Assessment of potassium and sodium excesses in rainwater

Marelo S. Vieira-Filho[a], Jairo J. Pedrotti[b], Adalgiza Fornaro[a]

[a] Departamento de Ciências Atmosféricas, IAG/USP, Rua do Matão, 1226, 05508-090, Cidade Universitária, São Paulo, SP, Brasil.
[b] Departamento de Química, Universidade Presbiteriana Mackenzie, Rua Consolação, 930, 01302-090, Consolação, São Paulo, SP, Brasil.

Keywords: rainwater, sea-salt, biomass burning, HYSPLIT, long-range transport

Author email: marcelovieira@model.iag.usp.br

Abstract

The surface winds and backward trajectories were analyzed to investigate sources of sodium and potassium ions measured in rainwater in the metropolitan area of São Paulo (MASP), Brazil from July-2002 to December-2005. This study evaluated the chemical composition of 315 rainwater samples with focus on precipitation events with high concentrations of sodium and potassium, where the cations concentrations were, at least 1.5 times higher than sulfate and nitrate concentration - which are common ions for urban regions. The meteorological dataset were obtained from the Meteorological Station of the Institute of Astronomy, Geophysics and Atmospheric Sciences (IAG/USP), The Center of Weather Forecast and Research (CPTEC/INPE), The Brazilian National Institute of Meteorology (INMET), and National Oceanic and Atmospheric Administration (NOAA). In the results from the total samples, the Na^+ and K^+ volume weighted mean (VWM) concentrations were 10.4 and 3.2 μmol L^{-1} respectively, while for the excess events the registered concentrations were 32.4 μmol L^{-1} and 11.1 μmol L^{-1}. From the sodium excess events, 45% showed an influence from ocean air masses by the wind direction evaluation while 57% of backward trajectories for excess potassium events indicated a contribution of biomass burning air masses from the northwestern region of the São Paulo State. Although some excess events points the pattern of long-range transport, these events represents less than 15% of total samples. The results suggest that the city itself is predominantly involved in the process of emission and removal of the compounds and the influence of external components are limited to circumstantial events.

Introduction

The relations between ionic species in rainwater samples are usually applied to identify potential sources for atmospheric pollution. Traditionally, the sodium ion has been used to identify marine influence by the presence of sea-salts in rainwater or in the particulate matter soluble phase. Keene and colaborators (1986) applied concentration ratios to estimate the sea-salt fractions in atmospheric samples, and also emphasize that the sodium ion may not always be appropriate, thus the evaluation criteria must be carefully analyzed for the region under study. Recently, Dos Satos et al. (2012) discussed the influence of the South Atlantic Ocean on sea salt mass concentrations in the urban atmosphere of Buenos Aires and highliths the episodes of high Na^+ concentrations when onshore winds speed were higher than 4.3 m s^{-1}. Moreover the potassium ion was identified as indicator of biomass burning processes and biotic sources (such as leaf fragments, pollen, log, etc.), in both wet and dry deposition (Forti et al., 2000).

In Brazil, agriculture is responsible for two major causes of air pollution: the sugarcane burning in the harvesting period and major forest fires in the Amazon region (Pauliquevis et al., 2007; Honorio et al., 2010). High potassium concentrations in rainwater and particulate matter were associated with these events by Allen (2004). Also it is important to note that the period of fires always coincides with drought or low rainfall seasons, mostly between the months of June and November (Cavicchioli et al., 2010).

We believe that for the Metropolitan Area of São Paulo (MASP), local anthropogenic sources of sodium and potassium are significant and could mask these ions origins. In this study, we evaluated the influence of mesoscale phenomena, such as the entry of sea breeze (wind speed and direction) and transport of air masses (HYSPLIT model) in rainwater K^+ and Na^+ concentrations. To identify events with excess of crustal species in rainwater samples, ratios between K^+ and Na^+ ions and anthropogenic ions (NO_3^- and SO_4^{2-}) were calculated. For the MASP, the environmental agency of São Paulo State (CETESB) attributes more than 80% of NO_X to vehicular emissions and around 60% of SO_X to fixed sources. Moreover, the precursors of ionic crustal species are related with land-using, marine air masses and other natural processes. The assessments for potassium and sodium compounds sources are mixed and little is known about the anthropogenic emissions of these species in urban areas. Therefore, this study aims to improve the discussion of possible relations from local or external crustal compound sources in atmospheric samples.

