Interannual variability of estimated monthly nitrogen deposition to coastal waters due to variations of atmospheric variables model input

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ABSTRACT

In this work, the influence of the interannual variation of meteorological input data on the nitrogen (N) deposition estimated applying atmospheric dispersion models is discussed. As a case study, the deposition of atmospheric oxidized N coming from the NO_x generated in the Metropolitan Area of Buenos Aires to waters of de la Plata River is evaluated for three years, considering high spatial (1 km^2) and temporal (1 h) resolutions. The interannual variation of monthly N dry deposition is in the range 10–160%, being mostly controlled by the photochemical activity of the atmosphere and the frequency of winds towards the river. The variation of monthly wet deposition values between years is in general greater than a factor of 2. It is mainly affected by the frequency of rainy hours and the precipitation rate during offshore wind conditions, and reaches a factor of 124 as a result of the variation of these variables in a factor of 4 and 3, respectively. These results show that estimated monthly N deposition to coastal waters may vary significantly between years. The evaluation of the atmospheric N that can be transferred to coastal waters can therefore be improved considering several years of atmospheric input data.

1. Introduction

The continuous increase of the population at coastal urban zones leads to greater emissions of air pollutants, which not only affects the human health and welfare but also produces diverse impacts on the environment. In urban areas, the major atmospheric N emission source is given by fossil fuel combustion that releases nitrogen oxides (NO_x). In an urban atmosphere, the NO_x are oxidized to form other nitrogen species such as nitrogen dioxide (NO_2), gaseous nitric acid (HNO_3) and ammonium nitrate (NH_4NO_3) aerosol. These compounds can be transferred to the aquatic surface through dry and wet deposition processes (Poor et al., 2001; Pryor et al., 2001; Gao, 2002; Whitall et al., 2003; Schlünzen and Meyer, 2007; Bencs et al., 2009). In the absence of precipitation, dry deposition occurs when species are transported downward mainly by atmospheric turbulence and then absorbed or adsorbed by the surface. Wet deposition is produced when the precipitation scavenges substances being present in the air column, transferring them to the surface. These processes depend on the physical and chemical characteristics of the substance (e.g., the diffusivity of the species in air, its solubility and reactivity in water) and meteorological conditions (e.g., atmospheric stability, wind speed, wind direction, and precipitation rate), which not only affect the chemical transformation rates between the different N species and hence their ambient concentrations, but also their deposition velocities. The complex relationships between dry and wet deposition processes and atmospheric

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and emission conditions make the deposition of nitrogen to coastal waters to vary considerably with time.

In previous papers (Pineda Rojas and Venegas, 2008, 2009), we estimated oxidized nitrogen (NO_2, gaseous HNO_3 and NO_3^- aerosol) deposition fluxes to coastal waters of de la Plata River (Buenos Aires, Argentina). The atmospheric dispersion model DAUMOD-RD (version 3) (Pineda Rojas and Venegas, 2009) was applied to area source emissions and CALPUFF model (Scire et al., 2000) to main point sources of NO_x in the Metropolitan Area of Buenos Aires (MABA). Maximum total oxidized N dry deposition fluxes (7–13 kg-N km^{-2} $month^{-1}$) to the de la Plata River were within the range of values obtained in other coastal sites of the world, and N wet deposition fluxes (1–4 kg-N km^{-2} $month^{-1}$) were consistently lower than values reported by other authors given the very low frequency of rain events with offshore wind and that only source emissions in the MABA were considered. The objective of this study is to discuss the variations of monthly N deposition values estimated considering three different years of meteorological input data. Interannual variability of monthly meteorological variables in the area for the period 1999–2001 is presented. The seasonal and interannual variations of estimated monthly dry and wet deposition of oxidized N species generated from NO_x emissions in the MABA to de la Plata River are discussed focusing on the influence of atmospheric variables on chemistry, transport, dispersion and subsequent deposition.

2. Estimation of N deposition to coastal waters of de la Plata River

The Metropolitan Area of Buenos Aires (MABA) is considered one of the ten greatest urban conglomerates in the world and the third mega-city in Latin America, following Mexico City (Mexico) and Sao Paulo (Brazil). It is composed of the city of Buenos Aires (200 km^2 − 2.8 million inhabitants) and the Greater Buenos Aires (3600 km^2 − 8.7 million inhabitants) (Fig. 1). In the urban area, there are numerous
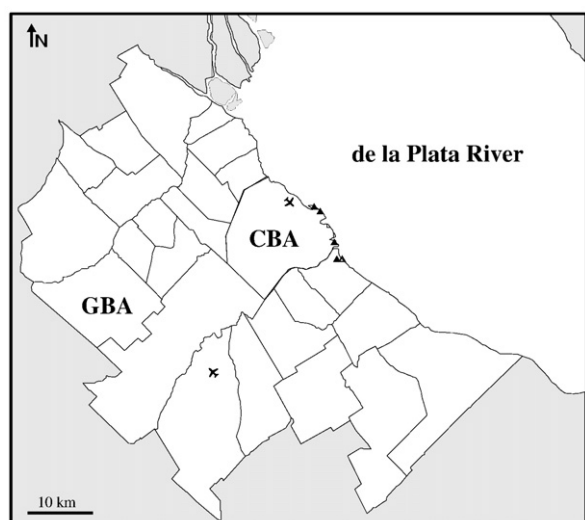

Fig. 1. Area of study: waters of de la Plata River in front of the Metropolitan Area of Buenos Aires (MABA) formed by the city of Buenos Aires (CBA) and the Greater Buenos Aires (GBA); domestic airport (✖); international airport (✖); power plants (▲); oil company (△).

NO_x emission sources coming from road traffic, residential, commercial and low industrial activities, and aircrafts at the main airports. Moreover, the main point sources located near the coast are the stacks of four Power Plants and a large oil company. Due to the geographical location of the MABA, pollutants released to the atmosphere are transported towards de la Plata River during great part of the year. De la Plata River is a shallow river-type estuary of 327 km long and with a width varying between 2 and 227 km. In front of the MABA, the river is 42 km width and shows a large zone where depths are less than 5 m. The river constitutes the main source of drinking water for the city of Buenos Aires and surrounding areas.

To estimate the deposition of atmospheric nitrogen (N), coming from the N emitted in the MABA, to surface waters of de la Plata River, the DAUMOD-RD (version 3) model was applied to area source NO_x emissions and the CALPUFF model to the emissions coming from the main point sources near the coast. Both models were applied over a surface of the river of 2339 km^2 (Fig. 1), considering spatial and temporal resolutions of 1 km^2 and 1 h, respectively. Three years (1999–2001) of hourly surface meteorological information measured in a coastal site within the domestic airport and sounding data from the site located in the international airport (Fig. 1), were used. The NO_x emission data belong to a high resolution emission inventory developed for the Metropolitan Area of Buenos Aires (Pineda Rojas et al., 2007) and the emissions from the stacks of the four Power Plants and the large oil company. The emission inventory includes area source emissions: residential, commercial, small industries, road traffic and aircrafts landing/take-off at both the domestic and the international airports. The emission factors used in preparing the emission inventory were derived considering: a) monitoring studies undertaken in Buenos Aires (Rideout et al., 2005); b) The EMEP/CORINAIR Atmospheric Inventory Guidebook (European Environment Agency, 2001); c) The US Environmental Protection Agency's manual on the Compilation of Air Pollution Emission Factors (US EPA, 1995). These factors were applied to fuel consumption, gas supply data and vehicle kilometres travelled within each grid square. Data on traffic flow and bus service frequencies was also available. Aircraft emissions were computed knowing the scheduled hourly flights, the type of aircraft, the information available on LTO (landing/take-off) cycles and NO_x emission factors (Romano et al, 1999, EMEP/CORINAIR, 2001). Table 1 includes

Table 1
Annual NO_x (expressed as NO_2) emission from the main point sources and area sources of the MABA considered for calculations.

Source category	Annual emission (ton-NO_x yr^{-1})
Main point sources	
4 Power plants	31484
Oil company	1794
Total point sources	*33278*
Area sources	
Road traffic	53883
Residential	7520
Commercial	702
Small industries	3839
Aircrafts (airports)	879
Total area sources	*66823*
Total annual emission	*100101*

the annual NO_x emission for each source category considered. Area sources account for 67% (66 823 ton-NO_x (as NO_2) yr^{-1}) of NO_x annual emissions in the MABA. The main contribution to this value comes from road traffic (81%). The emission inventory has a spatial resolution of 1×1 km and a typical diurnal variation. Fig. 2 shows the spatial distribution of annual emission of NO_x (as NO_2) from area sources in the MABA.

