 223–244.

Sather, M.E., Slonecker, E.T., Mathew, J., Daughtrey, H. and Williams, D.D. (2007). Evaluation of Ogawa Passive Sampling Devices as an Alternative Measurement Method for the Nitrogen Dioxide Annual Standard in El Paso, Texas. *Environ. Monit. Assess.* 124: 211–221.

Seguel, R.A., Morales, R.G.E. and Leiva, M.A. (2009). Estimations of Primary and Secondary Organic Carbon Formation in PM$_{2.5}$ Aerosols of Santiago City, Chile. *Atmos. Environ.* 43: 2125–2131.

Siefert, R.L. and Scudlark, J.R. (2008). Determination of Ammonia Emission Rates from a Tunnel Ventilated Chicken House Using Passive Samplers and a Gaussian Dispersion Model. *J. Atmos. Chem.* 59: 99–115.

SINCA (2011). Sistema de Información Nacional de Calidad del Aire (Information National System of Air Quality), Database Online: <http://sinca.conama.cl>, Ministerio del Medio Ambiente, Gobierno de Chile.

Solorzano, L. (1969). Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method. *Limnol. Oceanogr.* 14: 799–801.

Stelson, A.W. and Seinfeld, J.H. (1982). Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant. *Atmos. Environ.* 16: 983–992.

Walker, J.T., Whittall, D.R., Robarge, W. and Paerl, H.W. (2004). Ambient Ammonia and Ammonium Aerosol across a Region of Variable Ammonia Emission Density. *Atmos. Environ.* 38: 1235–1246.

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