Methodology

The wet-only samples were collected with an automatic rainwater collector G. K. Walter Eigenbrodt model (Königsmoor, Germany) within the campus of Mackenzie University (23º32'S, 46°39'W), in central area of MASP, from July 2002 to December 2005. The high density polyethylene flasks were maintained fully with deionized water until the time of use, in addition to receiving periodical maintenance for cleaning. For ionic chromatography analysis, the sample fraction was filtered with Millex membrane (pore 0.22 μm) and frozen (-18^{o}C) until analysis.

The hourly wind data at ground level were obtained from the Center for Weather Forecasting and Climate Studies (CPTEC/INPE), and meteorological data station from Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo (IAG/USP) were evaluated for the events of sodium and potassium excess. Backward trajectories were generated with 72 hours from HYSPLIT model (Draxler et al., 1997 and 2012; HYSPLIT - http://ready.arl.noaa.gov/HYSPLIT.php) obtained through the READY (Real-time Environmental Applications and Display System) platform from NOAA (National Oceanic and Atmospheric Administration). Meteorological data (Reanalysis) - products of NOAA / OAR / ESRL PSD, Boulder, Colorado, USA – from the global atmospheric model for the years 2002 to 2005 were used as input data (http://www.esrl.noaa.gov/psd/, accessed in November, 2012). The height levels trajectories used were 500, 1500 and 3000m above ground level (AGL) to avoid complicated local topography.

Results and discussion

Within the set of samples evaluated, it was identified samples with sodium and potassium concentrations higher than nitrate and sulfate concentrations. In order to characterize these events, the adopted criteria based on ratios higher than 1.5, i.e., $[K^+]/[NO_3^-]$ and $[K^+]/[SO_4^{2-}]$ or $[Na^+]/[NO_3^-]$ and $[Na^+]/[SO_4^{2-}] > 1.5$, were used to evaluate the possible long-range transport influence to the rainwater ionic composition in MASP. From this restriction, only 7 follow this condition for potassium, <3%, and 31 for sodium, ~10%.

Potassium Excess Events

The air masses backward trajectories calculated by the HYSPLIT model (Fig. 1) were analyzed to identify possible long range transport contribution for potassium excess events. This assumption is based on the incorporation of potassium compounds originated from areas with high fire spots (sugar cane plantations or/and forests) to the air mass across the 72 hour transport.