As the objective of this study is to evaluate the variations of monthly N deposition values estimated using three different years of meteorological input data, no interannual emission variation is considered in this opportunity.

On the other hand, both atmospheric dispersion models require ozone background concentration values to evaluate diurnal reaction constants. Unfortunately, at present the few local air quality monitoring stations do not report ozone concentrations in the city. However, several campaigns (Bogo et al., 1999; Mazzeo et al., 2005) reveal that ozone concentrations in the area are usually low. According to these reports, monthly mean values varying between 30 ppb in winter and 60 ppb in summer months were considered. Moreover, to estimate the ammonium nitrate aerosol formation rate, both models require ammonia background concentration values in the area. Due to the lack of measurements of NH_3 concentration in the MABA, in a previous paper (Pineda Rojas and Venegas, 2009) a typical representative value for an urban area was derived based on the analysis of values observed in more than 10 cities of the world. Results showed that monthly and annual mean concentrations of ammonia in urban areas varied between 1 and 9 ppb. According to the results showed in Pineda Rojas and Venegas (2009), an

ammonia background concentration of 5 ppb was considered for calculations.

It is worth noting that reduced N compounds (NH_x) as well as nitrogen species transported from regions outside the MABA (i.e., rural background pollution) could contribute to N deposition to the river. However, at present, there is no NH_x emission inventory or measurements of N species concentrations available for the outer area so as to include these possible sources of nitrogen in the estimations of deposition rates.

2.1. Brief description of the models used

The DAUMOD-RD model is an atmospheric dispersion model developed for urban area source emissions. The original version of the DAUMOD model (Mazzeo and Venegas, 1991) was developed to estimate the concentration of air pollutants without considering chemical reactions or deposition processes. Its performance has been evaluated in the city of Buenos Aires and in different cities of Europe and the United States (Mazzeo and Venegas, 1991, 2004; Venegas and Mazzeo, 2002, 2006). DAUMOD-RD (version 3) is the updated version of the model which includes modules to evaluate the formation of secondary nitrogen compounds (NO_2, gaseous HNO_3 and NH_4NO_3 aerosol) from NO_x emissions, and the dry and wet deposition of these species over an aquatic surface. A detailed description of the last version of DAUMOD-RD and its key assumptions can be found in Pineda Rojas and Venegas (2009).

The CALPUFF model (Scire et al., 2000) is an atmospheric dispersion model recommended by the United States Envi-
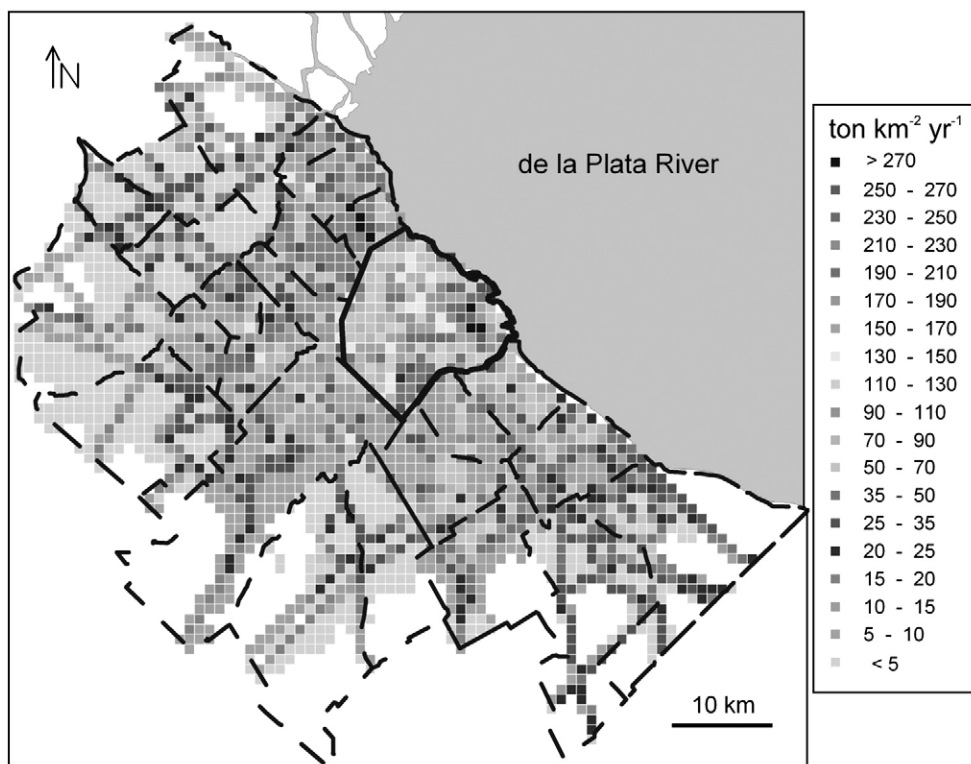

Fig. 2. Annual emission rates (ton km^{-2} yr^{-1}) of NO_x (as NO_2) from area sources in the MABA. Grid resolution is 1×1 km.

ronmental Protection Agency (US EPA). CALPUFF can be applied to estimate concentration and deposition of atmospheric pollutants emitted from point sources. Taking into account that the point sources considered in this study are located near the coast (Fig. 1) and that only the plume behaviour over the water surface is modelled, the CALPUFF model was applied in slug mode (to avoid errors associated to circular puffs near the emission source) and screening mode (i.e., spatial homogeneity of atmospheric variables is assumed).

The DAUMOD-RD (version 3) model was developed in order to evaluate deposition of nitrogen compounds to a water surface, when NO_x emissions come from a great number of area sources in a coastal city. Both CALPUFF and DAUMOD-RD models include the same parameterisations of chemical transformations and deposition processes. However, DAUMOD-RD model requires much less computation time than CALPUFF when it is applied to a great number of area sources. Area source emissions of NO_x in the MABA are given using a grid net with a resolution of 1×1 km that includes 2203 area sources. The application of CALPUFF to all these sources would require a considerable amount of computation time, so DAUMOD-RD (version 3) was applied to area source emissions.

The chemical transformation scheme included in both models assumes that nitrogen oxides ($NO_x = NO + NO_2$) are all transformed to nitrogen dioxide (NO_2), which is then oxidized to gaseous nitric acid (HNO_3) and organic nitrates (RNO_3). HNO_3 can then react with gaseous ammonia (NH_3) present in the atmosphere to produce ammonium nitrate (NH_4NO_3) aerosol (Atkinson, 2000; Jenkin and Clemitshaw, 2000; Seinfeld and Pandis, 2006). RNO_3 is not subject to subsequent reactions or deposition. The chemical transformations through which NO_2 is lost and gaseous HNO_3 is formed are considered as pseudo-first-order reactions. The reaction constants for these transformations are evaluated as functions of ozone (O_3) background concentration (precursor of the hydroxyl radical), the atmospheric stability index, varying between 2 (moderate unstable) and 6 (moderate stable) according to the Pasquill–Gifford–Turner classification (Gifford, 1976), and the vertically averaged NO_x concentration (Scire et al., 1984, 2000). In addition, at each hour the models evaluate the fraction of NH_4NO_3 aerosol being in equilibrium with gaseous HNO_3 and NH_3, as a function of the equilibrium constant for this reaction, the concentration of available gaseous HNO_3 and the background concentration of gaseous NH_3. The equilibrium constant is a nonlinear function of temperature and relative humidity and it is estimated through a double linear interpolation algorithm on these variables, following the relationships obtained by Stelson and Seinfeld (1982). It is assumed that the available HNO_3 concentration results from the NO_x oxidation.

The wet removal of gaseous species occurs when substances are dissolved within falling drops and can therefore be important in the case of soluble gases such as HNO_3. On the other hand, the precipitation scavenging of aerosols is one of the most effective mechanisms to remove pollutants from the atmosphere and occurs when drops "collide" or "impact" with particles. This mechanism is very effective to remove aerosols such as nitrate. A simple approach that has shown to give realistic estimates of the long-term wet removal of gases and aerosols, is the scavenging coefficients method (Maul, 1980; Scire et al., 2000). Through this methodology, the wet deposition flux can be estimated as (Seinfeld and Pandis, 2006):

$$F_w = \Lambda h C_m \tag{1}$$

where h is the vertical extension of the pollutant plume below the cloud, C_m is the vertically averaged species concentration within the pollutant plume before the wet removal process and Λ is the scavenging coefficient given by $\Lambda = \lambda(p_0/p_1)$, where p_0 is the precipitation rate, p_1 is a constant ($= 1$ mm h^{-1}) and λ is a washout coefficient (s^{-1}) dependent on the pollutant (Scire et al., 2000). The values of λ considered in both models are: 6.0×10^{-5} s^{-1} for gaseous HNO_3, 1.0×10^{-4} s^{-1} for NO_3^- aerosol and zero for NO_2 due to its low solubility in water (Lee and Schwartz, 1981). After the wet removal, the species concentration (C') that remains in the air is evaluated as:

$$C' = C \exp(-\Lambda \Delta t) \tag{2}$$

where C is the pollutant concentration before the rain scavenging and Δt is the time step of the model.

