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A first record of bulk atmospheric deposition patterns of major ions in southern South America

D. A. Carnelos · S. I. Portela · E. G. Jobbágy · R. B. Jackson · C. M. Di Bella · D. Panario · C. Fagúndez · J. M. Piñeiro-Guerra · L. Grion · G. Piñeiro

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Abstract Despite the importance of long-term atmospheric deposition of ions for vegetation productivity and biogeochemistry, southern South America lacks long-term deposition records. We report a 6-year-long record of atmospheric deposition measurements of Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and NH_4^{+} in the plains of southern South America, which encompass one of the most important agricultural basins and urban clusters of the continent. After establishing a deposition measurement network across four sites in Argentina and Uruguay, we collected bulk atmospheric deposition monthly form January 2007 through December 2012 in an east–west transect of 700 km. Spatial changes in the sea-salt component of atmospheric deposition were primarily associated with proximity to the sea—as observed in other regions of the world—whereas non-sea-salt components of atmospheric deposition of terrestrial origin were primarily associated with the size of the human population surrounding collection sites. Atmospheric deposition showed a strong interannual variability (CV 50%) mainly associated with variations in the non-sea salt components of terrestrial origin and were within observed values for other relatively unpolluted sites of South America and globally. However, atmospheric deposition appears to be increasing in

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D. A. Carnelos (✉)
Facultad de Agronomía, Catedra de Climatología y Fenología Agrícolas, Universidad de Buenos Aires, Buenos Aires, Argentina
e-mail: carnelos@agro.uba.ar

D. A. Carnelos · J. M. Piñeiro-Guerra · L. Grion · G. Piñeiro
LART- Laboratorio de Análisis Regional y Teledetección, Buenos Aires, Argentina

D. A. Carnelos · J. M. Piñeiro-Guerra · L. Grion · G. Piñeiro
Departamento de Recursos Naturales y Ambiente, Facultad de Agronomía, Catedra de Ecología, Universidad de Buenos Aires, Buenos Aires, Argentina

D. A. Carnelos · J. M. Piñeiro-Guerra · L. Grion · G. Piñeiro
CONICET - Universidad de Buenos Aires, Instituto de Investigaciones Fisiológicas y Ecológicas vinculadas a la Agricultura (IFEVA), Buenos Aires, Argentina

S. I. Portela
Estación Experimental Agropecuaria Pergamino, INTA (Instituto Nacional de Tecnología Agropecuaria), Buenos Aires, Argentina

E. G. Jobbágy
Grupo de Estudios Ambientales, IMASL, CONICET & Universidad Nacional de San Luis, San Luis, Argentina

the region, particularly for SO_4^{2-} and other ions around Buenos Aires, Argentina, which may represent an early warning of increased air pollution in the area. Average annual regional deposition of sulfate (SO_4^{2-}) was 12.7 kg S hectare^{-1} and nitrate (NO_3^-) was 9.2 kg N hectare^{-1}. Weighted average concentrations of base cations (sum of Mg^{2+}, Ca^{2+}, Na^+ and K^+) was 0.27 mg L^{-1}, and weighted average concentrations of SO_4^{2-}, NO_3^- and NH_4^+ were 0.094, 0.018 and 0.046 mg L^{-1}, respectively. Our work highlights the need for long-term networks recording atmospheric deposition in the region, increasing knowledge of nutrient cycling and establishing a baseline for future atmospheric pollution measurements.

Keywords Atmospheric deposition · Soluble ion · Regional patterns

Introduction

Atmospheric deposition is a key component of nutrient cycling in ecosystems and helps determine and trace biogeochemical fluxes in the land at multiple scales. By definition, deposition includes the flux of a chemical compound to the earth's surface dissolved in rain water (wet deposition) and the flux of trace gases and particles via turbulent exchange and gravitational settling followed by the interaction with exposed surfaces (dry deposition) (Schlesinger 2000; Fowler et al. 2009; Vet et al. 2014). Bulk atmospheric deposition (the sum of wet plus dry deposition) is one of the major pathways of nutrient inputs to ecosystems and contributes to the spatial redistribution of elements across landscapes and regions (Baker et al. 2007). Human activities have modified the chemical composition of the atmosphere and thus atmospheric deposition, causing extensive alterations in the biosphere's functioning (Holland et al. 1999; Conradie et al. 2016; Xing et al. 2017). In this sense, temporal or spatial comparisons of deposition throughout the world have been crucial to detect the imprint of human activities on biogeochemical cycling and ecosystem functioning (Migliavacca et al. 2005; De Souza et al. 2006; Marticorena et al. 2017; Xing et al. 2017).

While numerous studies have quantified atmospheric deposition in other regions, to our knowledge, there is only one long-term record for southern South America, a study performed in Torres del Paine, between 1984 and 1993 in a national park of Southern Chile (Galloway et al. 1996). In the United States and Europe there are extensive networks that periodically collect atmospheric deposition, such as the National Atmospheric Deposition Program (NADP) (http://nadp.sws.uiuc.edu/Default.aspx) (Rogora et al. 2006; Padgett and Minnich 2008; Vet et al. 2014). These records have provided the foundation for numerous studies quantifying the spatial and temporal distribution of element inputs to ecosystems, with important implications for agriculture and conservation (e.g., Munger and Eisenreich 1983). In addition, continuous monitoring of atmospheric deposition allows the detection of temporal trends in environmental quality, such as changes in acid deposition or other pollution processes associated with human activities (Walker et al. 2000; Fowler et al. 2009; Fayiga et al. 2017; Geilfus 2019). In southern South America, a limited number of short-term studies report deposition for a particular location and for one or few ions (Lavado 1983; Hedin et al. 1995; Zunckel et al. 2003). These