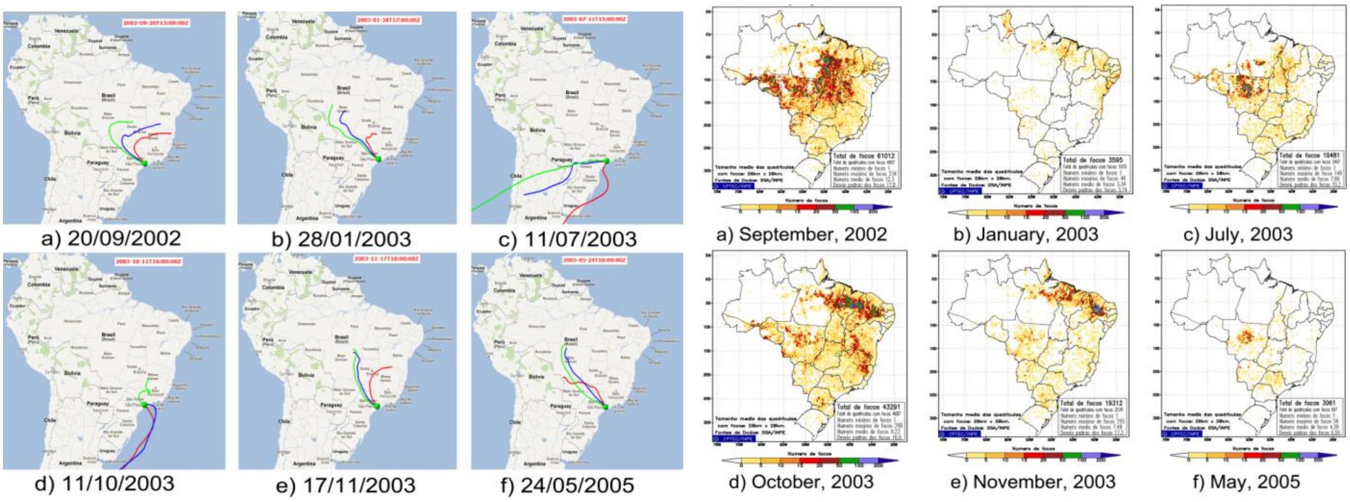

Figure1. Left Panel: backward trajectories plots from HYSPLIT model for the days that excess potassium concentration were registered in the rainwater samples of MASP. The above ground levels are 500m (red), 1500m (blue) and 3000m (green). Right Panel: spatial distribution of number of monthly spot fires in Brazil based on data from satellite NASA GSFC, calculated by INPE.

One factor that contributes to the biomass burning is the sugar cane management in the state of São Paulo. The sugar cane fields cover about 5.3 million hectares in São Paulo State. The central-north region of the state accounts for a substantial part of this total. In the sugar cane management cycle, the burning occurs before the manual harvest, from May to November (Cuadra et al., 2012). It is important to highlight that 6 out of 7 excess potassium events occurred in this period.

Concerning the fires, it is important to quote that in the literature, Setzer (1993) was one of the pioneers to use the term "arc of fire" for the Midwest and North of Brazil. This region comprises the States of Acre, Rondonia, Mato Grosso, Pará, Tocantins and Maranhão, where fires are related to the forests burning, besides the intense agricultural and pastoral activities. Also the drier months, period from June to October offers favorable conditions for these fires to spread (Fig. 1)

For some potassium excess events (57%), air masses from regions with high fire spots numbers move towards MASP, characterizing an external source. Nonetheless, not all the excess events presented this characteristic. Therefore, it would be inaccurate to link potassium in atmospheric samples only with external sources.

Sodium Execess Events

The land use changes and urbanization could cause alteration on atmospheric on circulations, changing surface fluxes and dispersal of pollutants (Morris et al. 2001; Freitas et al. 2007).