The dry deposition flux is estimated as the product of the species concentration (C') and the species deposition velocity (v_d) at a reference height near the surface (as deposition is estimated over a water surface, the reference height is considered 1 m)

$$F_d = v_d C' \tag{3}$$

Among the most widely used methodologies to estimate the deposition velocity is the resistance method (Seinfeld and Pandis, 2006). Under steady-state conditions, the deposition velocity (cm s^{-1}) of a gaseous substance over an aquatic surface can be expressed as:

$$v_{dg} = [r_a + r_{dg} + r_w]^{-1} \tag{4}$$

where r_a is the aerodynamic resistance representing the effect of turbulent transport through the atmospheric surface layer, r_{dg} is the quasi-laminar layer resistance for gaseous species including the effect of molecular diffusion in this sub-layer, and r_w is the water surface resistance which represents the tendency of the surface to "capture" the species once they come into contact. In the case of aerosols, deposition is also favoured by particle settling due to the action of gravity. The deposition velocity for aerosol particles (v_{dp}) can be estimated by:

$$v_{dp} = [r_a + r_{dp} + r_a r_{dp} v_s]^{-1} + v_s \tag{5}$$

where r_{dp} is the quasi-laminar layer resistance for aerosols and v_s is the gravitational settling velocity, being both parameters dependent on the aerosol particle size. In the models, the resistances are parameterised as a function of the species diffusivity in air, its solubility and reactivity in water, the atmospheric stability and the friction velocity, following the methodology described in Seinfeld and Pandis (2006). To include r_{dp} and v_s dependencies on particle size, a log-normal distribution with typical geometric mean diameter (0.48 μm)

and standard deviation (2.0 μm) for nitrate aerosol is considered (Scire et al., 2000).

3. Results and discussion

3.1. Meteorological variables in the area during 1999–2001

3.1.1. Wind speed and direction

Wind is one of the variables with greatest influence on the transport and transference of pollutant substances from the atmosphere to the water surface. Due to the direction of the coast (Fig. 1), winds transporting pollutants from the Metropolitan Area of Buenos Aires towards de la Plata River come from the SE→NW sector. Annually, these situations occur during 40% of the year (Fig. 3a). Some of these directions are more effective in transporting pollutants from the MABA to the river. For example, winds from SW transport pollutants coming from almost all sources in the MABA to the river; but when wind blows from the SE or NW sector, only some sources located near the coast contribute to the deposition of nitrogen to the river. During offshore wind conditions, wind blows almost equally from the SW (16.4%),

SE (15.4%) or the NW (14.5%) sectors (Fig. 3b). On the other hand, wind speed can enhance deposition under certain atmospheric conditions and decrease it in others. Stronger winds lead to a greater atmospheric dispersion (i.e., lower concentration) at the same time they favour dry deposition of species to the aquatic surface (i.e., increasing deposition velocity). The mean wind speed registered for each wind direction is included in Fig. 3a. During offshore wind situations, higher mean wind speeds (>4 m s^{-1}) are registered between the SE and WSW directions (Fig. 3a).

Another important factor is the time of the day at which offshore winds occur, since daylight hours are more favourable for nitrogen deposition due to the greater emission of NO_x and conversion of NO_2 to HNO_3. Fig. 4 shows the monthly variation of the mean number of "diurnal" (8:00am–7:00pm) and "nocturnal" (8:00pm–7:00am) hours with offshore winds. The error bars indicate the variation (maximum and minimum) of monthly values in the three-year period. In general, the frequency of winds towards the river is greater in winter (June–August) than in summer (December–February), varying between 26% and 57%. The highest monthly mean percentage of diurnal hours relative to the total number of
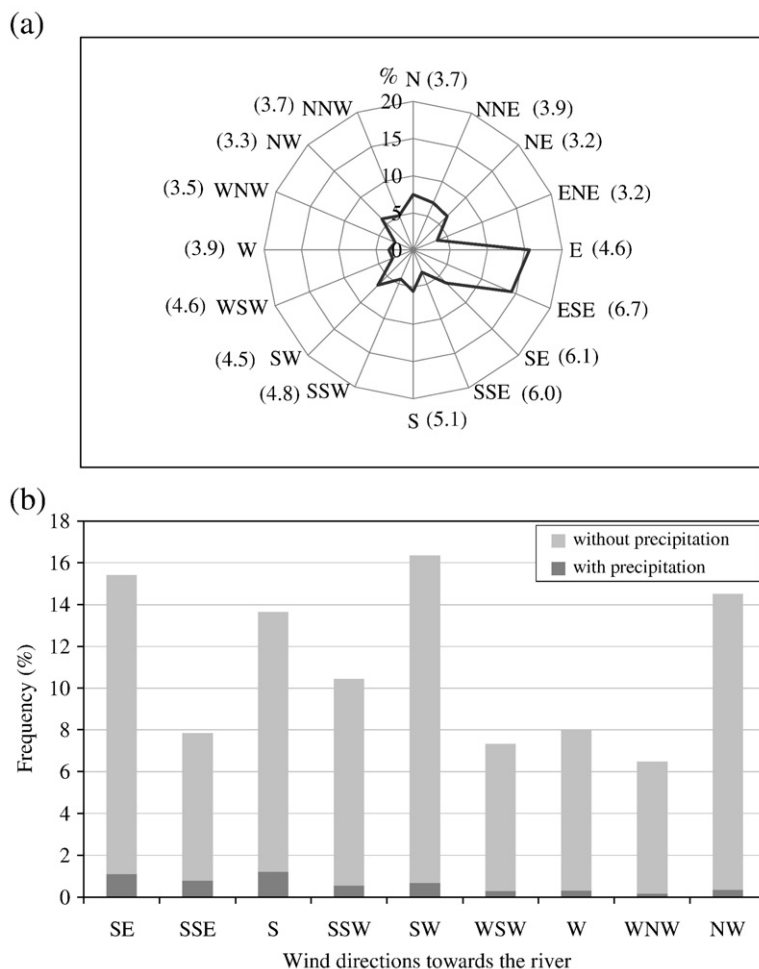

Fig. 3. (a) Annual wind rose indicating the mean wind speed in m s^{-1} (in parentheses) (1999–2001) and (b) annual relative frequency distribution of wind directions during offshore wind conditions only (1999–2001).
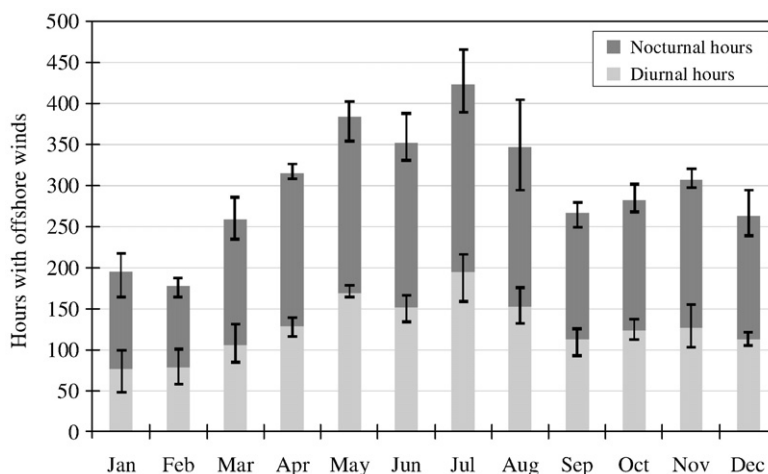
Fig. 4. Monthly variation of the mean (1999–2001) number of diurnal (8:00am–7:00pm) and nocturnal (8:00pm–7:00am) hours with offshore winds (the error bars indicate the variation of monthly values in the three-year period).

offshore wind hours occurs in July (46%) and the lowest in January (39%). The interannual variation of the monthly number of diurnal hours with winds towards the river varies between 9% (in May) and 106% (in January), while that of total hours (diurnal + nocturnal) with offshore winds ranges from 3% (April) to 69% (in January).

3.1.2. Air temperature and relative humidity

Air temperature and relative humidity play an important role in aerosol nitrate formation, through their effects on the dissociation constant for the equilibrium reaction between gaseous HNO_3 and NH_3 and NH_4NO_3 aerosol (Stelson and Seinfeld, 1982). Lower temperature and greater relative humidity values favour nitrate aerosol formation; hence, a higher percentage of NH_4NO_3 aerosol formation (i.e., greater gaseous HNO_3 removal) during nocturnal hours and in winter months is expected. On the other side, the equilibrium constant is more sensitive to temperature changes, varying more than three orders of magnitude for the range

of observed temperatures 0–40 °C (Stelson and Seinfeld, 1982). In the area of study, hourly air temperature during offshore wind conditions varied between 1.1 and 35.1 °C. The variation of the monthly mean (1999–2001) air temperature (calculated considering only values registered during offshore winds) and the range of variation of monthly temperature in the three-year period is shown in Fig. 5. During hours with winds towards the river, monthly temperature varied between 8.2 °C in July 2000 and 23.8 °C in January 2001.

Hourly values of relative humidity varied between 11 and 100%. Fig. 6 shows the variation of the monthly mean relative humidity for the cases of offshore winds only. Lower mean values were observed in summer months and greater ones in winter. Monthly relative humidity varied between 57% in December 2000 and 81% in June 2000. The interannual variation of the monthly values may be small as observed in July or as large as in March when the highest monthly relative humidity resulted 28% greater than the lowest one.
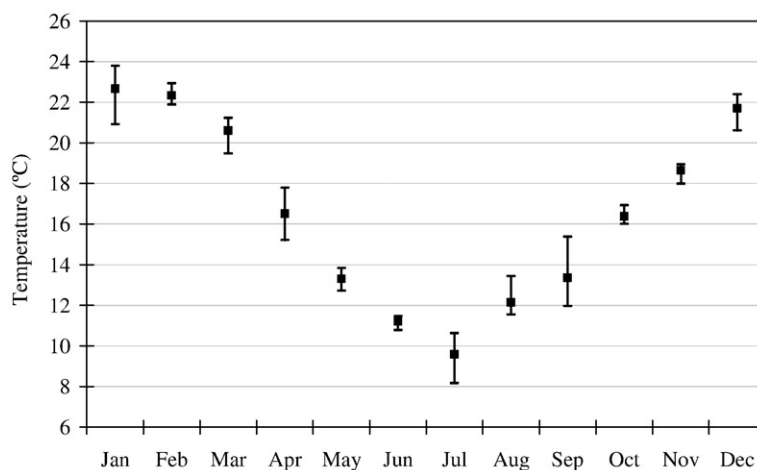

Fig. 5. Monthly variation of the mean (1999–2001) air temperature during offshore wind conditions.
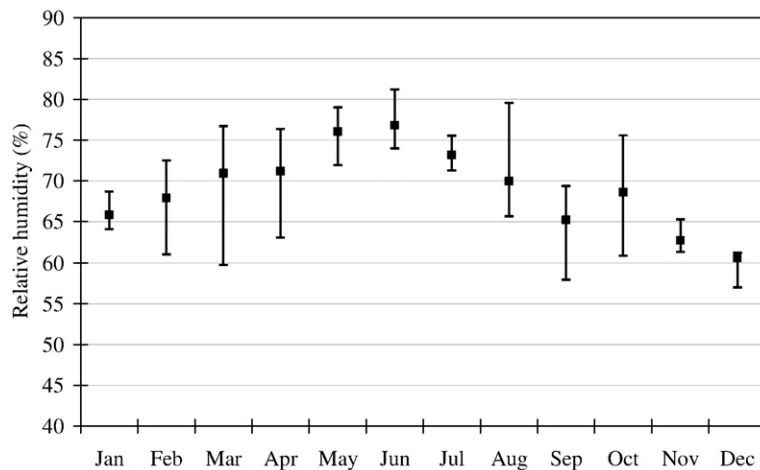
Fig. 6. Monthly variation of the mean (1999–2001) relative humidity during offshore wind conditions.

3.1.3. Precipitation

Wet deposition of antropogenically derived species to coastal waters depends on the occurrence of situations with offshore wind and rain (hereafter, "OWR") and on the precipitation rate. In the area of study, the former have very low frequency (2% on the annual average) and rains are generally light (less than 5 mm h^{-1}). The mean annual precipitation in the area was 1040 mm, while it was 442 mm during offshore winds.

The histogram of hourly precipitation rates during offshore wind conditions observed in the analyzed period (1999–2001) is included in Fig 7. Precipitation rates lower than 3 mm h^{-1} were more frequent (75%) and heavy rains (more than 20 mm h^{-1}) were rare (1%).

Fig. 8 shows the monthly variation of (a) the mean precipitation rate during offshore winds and (b) the mean number of "OWR" hours. The bars in this Figure indicate the interannual variation range of monthly mean values in the three-year period. Precipitation rates (Fig. 8a) are higher from January to March. The interannual variation of the monthly mean precipitation rate is in general significant. Monthly

mean values vary between years a factor ranging from 2 to 6, except in February, May and December when this variation is smaller. Fig. 8b shows a marked variation of the mean frequency of "OWR" cases, with greater values (up to 26 h) in May–August. However, these months also show the lowest mean precipitation rates (around 2 mm h^{-1}). On the other hand, comparing Figs. 4 and 8b, it can be observed that the percentage of hours with precipitation during offshore wind situations varies between 3% in September and 9% in February. The number of "OWR" hours may also show a considerable interannual variability. The highest interannual variation was observed in May, when the greatest frequency of "OWR" exceeded the least one by a factor of 8, and the lowest interannual variation (36%) was obtained in February.

3.2. Monthly variation of parameters involved in deposition parameterisations

3.2.1. Diurnal NO$_x$ oxidation rates

Figs. 9 and 10 present the monthly variation of the mean (1999–2001) diurnal rates for the loss of NO$_2$ and formation of
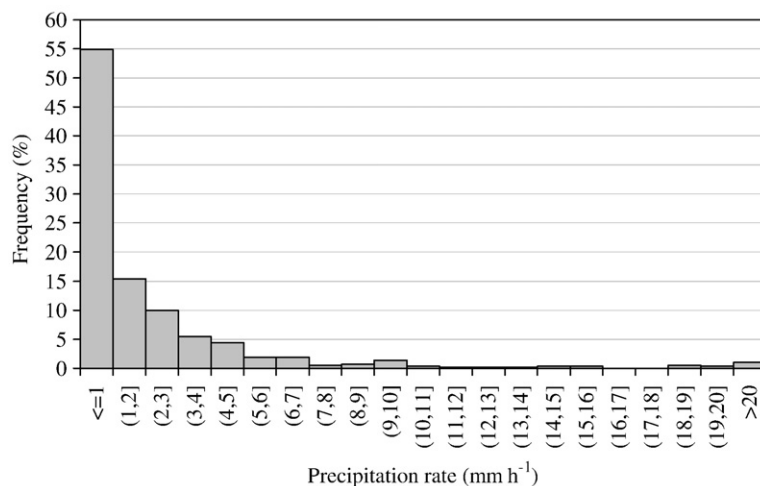