R. B. Jackson
Department of Earth System Science, Woods Institute for the Environment, and Precourt Institute for Energy, Stanford University, Stanford, CA, USA

C. M. Di Bella
Instituto de Clima y Agua, CIRN-CNIA- INTA Castelar, Buenos Aires, Argentina

C. M. Di Bella
Departamento de Métodos Cuantitativos y Sistemas de Información, Facultad de Agronomía, Universidad de Buenos Aires, Buenos Aires, Argentina

D. Panario
UNCIEP, Instituto de Ecología y Ciencias Ambientales (IECA), Facultad de Ciencias, Universidad de la República, Montevideo, Uruguay

C. Fagúndez
CURE, Centro Universitario Regional del Este, Sede Rocha, Universidad de la República, Rocha, Uruguay

G. Piñeiro
Grupo de Ecología, Departamento de Sistemas Ambientales, Facultad de Agronomía, Universidad de la Republica, Montevideo, Uruguay

short-term studies have highlighted particular elevated deposition events in the region (Lara et al. 2001).

Regional studies of atmospheric deposition in southern South America are almost completely lacking. Studies in the United States and elsewhere show that atmospheric deposition in coastal areas is primarily composed of Cl^-, Na^+, Mg^{2+} and SO_4^{2-} transported from ocean to land (marine origin) (Junge and Werby 1958; Hedin et al. 1995; Vet et al. 2014). In contrast, inland (or continental) atmospheric deposition typically has higher concentrations of elements transported from soils, such as Ca^{2+} and K^+ (terrestrial origin) (Young et al. 1988; Sequeira 1993). Ions can be loaded to the atmosphere from natural sources, either marine or terrestrial, or from anthropogenic ones, including industrial sources such as fossil fuel burning or agricultural activities associated with livestock, croplands, and fertilizers (Loye-Pilot and Morelli 1988; Zunckel et al. 2003; De Souza et al. 2006). For elements emitted from both ocean (sea-salt origin) and terrestrial sources, it is often possible to discriminate the portion coming from each source. The proportion of an element that is emitted from the ocean (sea-salt origin) can be estimated using the ratio of the ion to a reference element (usually Cl^- or Na^+) that is assumed to come only from the ocean (Keene et al. 1986; Vet et al. 2014). The spatial redistribution of chemical compounds that are emitted from the earth's surface depends on the distance traveled before redeposition, which is mainly determined by the intensity and direction of winds and the average residence time of the ions in the atmosphere (Schlesinger 2000; Wei et al. 2017). These proportions change for different ions with different sources of emissions in the region and different mean residence times in the atmosphere. Both the residence time and the origin of the ion will determine the pattern of spatial and temporal deposition.

The aim of this paper was to quantify atmospheric deposition of major ions (Mg^{2+}, Ca^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^- and NH_4^+) in the Rio de la Plata region of Argentina and Uruguay. We measured atmospheric deposition for 6 years across four sites spanning a 700-km gradient. We report temporal and spatial distributions and changes, characterizing atmospheric deposition in this poorly studied region. We hypothesize that regional differences in atmospheric deposition between sites (spatial variation) will be greater than changes across years (temporal variation) because we expect atmospheric deposition in the region to be dominated by relatively constant local sources.

Materials and methods

Study area

Southern South America has two semi-permanent anticyclones that are located at $\sim$ 30° south latitude, on both sides of the South American continent over the oceans. A low-pressure system known as the depression of Northwest Argentina (DNOA) occurs in the northern portion of Argentina, with dominant air flows coming from the West around 35° latitude south (Erich 1980). There is a transition zone in the north of Patagonia where this flow is maintained in winter but changes to the north in summer. Precipitation in the region occurs mainly as fronts, with some convective storms in summer. The average precipitation varied from 1000 to 1300 mm $year^{-1}$ over 1991–2000 timeframe (Murphy et al. 2008).

Bulk atmospheric deposition sampling

We established an atmospheric deposition network in Argentina and Uruguay (Fig. 1) in an east–west transect of 700 km, including two large cities (Buenos Aires and Montevideo), a small village near the Atlantic Ocean (La Paloma in Rocha department) and a town located in an inland agricultural site (Pergamino). Atmospheric deposition samplers collected bulk deposition (sum of wet and dry) monthly for 6 years, from January 2007 to December 2012 at all sites. Collectors were installed 1.5 meters above ground level. They were constructed using 3-l amber glass bottles with a 10 cm-diameter glass funnels on top and a 100-micron stainless steel mesh fitted in the bottom of the funnel. The steel mesh kept the water collected clean inside the bottle and reduced evaporation. Evaporation from the collectors was relatively small based on the close correspondence between precipitation depth computed from the collection volume and rainfall measured at nearby weather stations (see Fig. SP1). Bottles were placed into PVC tubes to minimize the impact of sunlight.

A total of four collectors (subsamples) were installed at each site and any contaminated samples

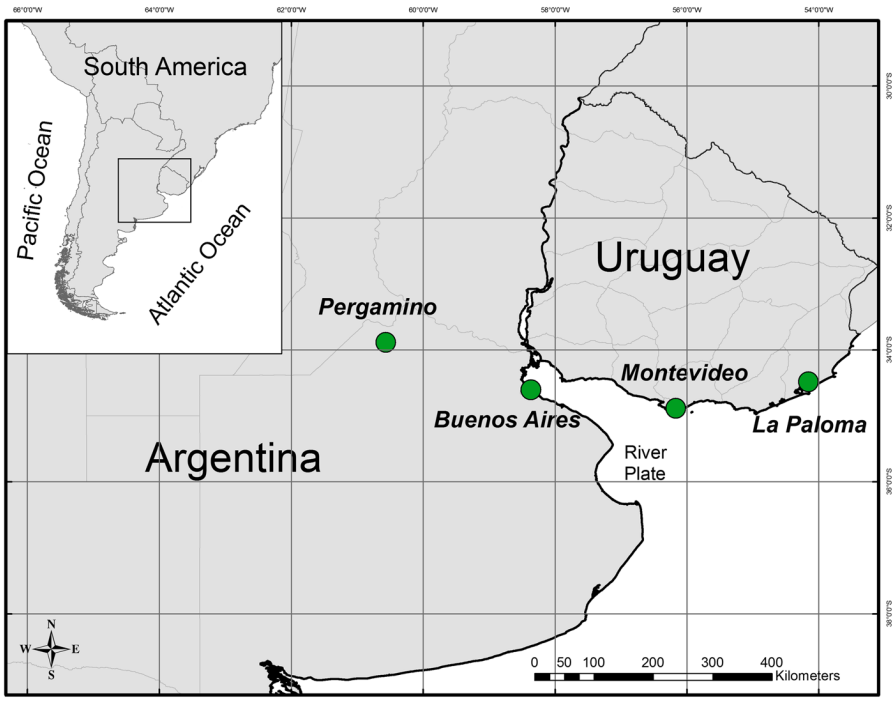

Fig. 1 Location of the four sites included in the atmospheric deposition network. Sites were established in Montevideo (Uruguay) and Buenos Aires (Argentina) cities, and in the towns of Pergamino (Argentina) and La Paloma (Uruguay)

(i.e. by birds faces, insects, etc.) were discarded. Rainwater was collected monthly. Bottles, funnels and 100-micron filters were washed after each collection interval using a laboratory detergent followed by 18 megaohm deionized water. Bottles were additionally rinsed with 5% HCl and rinsed with 18 megaohm deionized water. In the initial years of the project, thymol was added (0.4 mg) to two of the four bottles during some months to see if microbial degradation of the samples was occurring during the 1-month sampling interval. Thymol is a biocide that prevents the growth of algae and bacteria that may consume nutrients (Ayers et al. 1998). There were no significant differences between the concentrations of most ions in the collectors with or without thymol and because of the difficulty related to its manipulation, its use was discontinued. However, ammonium concentrations were significantly higher in thymol treated samples (Table SP2) and ammonium concentrations in non-thymol samples were corrected for this bias using the following equation:

$$NH_4^+ \text{ corrected } \left(\text{mg L}^{-1}\text{year}^{-1}\right) = NH_4^+ \text{ uncorrected } \left(\text{mg L}^{-1}\text{year}^{-1}\right) \cdot Z \quad (1)$$

where Z was the estimated bias in Table SP2; 1.91 for the region.

Fifty-ml samples were obtained from each collector and immediately filtered through a combination of a 0.70 micron Versapor 800 membrane and a 0.45-micron nylon membrane to remove suspended particles to preserve the samples (Ayers et al. 1998; Michel 2012). When there were no rains during the month, the 50-mL sample was obtained from the rinsing of the bottles with 100 ml of 18 megaohm deionized water (which would represent dry deposition). Samples were transported and stored in the dark at 5 °C. Cation concentrations were analyzed (Mg^{2+}, Ca^{2+}, Na^+ and K^+) by an Atomic Absorption Spectrophotometer (AAnalyst 300 Perkin Elmer Laboratory for Special Analytical Services, LAB-FAUBA). Ten milliliter subsamples were sent to Duke University, USA, and analyzed for Cl^-, SO_4^{2-}, NO_3^- concentration by ion chromatography and NH_4^+ concentration with a continuous flow meter (QuikChem 8000, Lachat instruments).

To estimate the proportion of non-sea-salt (nss) ion concentration in a sample (the proportion of total atmospheric deposition of a particular ion that was not emitted from the ocean), we used the observed concentrations of Cl^- as a reference element (Keene et al. 1986). Therefore, we assumed that all Cl^- in the collected samples had a seawater origin because the

distance from the site that is closest to a possible ground source of chloride (600 km) is greater than the distance from this site to the sea (400 km) (i.e., it is unlikely that Cl^- will be deposited from terrestrial origin). The non-sea-salt concentration of anion "X" was calculated based on the following equation:

$$[X_{nss}] = [X_{sample}] - \left\{ \left[Cl^-_{sample} \right] \times \left(\frac{X}{Cl^-} \right)_{seawater} \right\} \quad (2)$$

where X_{nss} is non-sea-salt concentration of element "X"; X_{sample} is the concertation of element "X" in the water sample, Cl^-_{sample} is the concentration of Cl^- in the water sample and $X/Cl^-_{\ sea\ water}$ is the ratio of element "X" to Cl^- in sea water (using average values of oceans reported by Schlesinger 2000). The proportion of the element coming from the ocean (sea-salt component) was estimated by subtracting the non-sea-salt component to the total deposition recorded.

Statistical analysis

Monthly deposition rates were estimated as the product of the concentration and the amount of monthly rainfall recorded at nearby weather stations. Annual bulk deposition values were the sum of monthly deposition during each year. Analysis of variance (ANOVA) was used to compare the annual bulk deposition values between sites and Tukey's range test was used for mean comparisons. Spatial and temporal variations of bulk atmospheric deposition were evaluated through principal component analyses (PCA). PCA is a descriptive multivariate analysis that allows sorting the differences and similarities between sites and years separately. To study spatial patterns of atmospheric deposition, a PCA was performed for all sites separately and averaging across years. Finally, potential trends in atmospheric deposition were evaluated by regression analysis between annual bulk deposition values and time (years).

Results

Spatial variations in bulk atmospheric deposition

The influence of the ocean dominated the observed patterns. For example, the sea-salt components of atmospheric deposition decreased with distance from the ocean for all elements (from La Paloma, the closest site to the ocean, to Pergamino, the farthest away), whereas the non-sea-salt components were relatively constant across sites, and usually higher in Buenos Aires, the most populated site (Fig. 2). Elements such as Na^+, Cl^- and Mg^{2+} had higher proportions of sea-salt than non-sea-salt components, suggesting a mainly marine origin, and showed very high deposition rates in sites closer to the ocean (Fig. 2a–c). On the other hand, Ca^{2+} and K^+ had higher proportions of non-sea-salt components in all sites, suggesting an important terrestrial origin (Fig. 2d, e). SO_4^{2-} had higher proportions of sea-salt in La Paloma but a higher non-sea-salt component in the other sites, suggesting that sulfates came from both marine and terrestrial sources (Fig. 2f). Finally, NH_4^+ and NO_3^-, which are not typically released from the ocean but primarily from the land, did not show strong differences in deposition across sites (Fig. 2g, h).

In the principal component analysis, where single deposition collections (sites × period) are "sorted" according to the relative contribution of each ion to the total deposition, the four sites were separated in the first axis displaying a clear marine-terrestrial gradient The first PCA axis (CP1) explained 62.8% of the total data variation and displayed a strong correlation with distance from the ocean ($r = -0.81$). Therefore, Pergamino and Buenos Aires had similar ion deposition patterns, with elevated deposition of terrestrial ions, whereas Montevideo and La Paloma had higher relative deposition of elements of marine origin (Cl^-, Mg^{2+} and Na^+) (Fig. 3a). Buenos Aires was characterized by atmospheric deposition with higher proportions of Ca^{2+}, K^+, SO_4^{2-} and NH_4^+. As expected, La Paloma showed the highest proportion of marine ions relative to other elements, followed by Montevideo. Montevideo had higher deposition of terrestrial elements during winter, whereas this pattern was the opposite in La Paloma, though somewhat weaker. On the other hand, Pergamino and Buenos Aires (to a lesser extent), had elevated proportions of Na^+, NH_4^+, NO_3^- during summer in their deposition and higher proportions of Mg^{2+}, Ca^{2+} and SO_4^{2-} deposition in winter (Fig. 3a, see PCA axis 2). The relatively high proportion of terrestrial Na^+ in the atmospheric deposition of Pergamino during summer was surprising and responsible for the second PCA axis (Fig. 2a, 3a).

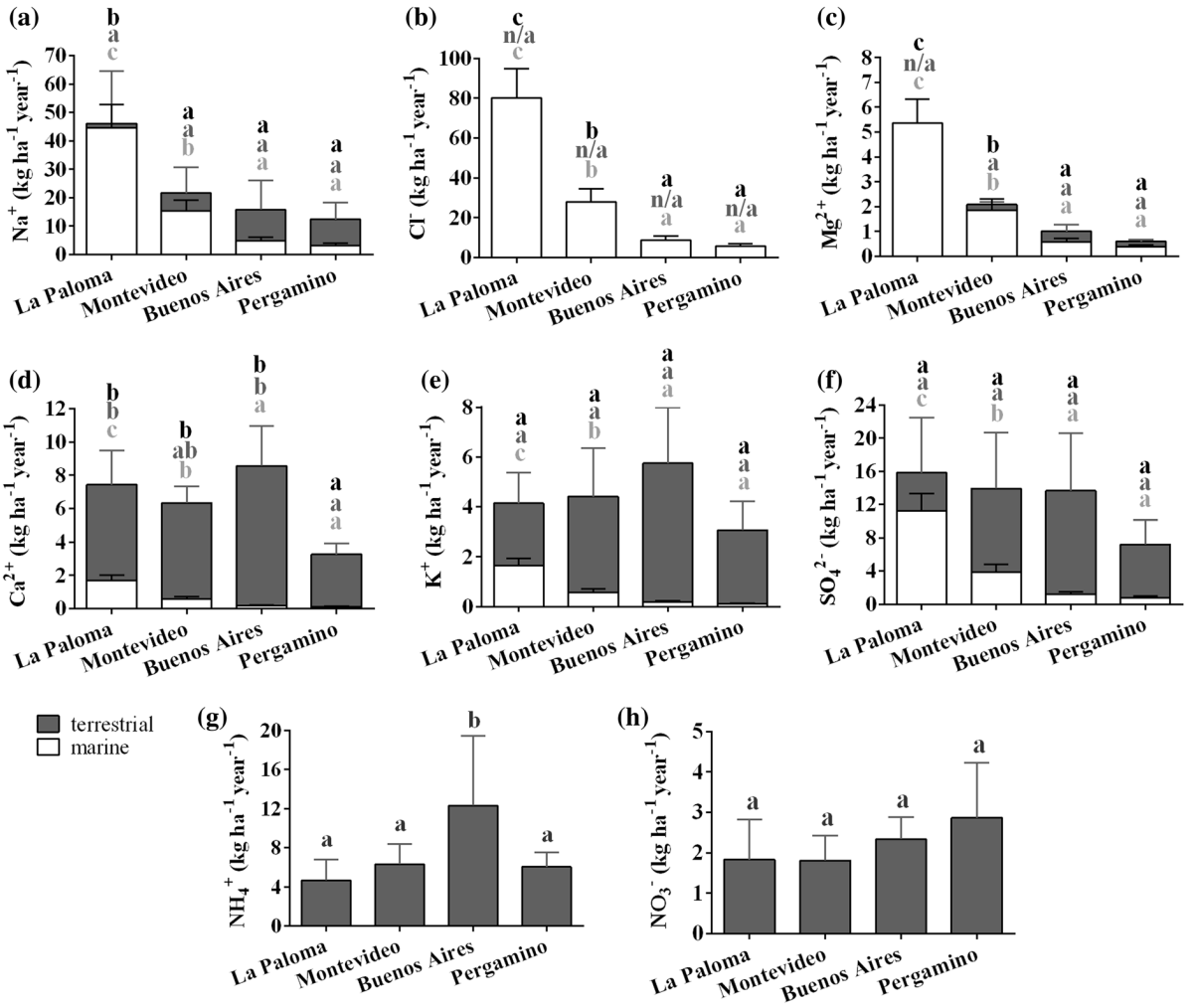

Fig. 2 Annual bulk atmospheric deposition partitioned into non-sea-salt (grey) and sea-salt components (white) for each ion at the four study sites. Sites are sorted according to their distance from the sea, with La Paloma being the closest and Pergamino the farthest (Fig. 1). Values are 6-year averages from 2007 to 2012. Black letters show significant differences between mean atmospheric deposition of ions. Dark gray letters show significant differences between the mean values of atmospheric deposition of the non-sea-salt components (terrestrial origin) and light gray letters show significant differences between sea-salt components (marine origin). NH_4^+ and NO_3^- are considered non-sea-salt ions and Cl^- is considered to be completely derived from ocean emissions

Temporal trends in bulk atmospheric deposition

Atmospheric deposition appeared to increase with time across the 6-year sampling period from 2007 through 2012. In particular, SO_4^{2-} had a 3.3-fold increase in Buenos Aires (SO_4^{2-}), which was not explainable by trends in precipitation quantity (Figs. 4f, i). Atmospheric deposition of marine elements such as Na^+, Cl^-, and Mg^{2+} doubled in Buenos Aires over the 6-year period (Fig. 4a–c). Deposition of some elements, such as Na^+, increased 3.5 times during 2009, a wetter year, compared to 2008, a drier year. A similar pattern was observed for SO_4^{2-} which also increased its deposition in 2009 and 2012 (wet years) that were 2.4 and 3.3 times greater than in 2007. However, atmospheric deposition was only occasionally associated with precipitation amount for a few ions and at some sites (see Supplementary Material Figures SP2). Terrestrial ions had different patterns of variation over time at each site. Ca^{2+} increased 1.2-times in Buenos Aires during the study period and slightly in Pergamino and Montevideo (near 40%),

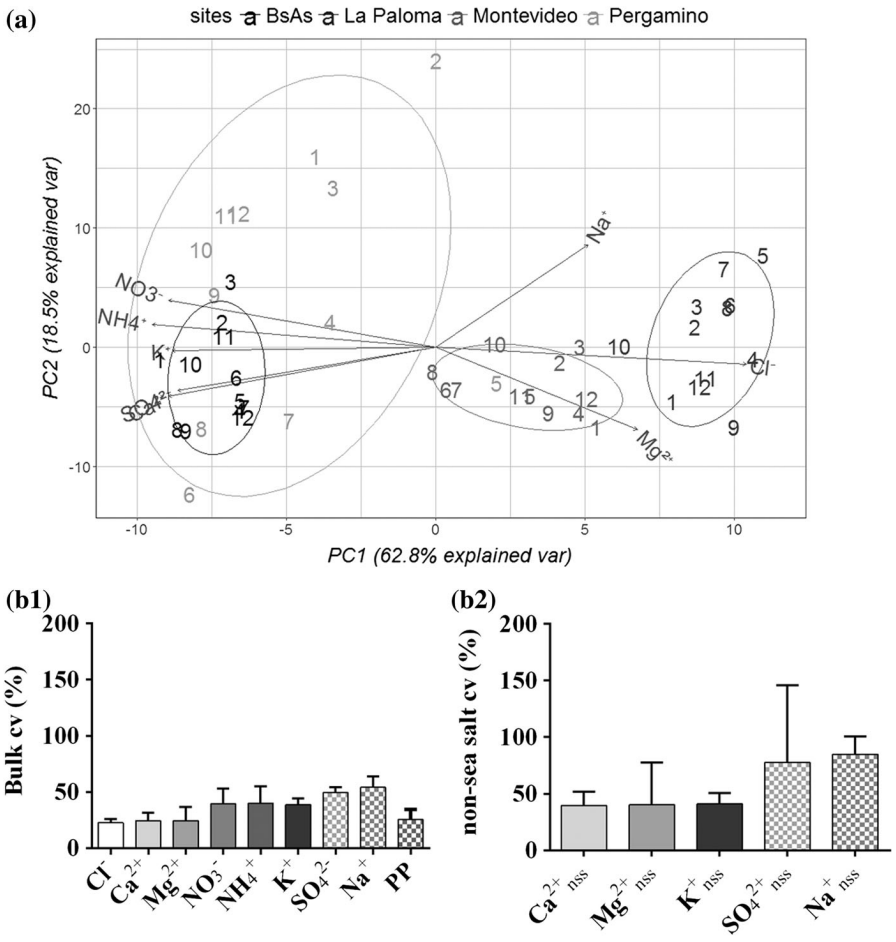

Fig. 3 Panel a, principal component analysis (PCA) scatter plot of monthly bulk atmospheric deposition at each site (spatial analysis). Each number in the plot represents the average atmospheric deposition of a site in one particular month, from January = 1 to December = 12 (average deposition of the 6 years studied). The grey arrows indicate the relative contribution of each ion in the PCA axes. Panel b, interannual coefficient of variation (CV) of atmospheric deposition of each ion studied. Panel b1 shows the average CV for total deposition and panel b2 shows average CV for the non-sea-salt component of the deposition

whereas NH_4^+ deposition decreased in La Paloma (0.7 times lower than in 2007) but had variable trends at the other sites (Fig. 4d, h). SO_4^{2-}, Na^+ and NO_3^- showed a deposition peak during 2009 in most of the sites. Finally, K^+ had a similar increase during 2009 but only in the two larger cities evaluated, a 70% increase in Montevideo and 1.4-fold increase in Buenos Aires.

Most ions showed strong interannual variations that can be mainly attributed to variations in their non-sea-salt components of deposition (Figs. 3b1, 2). Chloride, considered to be derived from marine sources, had the smallest interannual coefficient of variation for total bulk disposition (22.7%). The interannual variations of non-sea-salt components were higher for Ca^{2+}, Mg^{2+}, SO_4^{2-} (39.7%, 40.2% and 77.5%) and Na^+ (84.7%) but similar for K^+ (41%), suggesting that most of the variation in annual deposition came from terrestrial sources. In addition, the coefficient of variation for precipitation was lower (25.5%) than that of most individual ion's coefficient of variation. The first 2 years of our study period, 2007 and 2008, were similar but differed from the later years, because they had higher relative proportions of Na^+ and SO_4^{2-} compared with the other elements. This pattern may be associated with the severe drought that occurred in 2008 (Fig. 4i), but also to the increases in Na^+ and SO_4^{2-} deposition that occurred across the study period (see Fig. 4f). Finally, precipitation records obtained on-site or from nearby weather stations do not seem to show a clear trend in time and showed similar rainfall patterns across all sites (see Fig. 4i).

Discussion

As observed in other regions of the world, spatial changes in the sea-salt component of atmospheric deposition were mainly associated with proximity to

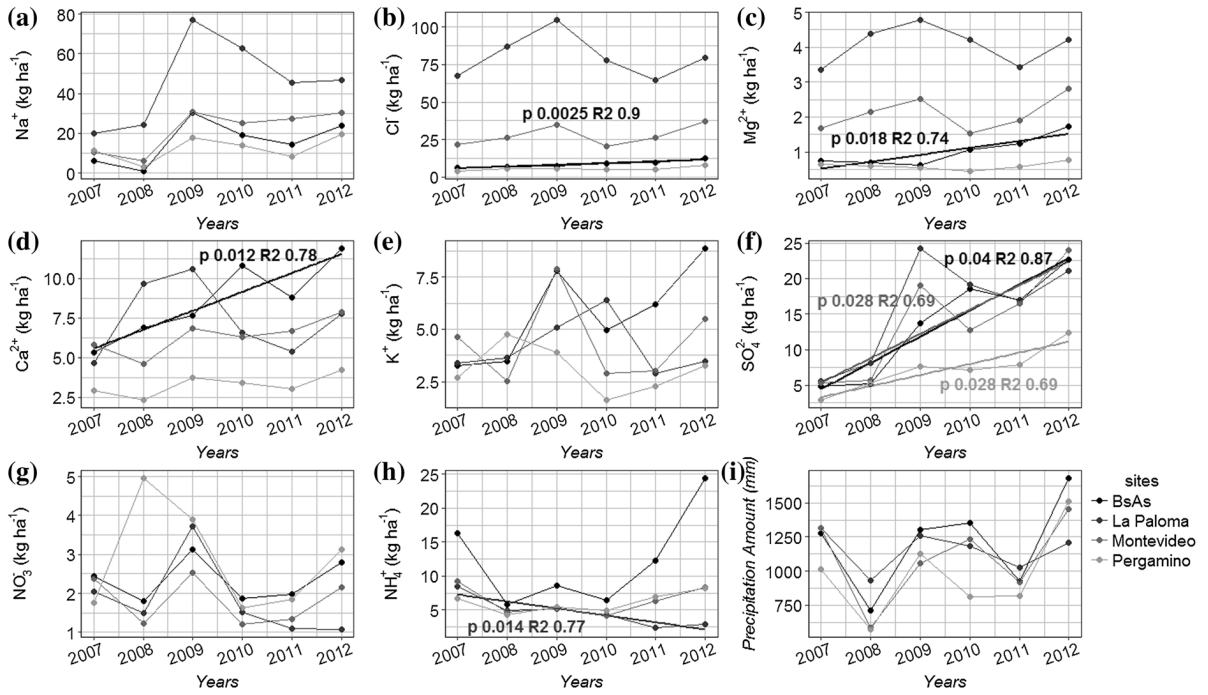

Fig. 4 Trends in annual bulk atmospheric deposition of different ions and precipitation depth from 2007 to 2012 for each site. Regression lines are shown only for the elements and sites with statistically significant regression parameters

the sea, whereas non-sea-salt components of atmospheric deposition (of terrestrial origin) were mainly associated with the size of the human population surrounding collection sites. Atmospheric deposition of marine elements, Cl^-, Mg^{2+} and Na^+, were an order of magnitude higher in coastal than in continental sites, consistent with previous short-term measurements (Hedin et al. 1995; Norman et al. 2001). As in other studies, variations in atmospheric deposition between sites were lower for terrestrial elements than marine elements (Conradie et al. 2016; Nanus et al. 2017; Norouzi et al. 2017). In our sites the ocean accounts for one-fourth to more than three-fourths of the deposition (La Paloma, 85%, Montevideo, 62%, Buenos Aires 25%, Pergamino, 27%). Similar proportions were found in South Africa, where marine contribution from the Indian Ocean accounted for 37% and 6% of the deposition 140 km and 490 km away from the coast, respectively (Conradie et al. 2016).

The relative proportions of elements deposited help to characterize the origin and emission sources of elements. Atmospheric deposition of exclusively marine origin should have a similar stoichiometry to seawater (Connors and Kester 1974; Schlesinger 2000). On the other hand, if ions come from terrestrial sources their stoichiometry will be more similar to that of soils (Jobbágy and Jackson 2001) or plants. To compare the stoichiometry of atmospheric deposition in our study sites we searched in the literature for bulk deposition measurements reported for sites in South America. Based on their stoichiometry, rainwater from La Paloma, located on the coast, had a similar stoichiometry as the ocean, and rainwater from Montevideo, which is located on a transition zone between the river and the ocean, had a similar stoichiometry to Sinhagad, a rural site located 100 km away from the Arabian Sea coast in India (Norman et al. 2001).

Buenos Aires is located on the shores of Rio de la Plata (fresh water), 250 km away from the ocean, and had a similar atmospheric deposition stoichiometry as land sources from vegetation and soil and to other industrial cities reported in the literature. We found a set of cities, mainly inland cities, that all presented similar deposition stoichiometry. Porto Alegre, with a strong petrochemical industry, steelworks, tanneries, coal-fired power stations, and more than 4 million inhabitants (Migliavacca et al. 2005), had a similar stoichiometry toBuenos Aires and Braganca or Campinas other cities with less industrial activities located

in southeastern Brazil (Lara et al. 2001) (Fig. 5). Pergamino, located 450 km from the ocean and surrounded by agricultural lands, was expected to have a lower contribution of elements from marine origin and to have a stoichiometry similar to soils or vegetation. However, unexpectedly, Pergamino showed a high proportion of Na^+ of terrestrial origin. One possible explanation for this result is that the saline-sodic basins in the region near the sampling site dry up during periods of drought, leaving Na^+ salts in the surface soil that are blown by the wind and redeposited in the region. In the alkaline wetland soils of the Pampas, Na^+ is accompanied by bicarbonate rather than choride or suflate (Jobbágy et al. 2017), explaining its departure from the expected stoichiometric of marine aerosols (Losinno et al. 2002); therefore, atmospheric deposition in Pergamino may reflect the very particular ionic imprint of alkaline basins in the principal component analysis (Fig. 5a).

We also compared the total amount of annual atmospheric deposition measured in our study sites with values reported in the literature for southern Brazil and from the total deposition of Global Atmosphere Watch (GAW) of the World Meteorological Organization. Atmospheric loadings in our region were medium to high compared to other sites and with the global assessment of precipitation chemistry and deposition (Vet et al. 2014), mainly due to the elevated contribution of Cl^- and Na^+. La Paloma is the site with the highest total annual deposition across the database (164.4 kg ha^{-1} $year^{-1}$ in total for all ions measured), with a high proportion of Cl^- and Na^+. The deposition of chloride in La Paloma was tenfold greater than in Porto Alegre (Fig. 5). The high levels of atmospheric deposition in La Paloma can be attributed mainly to natural emission sources such as the ocean. Montevideo also showed high values of total annual atmospheric deposition (84.3 kg ha^{-1}), with almost 61% coming from Cl^- and Na^+ (Fig. 5). Buenos Aires and Pergamino had different total annual deposition of 68.1 and 41.1 kg ha^{-1}, respectively. Buenos Aires value was similar to cities of Brazil, such as Campinas (76.5 kg ha^{-1}) and Braganca (67.9 kg ha^{-1}) (Lara et al. 2001), but, these cities showed higher NO_3^- and SO_4^{2-} deposition, suggesting a relatively low contamination due to human activities in Buenos Aires and Pergamino, particularly with NO_3^- (Fig. 5). Porto Alegre, another Brazilian city, located 900 km northeast of Buenos Aires, showed similar proportions of elements, but slightly less amounts of total

Ion	*Pergamino*	Porto Alegre[1]	Braganca[2]	*Buenos Aires*	Campinas[3]	*Montevideo*	*La Paloma*
Ca^{2+}	3.3	9.0	1.9	8.6	2.0	6.3	7.4
Cl^-	5.7	8.8	4.2	8.7	5.5	27.8	80.3
K^+	3.1	4.5	2.7	5.8	2.3	4.4	4.1
Mg^{2+}	0.6	2.1	0.4	1.0	0.5	2.1	4.1
Na^+	12.3	6.0	1.4	15.8	1.8	21.6	46.1
NH_4^+	6.1	11.5	10.0	12.3	8.3	6.3	4.7
NO_3^-	2.9	4.4	26.3	2.3	30.5	1.8	1.8
SO_4^{2-}	7.2	19.6	21.0	13.7	25.6	13.9	15.8
Sum	**41.1**	**65.9**	**67.9**	**68.1**	**76.5**	**84.3**	**164,4**

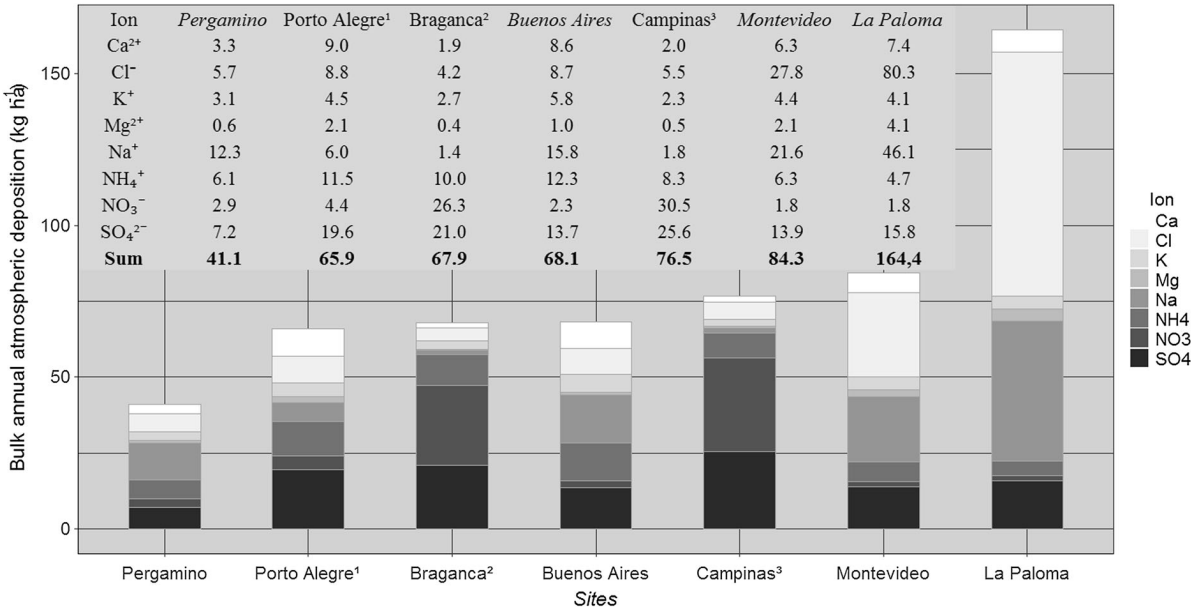

Fig. 5 Annual atmospheric deposition at three different sites in southern Brazil (including our sites). Each bar represents the sum of all ions deposited and grey scale denote the magnitude of each ion. References: 1 (Migliavacca et al. 2005); 2 and 3 (Lara et al. 2001), the other sites are from this study

atmospheric deposition, suggesting a common regional circulation pattern.

Increases in SO_4^{2-} deposition through time were observed in our region (Fig. 4f) and may be attributable to population growth and increased human activities. Buenos Aires had the clearest trend in increasing SO_4^{2-} and also Cl^-, Mg^{2+} and Ca^{2+} deposition through time, probably because it is among the most populated cities in the world with 13.5 million inhabitants (growth of 2.1 million inhabitants between 2001 and 2011) and is projected to grow to 15.5 million people by 2025, increasing projected emissions (Baklanov et al. 2016). Sulfate (SO_4^{2-}) is derived from both anthropogenic (Norman et al. 2001) and natural sources. When it is derived from anthropogenic sources it is generally accompanied by nitrate because both are emitted by the combustion of fossil fuels. However, in our data this association was not observed (Fig. 4). Therefore, the upward trend in SO_4^{2-} deposition in Buenos Aires may not be due entirely to anthropogenic emissions of sulfur.

We report the first long-term records of atmospheric deposition in southern South America, an economically and socially important region of the world. Our work highlights the absence of long-term records of atmospheric deposition in the region. Quantifications of atmospheric deposition increases knowledge of global element cycling and spatial redistribution of material between the oceans and land, including the impacts of human activities such as agriculture and fossil fuel combustion. For example, our data can be used to inform nutrient budgets in agricultural landscapes, with implications for fertilization management and soil conservation. Both the stoichiometry and total amount of atmospheric deposition in southern South America suggest a strong ocean influence. The deposition rates for N and S at our study sites are relatively low compared to more polluted regions of the Northern Hemisphere. However, we detected increases in sulfur deposition at most sites from 2007 to 2012, which suggests an early warning of increased air pollution in the region. The maintenance of atmospheric deposition collection in the region will allow investigators to evaluate patterns in longer timescales, including drier and wetter years, and will serve as a baseline for evaluating future changes in environmental policies or other human activities. Development of durable funding sources from governments in the region is strongly suggested to maintain these measurements through time, generating collaborative networks similar to those in the United States and the European Union.

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