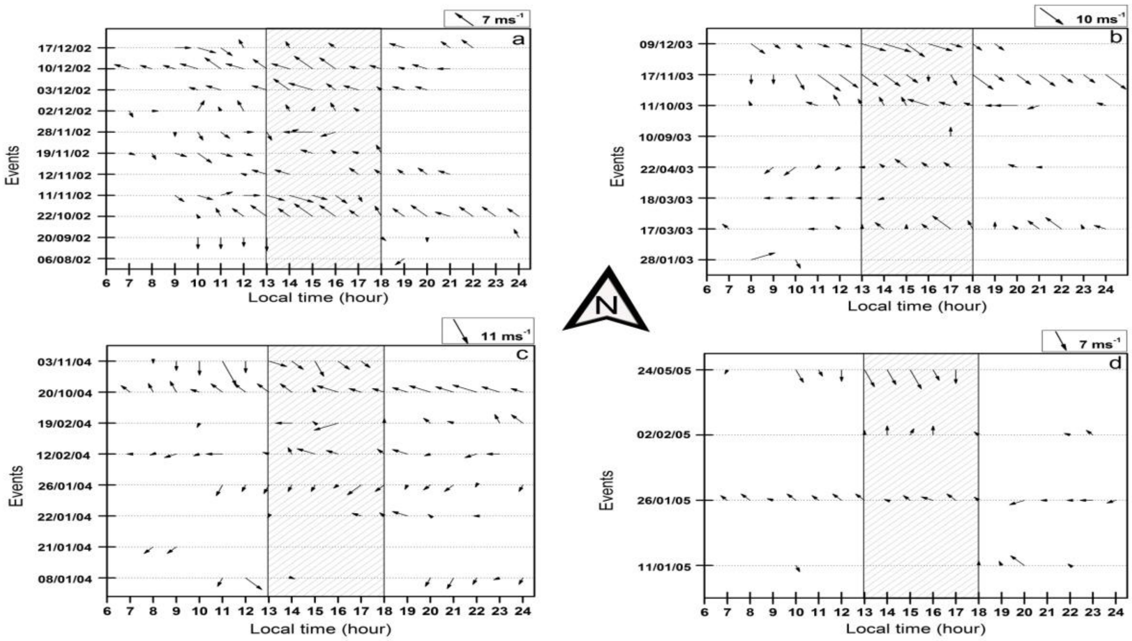

Figure 2. Hourly wind variation for the events with higher sodium concentrations in rainwater samples collected in MASP. The events are separated by year: a) 2002. b) 2003. c) 2004 e d) 2005. Data were from automatic wheater station of IAG/USP (Instituto de Astronomia, Geofísica e Ciências Atmosféricas / Universidade de São Paulo). The shaded hours represents the sea-breeze occurrence period.

The MASP is located at a distance of ~ 50 km from the coastline, and there is a mountain range with ridges up to 1000m (Serra do Mar) between this region and the sea coast, therefore the oceanic air masses need to overcome this natural barrier. In order to observe the phenomenon of the incoming sea breeze, data from IAG/USP weather station, located in the path of the incoming breeze toward the MASP were analyzed.

The winds vectors are shown in Figure 2 for each year of study. The maximum scale for velocity are indicated in the upper right for each year, and the vector absence corresponds to calm condition (<1 m s^{-1}). The wind intensity distribution indicates 47% of the data as calms; furthermore only 10% reaches values higher than 6 m s^{-1}. For the 31 days with sodium excess, 45% exhibit the sea breeze wind direction pattern for MASP. In these 14 days, the wind maximum intensity occurred during the mid-afternoon, within the period of the sea breeze occurrence (Oliveira, 2003; and Vemado, 2012).

The Pearson correlation divided by rainy and dry seasons were evaluated for excess events (Tab.1). The corresponding p-values indicate a high significant level for sodium and chloride correlations, and also the association is stronger in the rainy season (0.88). This value implies that these species could be originated from similar sources, for instance, the sea-spray. However, the ratio between these species is closer to the seawater value (1.17) in the dry season, which mixes the hypothesis about the similarity of the sources and suggests a Cl^- depleted state on the rainy season. The samples with sodium excess (n = 31), predominantly presented chloride deficiency.

Table 1. Pearson correlation between sodium, chloride and potassium ions identified in the São Paulo rainwater samples, also the chloride and sodium ratio is presented. The values are divided by dry and rainy seasons.

	N	$[Cl^-] / [Na^+]$	$[Na^+]$ *x* $[Cl^-]$	$[K^+]$ *x* $[Cl^-]$	$[Na^+]$ *x* $[K^+]$
Rainy (Oct - Mar)	231	0.78	0.88**	0.27**	0.38**
Dry (Apr- Set)	84	1.05	0.74*	0.42*	0.39*

* p values lower than 0.0003; ** p values lower than 0.00003

However the loss of Cl^- due to the incorporation of nitric acid (HNO_3), nitrogen dioxide (NO_2), sulfuric acid (H_2SO_4) or sulfur dioxide (SO_2) in the droplets, is dependent on the acidity, and statistically significant (~ 89%) under conditions of high acidity, pH <3 (Keene et al., 1998). No significant pH effect on Cl^-/Na^+ ratios was observed, so it is not reasonable to evaluate the sodium excess due to the hydrochloric acid, HCl, volatilization (chloride loss). Considering the above discussion, it is possible to consider other sodium compounds sources, rather than only the sea-spray sodium chloride for the MASP.

Conclusions

In this study the wet deposition was measured continuously at a high urbanized site in São Paulo, Brazil for four years (2002 – 2005) with representativeness higher than 70%. In order to identify external sources of sodium and potassium compounds a strong restriction was imposed, i.e, the concentration of these ions must exceed 1.5 times the sulfate and nitrate. From backward trajectories, we observed that half out of these potassium excess events, presented concentrations directly proportional to spot fire numbers, which means that some maximum potassium concentrations in rainwater samples could be associated with biomass burning areas. However, it was not possible to distinguish the sugar cane management from the long-range transport from forest biomass burnings in Brazilian central-northern regions. For the sodium events it was observed that the ocean influence is not mandatory for the occurrence of the excess concentrations, just half of these events were preceded by the sea breeze. The majority of sodium excess events presented a high Cl^- deficiency; and no relation between acidity rainwater and Cl^- loss could be associated, which indicated that the local sources contributed for sodium high concentrations, rather than the volatilization of HCl. This high concentration implies a considerable bias in the estimative of non-sea salt fraction for atmospheric deposition, if the assumption that the sodium is originated only by oceanic processes is considered.