Fig. 7. Relative frequency distribution of precipitation rates observed during offshore wind conditions in 1999–2001.
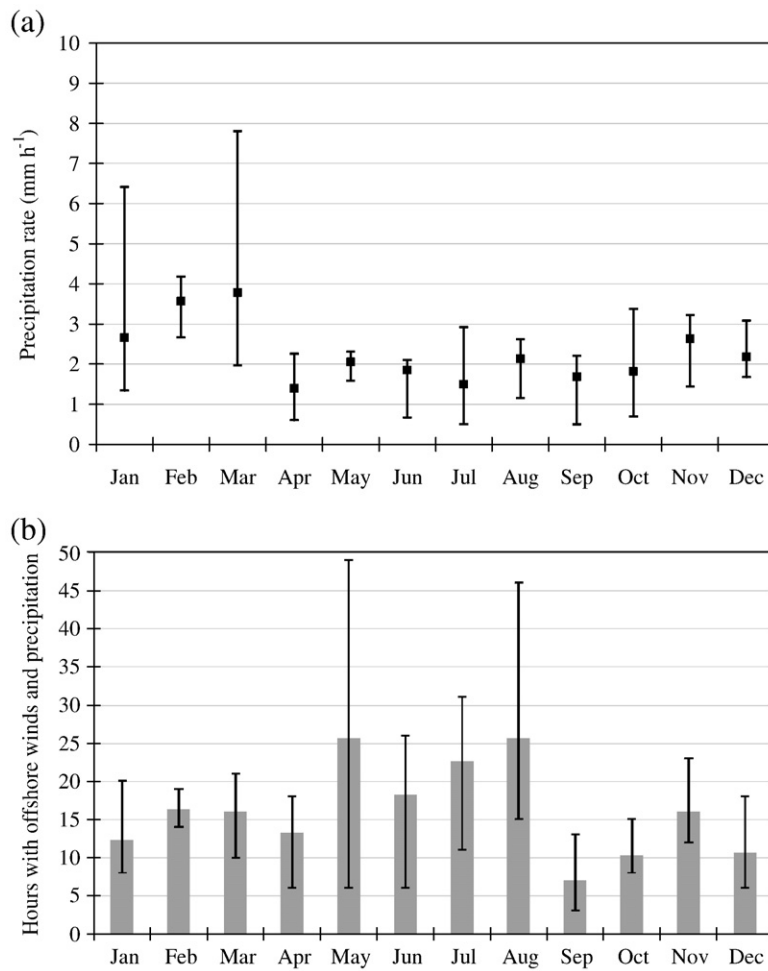
Fig. 8. Monthly variation of the mean (1999–2001) (a) precipitation rate and (b) number of hours with precipitation during offshore wind conditions.

gaseous HNO_3, respectively. Monthly mean values of diurnal rates for the loss of NO_2 vary between 8 and 30% h^{-1}, while those for the formation of HNO_3 vary between 3 and 9% h^{-1}, similar to that obtained by other authors (Kelly, 1987; Lin and Cheng, 2007). Both are lower in winter and greater in summer as a consequence of the greatest photochemical activity of the
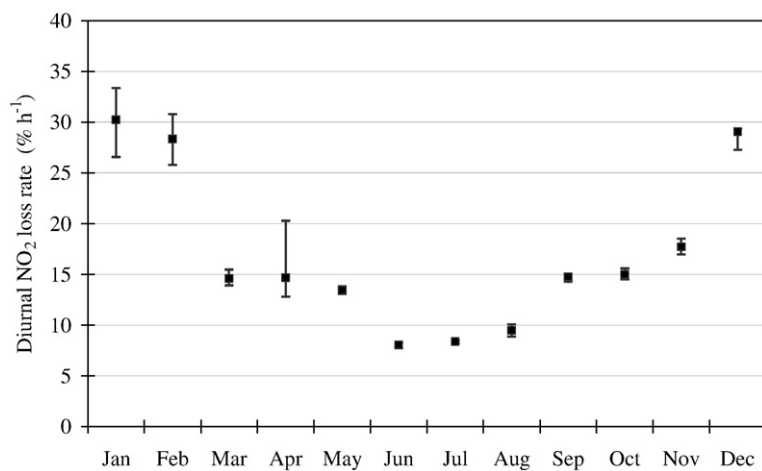

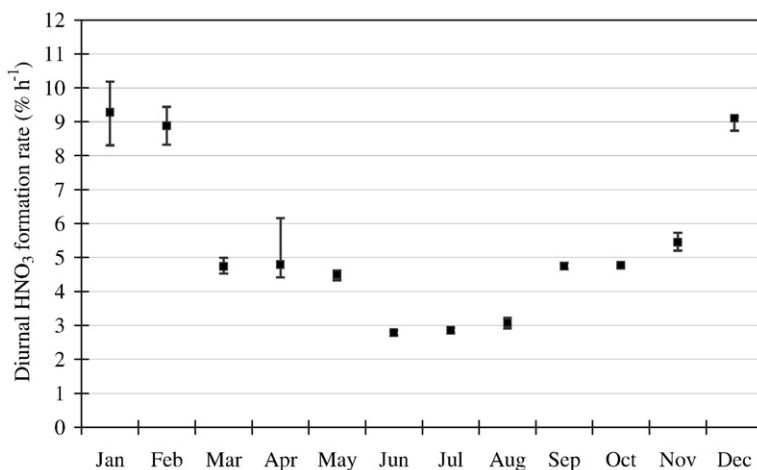Fig. 9. Monthly variation of the mean (1999–2001) diurnal oxidation rates for the loss of NO_2.

Fig. 10. Monthly variation of the mean (1999–2001) diurnal oxidation rates for the formation of gaseous HNO$_3$.

atmosphere, which is enhanced by greater ozone concentrations and unstable atmospheric conditions in warmer months. The interannual variation of monthly mean values of NO$_x$ oxidation rates is generally small, except in January, February and April. Taking into account that constant monthly O$_3$ background concentration values were considered, the greatest interannual variation obtained in summer resulted from the dependency of the diurnal oxidation rates on the rest of the variables. These transformation rates are sensitive to the variation of atmospheric stability. Particularly, diurnal rates present a greater spread when atmospheric stability varies among unstable conditions (i.e., in summer). The great interannual variation observed in April (59%) (Figs. 9 and 10), unlike the rest of the fall months (March and May), was due to a great interannual variation of the occurrence of unstable atmospheric conditions (in April 2000 the frequency of unstable conditions was 5 and 3 times greater than in April 1999 and 2001, respectively).

3.2.2. Nitrate aerosol formation rate

Fig. 11 shows the monthly variation of the mean percentage of gaseous nitric acid that is converted to nitrate

aerosol. As expected, the greatest values occur in winter and the lowest in summer, mainly due to the influence of the air temperature (Fig. 5) and the relative humidity (Fig. 6) on the equilibrium constant for the reaction between gaseous HNO$_3$ and NH$_3$ and NH$_4$NO$_3$ aerosol. In the analyzed period, the monthly mean percentage of NO$_3^-$ aerosol formation varies between 27% in January and 87% in July. The interannual variation of monthly mean values ranges between 0.4% in August and 57% in January. In general, according to the results shown in Fig. 5, the variation of this parameter between years, responds to the interannual variation of the air temperature. During winter months this effect is less pronounced because the equilibrium constant is more sensitive to temperature changes at higher air temperatures (Stelson and Seinfeld, 1982).

3.2.3. Scavenging coefficients

In wet deposition calculations, the "effectiveness" of rain to remove a substance is expressed through the value of the scavenging coefficient (Λ). Based on the observed precipitation rates and the washout coefficient (λ) values considered in the models, 75% of Λ values are lower than 0.5 h^{-1} for
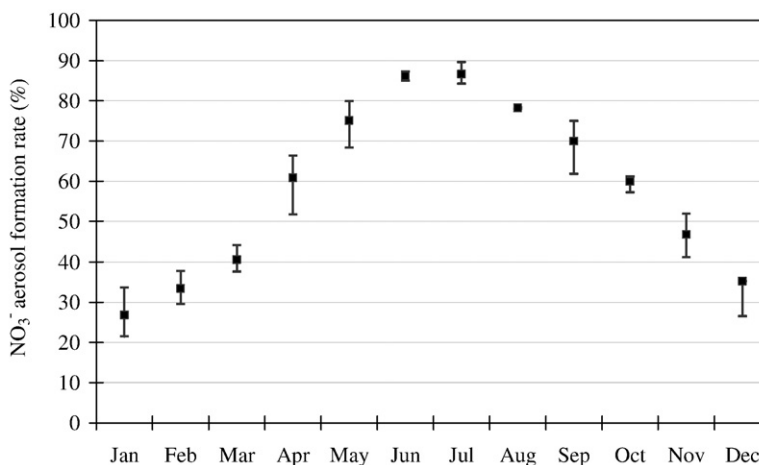

Fig. 11. Monthly variation of the mean (1999–2001) NO$_3^-$ aerosol formation rate (%).

gaseous HNO$_3$ and lower than 0.9 h^{-1} for NO$_3^-$ aerosol. According to the parameterisation of the scavenging coefficient, monthly variation of the mean Λ values follows the variation of the mean precipitation rate during "OWR" hours (Fig. 8a). The monthly mean values of Λ varied between 0.3 and 0.8 h^{-1} for HNO$_3$ and between 0.5–1.4 h^{-1} for NO$_3^-$. In general, the mean scavenging coefficients were greater from January to March, when greater precipitation rates occurred (Fig. 8a).

3.2.4. Deposition velocities

More than 90% of hourly deposition velocity (v_d) values were lower than 0.06 cm s^{-1} for NO$_2$, varied between 0.07 and 1.5 cm s^{-1} for gaseous HNO$_3$ and between 0.2 and 2.0 cm s^{-1} for NO$_3^-$ aerosol. These deposition values are similar to those reported in the literature (Kelly, 1987; Hauglustaine et al., 1994; Gao, 2002; Holloway et al., 2002; Sickles and Shadwick, 2002; Clark and Kremer, 2005). A comparison of our estimations of hourly deposition velocity values with those reported by other authors can be found in Pineda Rojas and Venegas (2009).

Fig. 12 shows the estimated monthly mean values of the deposition velocities for the three species, with their interannual variation ranges. Monthly mean values of v_d vary between 0.02–0.03 cm s^{-1} for NO$_2$, 0.7–0.9 cm s^{-1} for HNO$_3$ and 0.8–1.0 cm s^{-1} for NO$_3^-$. In all three cases, lower mean deposition velocities occur in June and greater ones in September. On the other hand, the interannual variation of monthly mean values of v_d is small in February, October and December, and large in others. In all cases, the greatest interannual variation occurred in May: 53% for NO$_2$, 68% for gaseous HNO$_3$ and 61% for NO$_3^-$ aerosol.

3.3. Variation of monthly N deposition

3.3.1. Dry deposition of N–NO$_2$

Fig. 13 shows the monthly variation of the mean dry deposition of nitrogen dioxide (expressed as N–NO$_2$) to 2339 km^2 of the river during 1999–2001, including the interannual variation of monthly deposition values. The monthly mean dry deposition varies between 1148 and 4153 kg-N month^{-1}. The highest values were observed in May–August and the lowest ones in January and February. This variation is mainly due to the monthly variation of the number of offshore wind hours (Fig. 4) and the rate for the loss of NO$_2$ by photochemical oxidation (Fig. 9).

On the other side, the interannual variation of monthly N–NO$_2$ dry deposition can be important, as results obtained for April and August. In April, the monthly deposition varied between years by a factor of 3. It was considerable lower in April 2000 due to a significantly higher frequency of unstable conditions which led to a considerably greater NO$_2$ loss rate and hence contributed further to the lowest N–NO$_2$ dry deposition in this month. In August, in turn, the greatest relative variation (80%) of N–NO$_2$ dry deposition between years was produced as a consequence of the interannual variation of the number of hours with offshore winds (in August 2000 it was 56% greater than in August 2001).

3.3.2. Wet deposition of N–HNO$_3$

Monthly variation of wet deposition of nitrogen in gaseous nitric acid (N–HNO$_3$) is included in Fig. 14. Mean values of wet deposition of this species vary considerably between 25 and 588 kg-N month^{-1}. Greater values are obtained in the warm months. This marked variation is strongly controlled by the monthly variation of the mean formation rates of gaseous HNO$_3$ (Fig. 10) and NO$_3^-$ aerosol (Fig. 11), given that in summer, not only more HNO$_3$ is formed from the NO$_x$ oxidation but also less HNO$_3$ is lost to form NO$_3^-$. Among months of the same season, when mean HNO$_3$ formation rates are similar, the monthly variation of mean N–HNO$_3$ wet deposition results as a consequence of the monthly variation of the mean precipitation rate and the number of "OWR" cases (Fig. 8). For example, even though December and February present similar mean formation rates of gaseous HNO$_3$, wet deposition of N–HNO$_3$ in February is 88% greater than in December. The reason for this is that in the considered period (1999–2001), the mean precipitation rate as well as
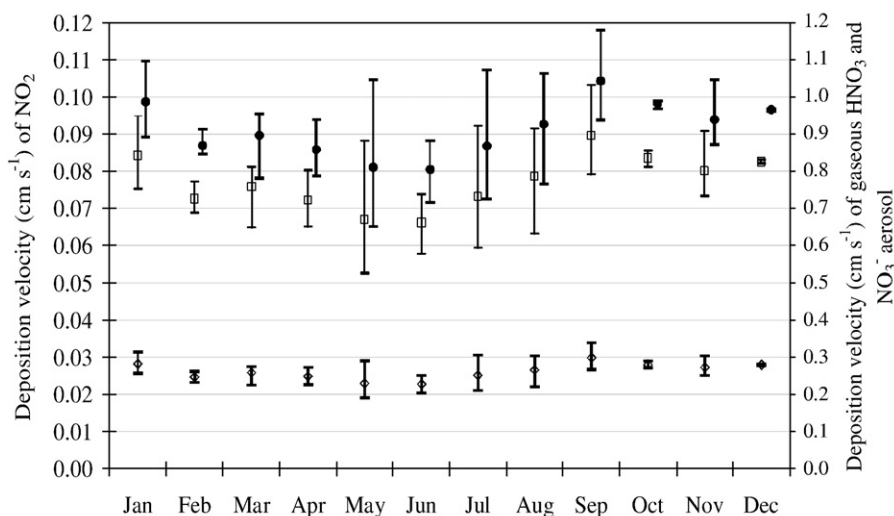

Fig. 12. Monthly variation of the mean (1999–2001) deposition velocities for NO$_2$ ($\Diamond$), gaseous HNO$_3$ ($\square$) and NO$_3^-$ ($\bullet$) aerosol.
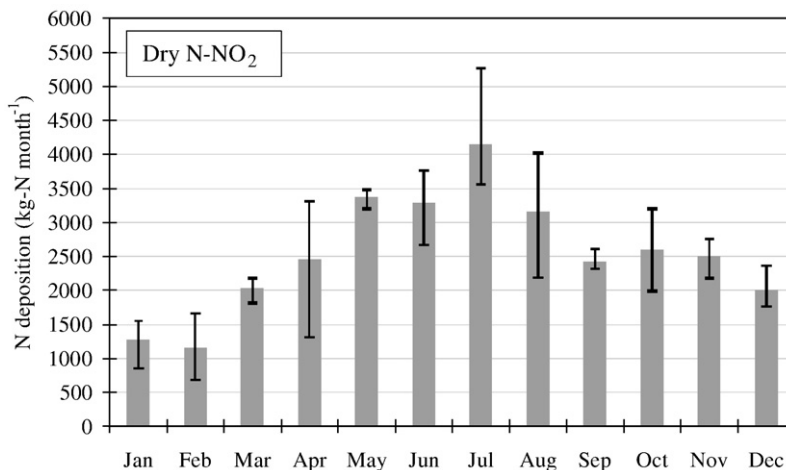
Fig. 13. Monthly variation of the mean (1999–2001) dry deposition of N–NO$_2$ in 2339 km^2 of the river.

the frequency of "OWR" hours is greater in February than in December (2 and 3 times, respectively). In the same way, the wet deposition of N–HNO$_3$ in March is notably greater than in the rest of the fall months, as a result of the greatest mean precipitation rate during that month.

The interannual variation of monthly wet deposition of N–HNO$_3$ is significant in all months. The ratio between the greatest and the lowest monthly deposition value obtained for each month in the three years varied between 2 and 245. This significant interannual variability is greater in colder months mainly due to the great interannual variation of the monthly frequency of "OWR" cases during the winter months (Fig. 8b). Among months of greater mean deposition, the greatest interannual variations were obtained in January, March, November and December. In these months, the relation between the number of these "events" in the years of the greatest and lowest deposition was approximately 2, except in December that it varied a factor of 3 (Fig. 8b). In addition, in January and November, the interannual variation of the mean precipitation rate also contributed to the great interannual variation of deposition. In these months, the

relative variation between the monthly mean precipitation rate in the years of the greatest and lowest deposition was 30% and 20%, respectively.

3.3.3. Dry deposition of N–HNO$_3$

The monthly dry deposition of N–HNO$_3$ is depicted on Fig. 15. Seasonal variations can be observed, with greater values in summer due to more photochemical activity during these months. Despite the mean formation rates of gaseous HNO$_3$ are generally low (as can be seen in Fig. 10), its high solubility makes the mean dry deposition of N–HNO$_3$ to the water surface to be comparable to that of N–NO$_2$, varying between 369 and 3119 kg-N month^{-1}. The mean N–HNO$_3$ dry deposition value obtained in December is particularly higher than in other summer months, being the number of diurnal hours with offshore winds responsible for this result. In December, this number is 48% greater than in January and 44% greater than in February (Fig. 4).

The greatest interannual variation of dry deposition of N–HNO$_3$ was obtained in February and reached a factor of 3. In general, the variation of monthly dry deposition between
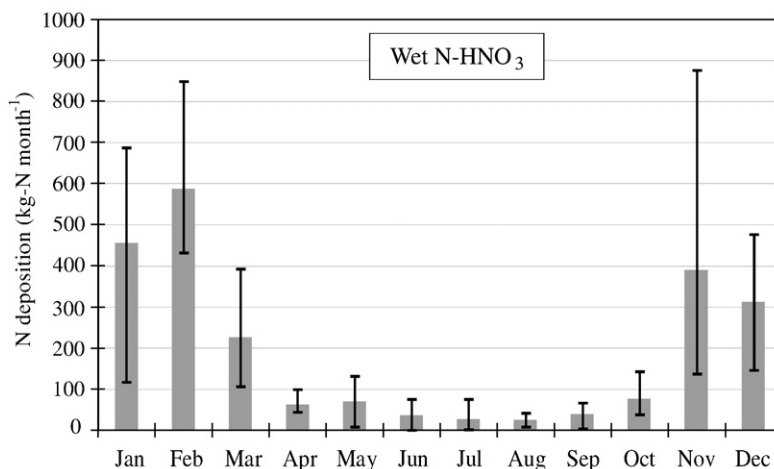

Fig. 14. Monthly variation of the mean (1999–2001) wet deposition of N–HNO$_3$ in 2339 km^2 of the river.
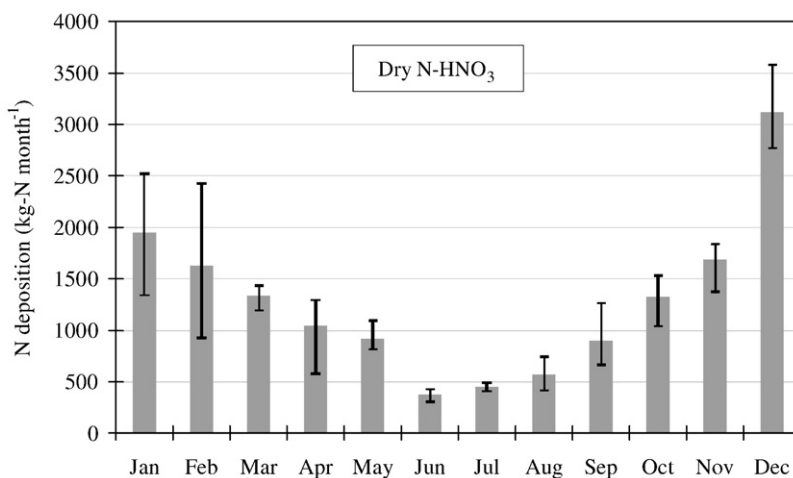
Fig. 15. Monthly variation of the mean (1999–2001) dry deposition of N–HNO$_3$ in 2339 km^2 of the river.

years resulted mainly from the interannual variation of the number of daylight hours with winds towards the river and the formation rate of gaseous nitric acid.

3.3.4. Wet deposition of N–NO$_3^-$

Monthly variation of wet deposition of nitrogen in nitrate aerosol (N–NO$_3^-$) is shown in Fig. 16. Mean values (1999–2001) of monthly deposition of this species vary between 233 and 1153 kg-N month^{-1}. As shown in Fig. 11, the greatest mean formation rates of nitrate aerosol occur in winter. However, the available nitric acid to form nitrate aerosol is formed mostly in summer (Fig. 10). Therefore, the mean "net formation rate" of nitrate aerosol varies uniformly between 2 and 3%, which is similar to that obtained by Lin and Cheng (2007). This explains the fact that no particularly high mean wet deposition values of N–NO$_3^-$ are estimated in a given season of the year.

Monthly N–NO$_3^-$ wet deposition (Fig. 16) shows a great interannual variation which mainly responds to the interannual variations of both the number "OWR" hours and the precipitation rate. The greatest variation was obtained in

June. In this month, the greatest N–NO$_3^-$ wet deposition estimated value (year 2000) resulted 119 times the lowest one (year 1999). The number of "OWR" hours in June 2000 was 4 times greater than in June 1999, while monthly mean precipitation rate varied by a factor of 3. On the other hand, in May, the greatest interannual variation of "OWR" cases (Fig. 8b) led to an interannual variation of nitrate wet deposition of a factor of 31.

3.3.5. Dry deposition of N–NO$_3^-$

The mean dry deposition of nitrate aerosol varies between 402 and 2202 kg-N month^{-1} (Fig. 17). As in the case of the deposition of nitrogen dioxide, the dry deposition of N–NO$_3^-$ aerosol varies following the monthly variation of the frequency of offshore winds (Fig. 4). Estimated values of monthly dry deposition of N–NO$_3^-$ showed a variation of 4–222% between years. Among months of greater monthly dry deposition estimations, April and August show the greatest interannual variation (222% and 117%, respectively). The large variation observed in August is due to the interannual variation of the number of hours with winds towards the
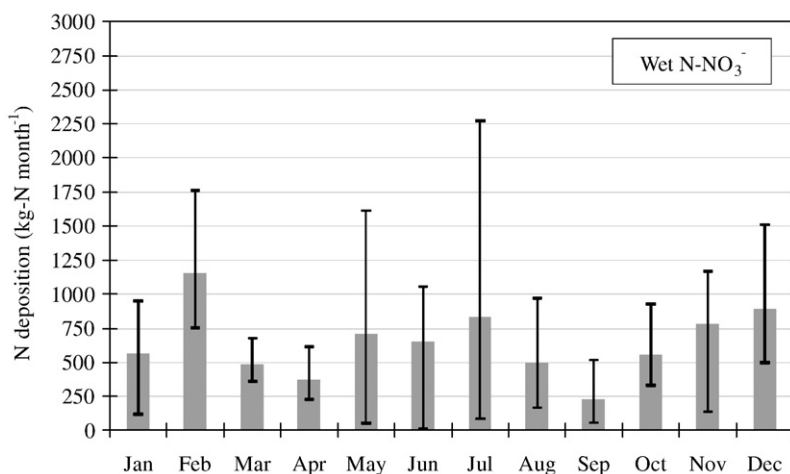

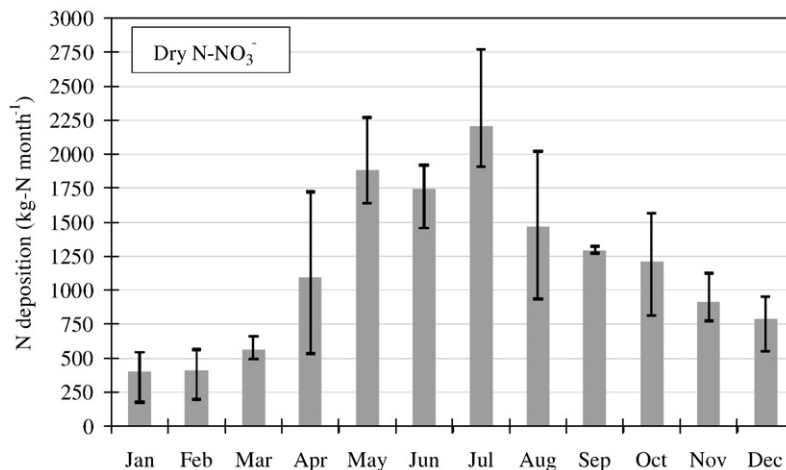**Fig. 16.** Monthly variation of the mean (1999–2001) wet deposition of N–NO$_3^-$ in 2339 km^2 of the river.

Fig. 17. Monthly variation of the mean (1999–2001) dry deposition of N–NO$_3^-$ in 2339 km^2 of the river.

river, similar to that of N–NO$_2$ dry deposition. In April, the greatest frequency of unstable atmospheric conditions in year 2000 seems to be responsible for the lowest dry deposition of all species.

3.3.6. Total N deposition and relative contributions of N species

Monthly mean values of total N ($=$N–NO$_2$ + N–HNO$_3$ + N–NO$_3^-$) deposition (dry + wet) vary between 4639 kg-N month^{-1} in March and 7669 kg-N month^{-1} in July (Fig. 18). However, due to the large interannual variation of deposition of the three species, not only estimated monthly deposition magnitudes but also months of minimum and maximum values may vary between years. For 1999 the minimum deposition was 4439 kg-N month^{-1} (June), for 2000 was 3134 kg-N month^{-1} (April) and for 2001 was 3182 kg-N month^{-1} (February). The maximum values were: 8876 kg-N month^{-1} for 1999 (December), 8528 kg-N month^{-1} for 2000 (July) and 6769 kg-N month^{-1} for 2001 (October). Greater mean N deposition values obtained in May–August respond to the greater frequency of offshore winds which are besides predominantly from the SW sector during these months. In

January, February, March and September, the predominant winds are from the SE and deposition is therefore affected by a lesser number of sources in the MABA most of the time.

Fig. 19 shows the monthly variation of mean relative contribution of each N species to total N deposition. Monthly contribution of N–NO$_2$ dry deposition varies between 23 and 55%, of N–HNO$_3$ total deposition between 6 and 52% and that of N–NO$_3^-$ total deposition between 21 and 40%. In May–August, total N deposition is mainly given by N–NO$_2$ and N–NO$_3^-$. The greatest contribution of N–HNO$_3$ deposition occurs in warmer months (December and January). From these results, it is possible to conclude that: i) the effect of the highest frequency of offshore winds and the least NO$_2$ loss by photochemical oxidation dominate in winter months; and ii) the greater photochemical activity of the atmosphere in summer increases the relative contribution of N–HNO$_3$ deposition by nearly 6 times compared to winter contribution.

3.3.7. Dry vs wet deposition of total N

The monthly variation of the mean dry and wet deposition of total nitrogen is shown in Fig. 20. Wet deposition of total N
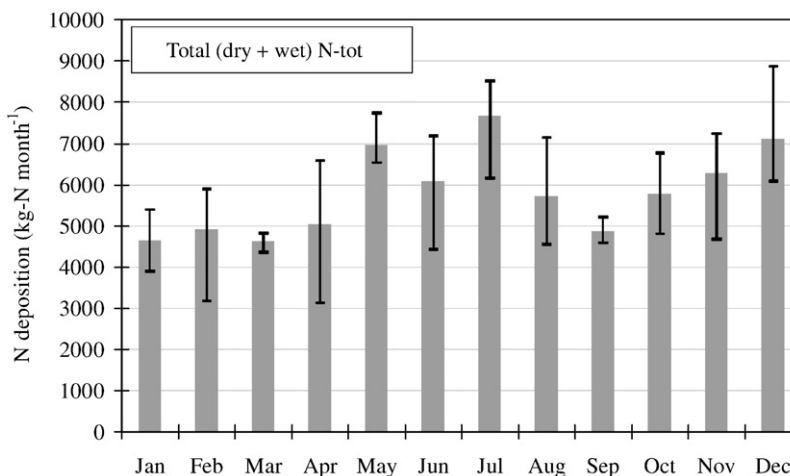

Fig. 18. Monthly variation of the mean (1999–2001) deposition (dry + wet) of total N (N–NO$_2$ + N–HNO$_3$ + N–NO$_3^-$) in 2339 km^2 of the river.
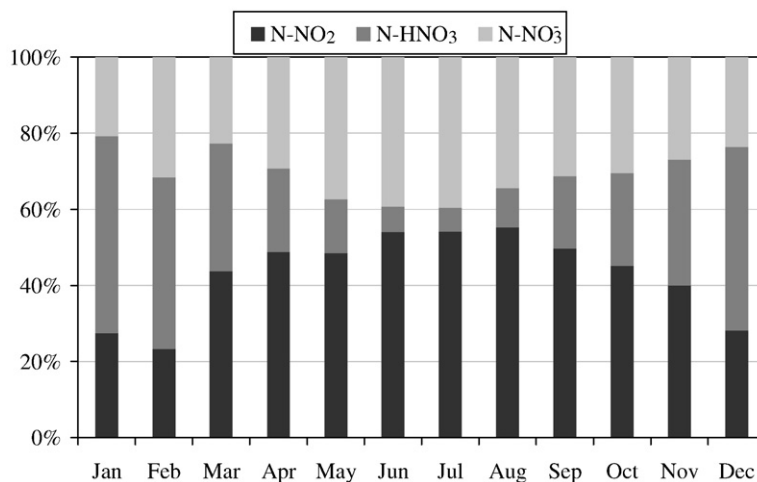
Fig. 19. Monthly variation of the mean (1999–2001) relative contributions of each N species to total N (N–NO$_2$ + N–HNO$_3$ + N–NO$_3^-$) deposition in 2339 km^2 of the river.

is, in general, considerably lower than dry deposition. During 1999–2001, monthly mean dry deposition of total N varied between 3180 kg-N month^{-1} in February and 6808 kg-N month^{-1} in July. On the other hand, monthly mean wet deposition of total N ranged from 272 kg-N month^{-1} in September (6% of total N deposition) to 1741 kg-N month^{-1} (35% of total N deposition) in February. Taking into account that in a rainy hour, the wet deposition process is much more efficient than dry deposition to transfer nitrogen from the atmosphere to the water surface, the low contribution of wet deposition to de la Plata River is a consequence of the very low frequency of "OWR" cases, as can be seen on Figs. 4 and 8b.

According to the interannual variations of monthly deposition of each species and their relative contributions, the interannual relative variation of monthly total N (= N–NO$_2$ + N–HNO$_3$ + N–NO$_3^-$) dry deposition varies between 10% (in May) and 160% (in April). The variation of monthly total N (= N–HNO$_3$ + N–NO$_3^-$) wet deposition between years is always greater than a factor of 2 (except in March when the

relative variation resulted in 60%) and reaches a factor of 124 in June. However, in the study area, it has a less pronounced effect on the interannual variation of monthly total (dry + wet) N deposition (which varied between 10 and 110%) due to its low contribution.

4. Conclusions

In this work, the interannual variations of estimated monthly N deposition values, obtained from the application of atmospheric dispersion models to three years of meteorological data, were evaluated. As a case study, the transfer of atmospheric oxidized nitrogen species (NO$_2$, gaseous HNO$_3$ and NO$_3^-$ aerosol), coming from NO$_x$ emission sources located at the Metropolitan Area of Buenos Aires (MABA), to coastal waters of de la Plata River was estimated. Atmospheric dispersion models DAUMOD-RD (version 3) and CALPUFF were applied considering hourly meteorological information for 1999–2001 and a spatial resolution of 1 km^2. Based on the present analysis, monthly mean total N deposition to waters
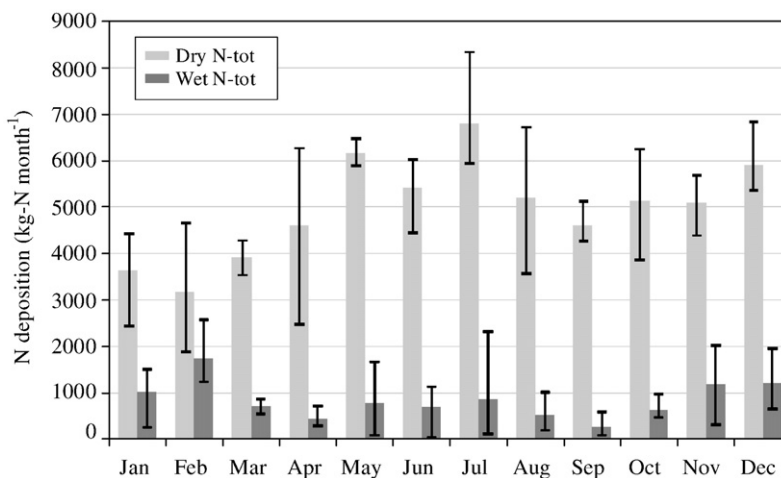

Fig. 20. Monthly variation of the mean (1999–2001) dry and wet deposition of total N (N–NO$_2$ + N–HNO$_3$ + N–NO$_3^-$) in 2339 km^2 of the river.

($2339 km^2$) of de la Plata River varies between 4639 and 7669 kg-N month^{-1}. The relative contributions of the different N species vary seasonally. During winter months, the greatest contribution is given by the deposition of N–NO_2 and N–NO_3^- aerosol, mainly controlled by the frequency of offshore winds and the NO_x oxidation rates. In summer, the greatest photochemical activity of the atmosphere leads to a greater contribution of gaseous N–HNO_3 deposition which can be 6 times higher than its contribution in winter.

The variation of monthly total N deposition between years is within the range 10–110%. The results show that the interannual variability of atmospheric conditions may lead to an interannual variation of monthly dry deposition of total nitrogen which can reach 160%. The main factors controlling these variations are the frequency of winds towards the river, the photochemical activity of the atmosphere and the frequency of unstable atmospheric conditions. On the other hand, the interannual variation of monthly N wet deposition is always significant (it varies between 60% and a factor of 124), suggesting the need of several years of meteorological input data when estimating monthly N deposition. In the study area, the greatest interannual variability of wet deposition was not reflected in total deposition values due to its low contribution.

Acknowledgements

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