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Factors controlling sea salt abundances in the urban atmosphere of a coastal South American megacity

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HIGHLIGHTS

- Sea salt is always present in $PM_{2.5}$ and $PM_{2.5-10}$ of the Buenos Aires aerosol.
- Oceanic influence under local and regional meteorological conditions is ratified.
- The ratio $\{[Cl^-]+[Mg^{2+}]+[Na^+]\}/PM$ best expresses variability in sea salt levels.
- Simple mathematical tools provide robust results to characterize sea salt patterns.
- Significant Cl^- depletion was registered from both, $PM_{2.5}$ and $PM_{2.5-10}$.

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ABSTRACT

The South Atlantic oceanic influence in the ambient air of Buenos Aires was studied on the basis of the measured concentrations of Cl^-, Mg^{2+} and Na^+, as chemical markers of marine aerosols. A total of 113 fine ($PM_{2.5}$) and 113 coarse ($PM_{2.5-10}$) samples were collected over a one-year period in an inland sampling site located ~250 km from the open sea and ~7.5 km from the shore of the La Plata River, which flows into the Atlantic Ocean. The ratio $r_{ion\text{-}PM}$ between the added concentrations of the three ions and the corresponding aerosol mass concentration was also used as a sea salt indicator. The behavior of these indicators under various meteorological conditions was used to identify and characterize the presence of sea salt in the urban aerosol. The influence of regional meteorological conditions was assessed by means of the Potential Source Contribution Function (PSCF) while that of local conditions was assessed by categorized percentile distributions analysis. The pattern of the PSCF for different ranges of the four sea salt indicators, exhibiting a transition from lowest values under continental influence to highest values under oceanic influence, provided robust evidence that the marine aerosol from the South Atlantic Ocean reaches the city of Buenos Aires. The $r_{ion\text{-}PM}$ ratio, which combines the opposite effects of wind speed on the aerosol mass and ion concentrations, was identified as the most sensitive indicator of sea salt aerosol variations. Percentile distributions of the $r_{ion\text{-}PM}$ ratio, disaggregated according to onshore (NE, E, SE, S) and offshore (N, NW, W, SW) winds and speeds above and below the median (4.3 m s^{-1}), clearly indicated that the highest levels of marine aerosol occurred under onshore winds and wind speeds > 4.3 m s^{-1}. In addition to characterizing the oceanic influence in Buenos Aires, we reported the expected sea salt levels under different conditions and estimated the magnitude of chloride depletion. This is the first study on sea salt levels in the urban atmosphere of this coastal megacity that reports and makes available a set of consistent concentrations of marine aerosol markers measured over a one-year period.

1. Introduction

The primary marine aerosol is produced by wind stress at the ocean surface resulting in the mechanical generation of sea-spray aerosol (O'Dowd and de Leeuw, 2007). Sea salt consists

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predominantly of chlorine (Cl) and sodium (Na) and carries also other chemical elements (Millero, 2004). Sea salt aerosol (SSA) plays an important role in many physical and chemical atmospheric processes at urban, regional and global scales. It influences radiative transfer directly by scattering solar radiation and indirectly by forming cloud condensation nuclei (CCN) and increasing cloud-top reflectivity (Yoon and Brimblecombe, 2002). When the halogens that are bound in the atmospheric particles are released to the atmosphere they play a significant role in atmospheric chemistry by intervening in a number of chemical reactions. Chlorine may be mobilized from SSA by: (*i*) the release of gaseous hydrochloric acid (HCl) through the reaction of sodium chloride (NaCl) with gaseous acids, particularly nitric or sulphuric acids (HNO_3, H_2SO_4); (*ii*) the formation of gaseous dichloride (Cl_2) through reactions of hydroxyl (OH^-) with Cl^- at the air water interface of deliquesced NaCl; and (*iii*) heterogeneous reactions at the surface of SSA, especially with nitrogen oxides that can promote the release of compounds such as nitrosyl chloride (ClNO) (Finlayson-Pitts, 2003; von Glasow, 2008).

The chlorine species released to the atmosphere from SSA take part of the inorganic halogen chemistry, which is closely intertwined with the complex chemical cycles that form and remove ozone from the troposphere (Finlayson-Pitts, 2003). Osthoff et al. (2008) have recently identified nitryl chloride ($ClNO_2$), mainly produced by the night–time reaction of dinitrogen pentoxide (N_2O_5) with chloride containing aerosol as a key precursor for enhanced ozone formation after sunrise.

For air quality assessment in coastal areas, it is necessary to take into account the large gradients in SSA levels along sea-inland directions. This feature is considered in a number of regional models, which include a description of sea salt. However, the verification of these models is severely hampered by the limited number of available ground-based measurements worldwide (Manders et al., 2010). This scarcity of data may be associated with the relatively low attention that air pollution researchers, traditionally more concerned with health impacts, have paid to the relatively benign SSA (White, 2008). Despite this situation, recent studies in Europe and the United States compiled measurements of concentrations of sea salt markers in aerosols collected in a significant number of ground-based monitoring sites. Manders et al. (2010) compiled Na concentrations measured in 89 sites distributed in 16 European countries to assess the spatial variability of sea salt concentrations and to provide a basis for the validation of a regional air quality model used to simulate sea salt distribution. White (2008) assessed the adequacy of using Cl^- as a SSA marker using the chemically speciated fine-particle concentrations measured at about 170 rural or remote sites from the IMPROVE network (interagency monitoring of protected visual environments) in the United States.

Assessments about the air quality situation of the metropolitan area of Buenos Aires (MABA) and other South American cities have also mostly overlooked SSA. In Buenos Aires, the city government operates an air pollution monitoring network, which reports carbon monoxide, nitrogen oxides and PM_{10}. Practically all information about $PM_{2.5}$ in the MABA has been reported by researchers (e.g., Magallanes et al., 2008 and references therein). Only three of these studies have considered the concentration of Na^+, Cl^- and other ions composing the SSA (Bogo et al., 2003; Magallanes et al., 2008; Dos Santos et al., 2009). Bogo et al. (2003) reported concentrations of eight ions in 30 PM_{10} samples collected in Buenos Aires between December 1998 and September 1999; levels of Cl^- and Na^+ were in the ranges 3.9–6.7 μg m^{-3} and 1.0–3.8 μg m^{-3}, respectively. The authors postulated a marine influence, based on the relatively high levels of Cl^- and Na^+ when compared to reference levels in the United Kingdom. Magallanes et al. (2008) applied a new multivariate analysis technique to a set of ion profiles of 18 PM_{10} samples. They identified three clusters; one of them contained the three samples with the highest Cl^- and Na^+ concentrations associated with back-trajectories mostly over the South Atlantic Ocean. Dos Santos et al. (2009) reported the concentration of 12 elements and four ions measured in 226 samples collected during a one-year monitoring campaign. The authors identified significant correlations in $PM_{2.5–10}$ (soluble fraction) of Cl^- with Na^+ and Mg and indicated that Na^+ and Cl^- were predominantly associated with $PM_{2.5–10}$. Although these studies reported valuable data about the ionic species present in the local aerosol, they did not advance in analyzing the role of SSA in the atmosphere of Buenos Aires.

This paper presents an analysis of the concentrations of chemical sea salt markers (Cl^-, Mg^{2+} and Na^+), measured by Dos Santos et al. (2009). It provides information on the distribution of sea salt in $PM_{2.5}$ and $PM_{2.5–10}$ in the MABA and examines the main local and regional meteorological conditions associated with sea salt abundances in the local urban atmosphere. The concentrations of ions analyzed constitute a unique set of ground-based observational data that together with the associated SSA estimates and, possibly combined with ship-based measurements, may be useful for the verification of regional transport models in areas influenced by the South Atlantic Ocean.

2. Studied area

The MABA is composed by the city of Buenos Aires (34°38′S, 58°28′W) and 24 neighboring districts (Fig. 1a). It has a surface of ~3800 km^2 and a population of ~16 million, which ranks it as the 11th megacity in the world and the third in Latin America. The MABA is located on the southern shore of the La Plata river (Río de la Plata), which has a funnel shape; ~300 km in length, oriented northwest to southeast. The limit between the Río de la Plata and the Atlantic Ocean has been defined as the line joining Punta del Este, Uruguay (34°58.5′ S, 54°57.5′W) and Cabo San Antonio, Argentina (36°18′S, 56°46′W) (Fig. 1b).

The estuary is characterized by high susceptibility to atmospheric forcing because of its large extension and shallow water depth. Guerrero et al. (1997) have characterized the seasonal influence of wind pattern on surface salinity distribution, with spring–summer dominated by onshore winds (NE, E, SE, and S), and fall–winter characterized by a balance between onshore and offshore winds (N, NW, W, and SW). For our purpose, the upriver marine influence may be simply characterized by the isolines of 5–10 su (salinity units, as reported by Guerrero et al., 1997) and the outer zone with salinity between 25 and 30 su (Fig. 1b).

Local climate is under the influence of the seasonal behavior of the semi-permanent systems, particularly, the subtropical South Atlantic anticyclone (SAA) and synoptic and mesoscale events, such as fronts and convective storms. Air moisture has high values throughout the year, with a slight increase in winter. The prevailing wind directions are in the NE to S sector, due to the influence of the SAA and the coastal location, during most of the year.

Air pollution potential in the Buenos Aires air shed was characterized in climatological studies in terms of mixing height and ventilation factor (Ulke and Mazzeo, 1998; Ulke, 2004). The estimated mean daytime mixing heights are 936 m in summer and 457 m in winter, and the annual mean is 695 m. These values are smaller than the critical one (1500 m) indicative of a reduced boundary layer for pollutants' dilution. The moderate intensities of wind speed translate to the mean ventilation factors, which are 11,000 m^2 s^{-1} in summer and 5500 m^2 s^{-1} in winter. The probabilities of reduced ventilation are 71% in winter and 55% on an annual basis.