Acknowledgments

This research has been supported by FAPESP (03/01194). The authors are grateful to the NOAA for the provision of the HYSPLIT trajectories model used in this publication, and also thanks to the Meteorological Station (IAG/USP), CPTEC/INPE and INMET for the other atmospheric data. We also thank to CAPES and CNPq for the student grants provided.

References

Allen, A.G., Cardoso, A.A., da Rocha, G.O., 2004. Influence of sugar cane burning on aerosol soluble ion composition in Southeastern Brazil, Atmospheric Environment 38, 5025–5038.

CETESB, 2005. Relatório de qualidade do ar no Estado de São Paulo 2004. Série Relatórios/Secretaria do Estado do Meio Ambiente, São Paulo. ISSN 0103e4103. http://www.cetesb.sp.gov.br/ar/qualidade-do-ar/31-publicacoes-e-relatorios.

Cuadra, S.V., Costa, M.H., Kucharic, C.J., da Rocha, H.R., Tatsch, J.D., Inman-Bamber, G., da Rocha, R.P., Leite, C.C., Cabral, O.M.R., 2012. A biophysical model of sugar cane growth. GCB Bioenergy 4, 36-48.

Draxler, R.R., Rolph, G.D., 2012. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, Silver Spring, MD.

Draxler, R.R., Hess, G.D., 1997. Description of the Hysplit_4 modeling system, NOAA Technical Memorandum ERL ARL-224, December, 24P.

Dos Santos, M., Dawidowski, L., Smichowski, P., Ulke, A.G., Gómez, D., 2012. Factors controlling sea salt abundances in th urban atmosphere of coastal South American megacity, Atmospheric Environment 59, 483-491.

Forti, M. C., Melfi, A.J., Astolfo, R., Fostier, A.H., 2000. Rainfall chemistry composition in two ecosystems in the northeastern Brazilian Amazon (Amapa State). Journal of Geophysical Research 105(D23) 28,895-28,905.

Freitas, E.D., Rozoff, C.M., Cotton, W.R., Silva Dias, P.L., 2007. Interactions of an urban heat island and sea-breeze circulations during winter over the metropolitan area of São Paulo, Brazil. Boundary-Layer Meteorology 122:43–6.

Honório, B.A.D., Horbe, A.M.C., Seyler, P. 2010. Chemical composition of rainwater in western Amazonia — Brazil. Atmospheric Research 98, 416–425.

Keene, W.C., Sander, R., Pszenny, A.A.P., Vogt, R., Crutzen, P.J., Galloway, J.H., 1998. Aerosol pH in the marine boundary layer: a review and model evaluation. Journal of Aerosol Science 29(3), 339-356.

Keene, W.C., Pszenny, A.A.P., Galloway, J.N., Hawley, M.E. 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation. Journal of Geophysical Research 91(D6), 6647-6657.

Morris, C.J.G., Simmonds, I., Plummer, N., 2001. Quantification of the influences of wind and cloud on the nocturnal urban heat island of a large city. Journal Applied Meteorology 40, 169–182.

Oliveira, A.P., Bonstein, R.D., Soares, K., 2003. Annual and diurnal wind patterns in the city of São Paulo. Water Air Soil Pollution Focus 3, 3–15.

Pauliquevis, T., Lara, L.L., Antunes, M.L., Artaxo, P. 2007. Aerosol and precipitation chemistry in a remote site in Central Amazonia: the role of biogenic contribution. Atmospheric Chemistry and Physics Discussions 7, 11465-11509.

Setzer, A.W., 1993. Operational satellite monitoring of fires in Brasil. International Forest Fire News, FAO-UN, 9, 8-11,

Vemado, F., 2012. Sea Breeze circulation analysis and its impacts over Metropolitan area of São Paulo precipitation using ARPS model. Dissertação (Mestrado) – Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo.