Article

The Chemical Composition of Winter Fogs at São Paulo Highway Sites

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Radiation and advection fogs were characterized at two sites nearby important roads next to São Paulo City, Brazil. Water-soluble ions, monosaccharides, other sugars and organic and elemental carbon (OC and EC) were determined. Both sites present a high number of fog events with mainly radiation fogs causing visibility problems to the automotive traffic (Castello Branco and Raposo Tavares roads). Samples were collected in nine events in 2009 and ten events in 2010, during wintertime. Two radiation and advection fog events have been herein presented. The radiation fog occurred in 2009 at Castello Branco Road (CBR), presented the highest concentration of pollutants comparing to all other events. The most abundant species are associated with biomass landfill and fossil fuel burning. Locally, the region has a strong impact by the fertilizer industries and traffic of heavy vehicles. The second most polluted event occurred also in 2009 at CBR, an advection fog presented species attributed to soil resuspension and anthropogenic emissions. The results are compared with rainwater composition studies.

Keywords: fog water, air pollution, industrial pollution, fog composition

Introduction

Fogs can affect the air pollution and human activities by different mechanisms. They cause limited visibility, which will affect driving conditions or airport activities. Moreover, they can affect local air quality by concentrating chemicals in small fog droplets, influencing the composition of the atmosphere by acting as a medium for chemical reactions or removing pollutants from the atmosphere through deposition processes.

Fog chemistry has been observed since the beginning of the last century with more intense studies at the end of the 1900s because of the increased interest in acid fog and its impact on human health and materials.[1-3] In recent years, the focus shifted from fog acidity studies towards organic matter in fogs and on how fog affects the secondary organic aerosol formation.[4] Amato *et al*.[5] suggested the possibility of bacterial activity in fogs and clouds.

Most of fog studies occurred in Europe, particularly in the Po Valley,[6] and in North America,[7] especially in the Central Valley of California.[2,8] In recent years, the observational database became substantially more diverse geographically with an increasing number of fog observation studies in Asia.[9,10] However, some areas of the world like Africa and South America have only reported a very limited amount of fog studies, especially in urban areas. In large urban environments like the São Paulo metropolitan area and surroundings, fogs and fog processing of atmospheric compounds has a profound impact on the visibility. Still to date only very limited information on precipitation chemistry is available.[11-13]

The formation and microphysical properties of fogs can be influenced by the abundance of water vapor, local environmental conditions and the occurrence of pollutants, especially those in the particle phase. The presence of high numbers of cloud condensation nuclei (CCN) can influence

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the size distribution of the fog droplet, optical density, and rate of water removal by droplet sedimentation.[2] Those CCN can be produced by industries, vehicular exhaustion or other anthropogenic sources, affecting the local fog formation.

The droplets that make up a fog can interact with trace species in the atmosphere. The accumulated solute species may participate in aqueous phase reactions, some of which can generate secondary inorganic mass that can remain as residual particles after evaporation.[14]

Many organic compounds were found in the fog samples: volatile carboxylic acids (acetic and formic acids) and mostly aldehydes.[7,15] Chapelon and Loones[16] reported that although only 10% of overall traffic occurs at night, one third of accidents and 50% of fatalities occurred during this period. According to this study, foggy conditions, in France, are associated with 2% of traffic-related deaths during the last ten years. Because fog events represent a real peril for traffic, highway managers are especially concerned about nighttime conditions that can give rise to dense fog formation.

In this study, observations on fogs and fog composition (water soluble ions, monosaccharides, other sugars, organic (OC) and elemental carbon (EC)) in the São Paulo motorways, nearby the São Paulo metropolitan area (SPMA), are presented.

Fog samples were collected at two sites nearby important roads surrounding the SPMA, in São Paulo State, Brazil. Fog type, meteorological conditions, fog chemistry, composition and sources are discussed. Since no other work on fog water study has been evaluated in São Paulo State, the results are compared with rainwater composition studies. The results can be useful to establish public politics, to the motorway managers and local government aiming the protection of people on the roads. In addition, it will be important to monitor the local air quality highly influenced by industrial emissions and biomass burning.

Experimental

Sampling procedures

Fog samples were collected at two sites using Caltech Active Strand Cloudwater Collectors (CASCC).[17] The CASCC collects fog droplets by inertial impaction on 6 inclined rows of 508 μm Teflon® strands. The airflow rate through the collector is 24 m^3 min^{-1} and the 50% lower size cut is 3.5 μm diameter. Collected droplets coalesce and run down the strands, aided by gravity and aerodynamic drag, into a Teflon® sample trough. Fog water was collected through a Teflon® tube into a polyethylene sample bottle. The collectors were cleaned prior to each event, using deionized water. The collectors worked manually when

fogs events were observed between 3:00 a.m. and 8:00 a.m. local time.

Weather and climate data are based on Weather Station (IAG) located in the campus of the University of São Paulo.

Sampling site characteristics

Samples were collected at the Raposo Tavares Road (RTR) and at Castello Branco Road (CBR). Both sites are located approximately 50 km from the São Paulo City Center. RTR is 654 km and CBR is 315 km long.

The RTR site is surrounded by a rural landscape (fisheries and agricultural activities) and presents low traffic (8,000 vehicles *per* day, which 800 are trucks). The CBR site is characterized by larger traffic volumes (four times higher than the traffic at RTR with 33,000 vehicles, which 9,000 are trucks) with industries (steel, dye and lime companies) in the surroundings. Additionally, pulp and fertilizer industries are also present on this road.

Analytical procedures

Water-soluble ions

Fog samples were filtered using 0.45 μm pore size membranes (Whatman plc, Middlesex, UK), and stored in clean polyethylene bottles. After pH measurement, ionic species were determined by ion chromatography (Metrohm AG, Herisau, Switzerland) with chemical suppression and conductivity detection. For anion detection (F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}), samples were injected via a 20 μL loop and eluted over a Metrosep A Supp 5 250/4.0 mm analytical column (Metrohm, Herisau, Switzerland). A mixture of 1.0 mmol L^{-1} $NaHCO_3$ and 3.2 mmol L^{-1} Na_2CO_3 was used as eluent. The system was regenerated using a solution of 50 mM H_2SO_4 pumped through a suppressor unit simultaneously with deionized water. A Metrosep C2-150 150/4.0 mm analytical column (Metrohm, Herisau, Switzerland) was used for cation detection (K^+, NH_4^+, Ca^{2+}, Mg^{2+} and Na^+) and the eluent used was a solution of 2.7 mmol L^{-1} oxalic acid in isocratic mode. The inorganic anions recovery were from 109 to 118%, from 80 to 101% for cations and from 87 to 107% for organic anions. The limits of detection (LOD, S/N = 4) ranged between 0.023-0.085 mg L^{-1} (inorganic anions), 0.046-0.157 mg L^{-1} (cations) and 0.004-0.010 mg L^{-1} (organic acids). Blank values were subtracted from sample determinations.[18]

Saccharides

The analysis was performed using a Dionex ICS-3000 system column (Dionex, Sunnyvalle, USA) consisting of

a quaternary pump and degasser, column compartment, electrochemical detector and gold electrode, and eluent organizer units. The waveform used for pulsed amperometric detection was the standard quadruple potential for carbohydrate analysis (Dionex Technical Note 21).[19] The separation was carried out on a Dionex CarboPac MA1 column (4 × 250 mm, Thermo Fisher, Waltham, USA) with a guard column (4 × 50 mm) at room temperature. This column is suited for separation of reduced monosaccharides. UP (ultrapure) water (eluent A) and 1.0 mol L^{-1} sodium hydroxide (eluent B) solution were used for the separation. The UP water was purged with helium for a minimum of 15 min to remove dissolved gases, particularly carbon dioxide. To prepare 1.0 mol L^{-1} sodium hydroxide eluent, 104.6 mL of 50% (m/m) sodium hydroxide solution was diluted to 2 L. The eluent flow rate was 0.4 mL min^{-1}. The sample injection loop was 25 mL. All eluent reservoirs were blanketed by helium to minimize carbon dioxide contamination from the air. Instrumental controls, data acquisition, and chromatographic integration were performed using Dionex Chromeleon software.[20]

The limit of detection was determined as the minimum concentration that was visible on the chromatogram and produced a peak height at least three times the signal to noise ratio. For galactosan and fructose, the minimum visible concentrations were taken as LOD values because they were much higher than S/N = 3. The LOD values were in the range of 0.002-0.08 mg L^{-1} corresponding to 0.1-2 ng absolute analyte mass injected using a 25 mL loop.

Determination of total carbon (TC), elemental carbon (EC) and organic carbon (OC) in liquid samples

For determination of TC in liquid samples, a commercial instrument (GOTOC 100, Gröger & Obst GmbH, Wolfratshausen, Germany) modified to a flow injection system was used. Catalytic combustion takes place at 850 °C. The evolving CO_2 is determined with a nondispersive infrared (NDIR) detector. To eliminate the influence of dissolved CO_2, the samples were acidified with nitric acid (100 µL 1 mol L^{-1} HNO_3 mL^{-1}), stripped with pure N_2, and then injected into the sample loop (300 µL). Standard solutions for calibration were prepared from phthalic acid (p.a., Merck, Darmstadt, Germany). The limit of quantification (6 s of the multiple (n = 9) injection of demineralized water) was 0.4 µg C mL^{-1}, corresponding to an absolute limit of quantification of 0.12 µg C. More details are given by Bauer *et al.*[21] Black carbon (BC) was again determined with the integrating sphere. OC was calculated as TC – BC.

Hysplit analysis

Hysplit (hybrid single-particle Lagrangian integrated trajectory) data analyses, from Draxler,[22] were performed in order to identify the air masses trajectories. The resulting figures show the origins of air masses at three different levels (500, 1000 and 1500 m) for fog events collected.

Overall meteorological conditions and fog occurrence

The winter of 2009 was wetter than the average due to the El Niño phenomenon,[23] with several record rainfall events between July and October in the SPMA. Rainfall totaled approximately 200 mm in July, four times higher than usual and this anomaly extended through the following months. The higher water vapor content in the atmosphere could increase the likelihood of fog events, but low temperatures are also important for radiation fog formation. Minimum temperatures were approximately 1 °C higher than the average (over 11 °C), decreasing the possibility of fog formation. Radiation fog events, in the study region, are generally favored during periods characterized by high-pressure systems (anticyclonic) with clear night skies, quick fall of air temperature and no wind. These conditions were less frequent, probably due to the prevailing El Niño conditions, where the low pressure system may increase. On the other hand, advection fog events are characterized by low-pressure systems (cyclonic), cloudy and sometimes with rain and drizzle, and with wind blowing from the sea side, bringing humidity and without a quick air temperature fall (due to the clouds).

On the other hand, the winter of 2010 was characterized by drier periods in July and wetter periods in August. The weather station recorded that July was warmer, with minimum temperatures over 1.6 °C above average (over 11 °C). However, there were wet periods during July as well as dry periods in August. The samples were collected during the fog events in the wet periods of July which presented advection fogs, mixed with rain and drizzle.

## Results and Discussion

Species concentration

Table 1 presents the chemical composition of the fog samples collected at both sites in 2009 and 2010. At CBR, with more intense traffic and more industries, water-soluble total ions concentrations (TIC) were higher (3821.8 and 888.8 µeq L^{-1}) than at RTR (934.0 and 619.7 µeq L^{-1}).

In 2009, the major ionic species at CBR were K^+ (average 1647 µeq L^{-1}), Cl^- (average 610 µeq L^{-1}) and NH_4^+ (average 483 µeq L^{-1}). At RTR were Ca^{2+} (183 µeq L^{-1}), NH_4^+

Table 1. Average concentration of water-soluble ions found in the fog samples collected in Castello Branco Road (CBR) and Raposo Tavares Road (RTR) in the years 2009 and 2010

	CBR-2009	RTR-2009	CBR-2010	RTR-2010
Inorganic anion / (μeq L^{-1})				
F$^-$	434	15	11	5.4
Cl$^-$	610	95	270	150
NO$_2^-$	111	37	14.4	38
Br$^-$	0.8	1.0	1.3	BDL
NO$_3^-$	41	60	12	16
PO$_4^{3-}$	1.7	6	4	6.3
SO$_4^{2-}$	336	138	36	36
Organic acid / (μeq L^{-1})				
Acetic	5.1	8	BDL	BDL
Formic	4.8	6	0.4	BDL
Oxalic	2.5	6	2.0	1.7
Fumaric	0.9	1.0	BDL	BDL
Succinic	1.5	1.0	3.0	BDL
Cation / (μeq L^{-1})				
Na$^+$	5	80	35	11.4
NH$_4^+$	483	157	21	80
K$^+$	1647	58	238	178
Mg^{2+}	5	82	28	11.6
Ca^{2+}	133	183	211	86

BDL: below detection limit.
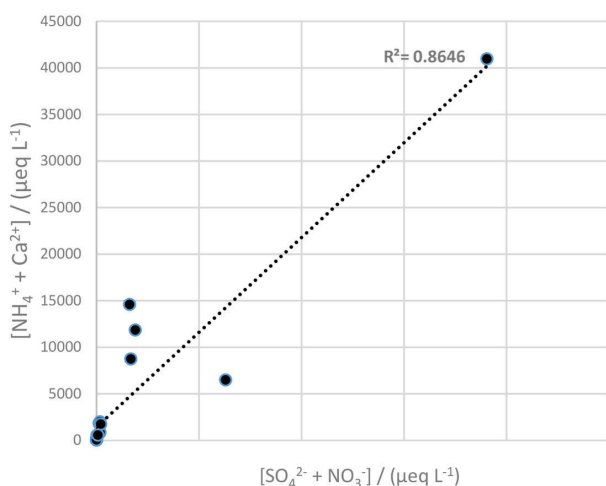
Figure 1. Correlation between the concentrations of the acidic inputs (nitrate plus sulfate) with neutralizing species.

(157 μeq L^{-1}) and SO$_4^{2-}$ (138 μeq L^{-1}). In 2010 the major ionic species at both sites were Cl$^-$, K$^+$ and Ca^{2+}.

In 2009, potassium made up 43% of the total ion concentration at CBR and chloride 30% in 2010. At RTR, calcium made up 20% (2009) and potassium 29% in 2010. Soil components and secondary species were ubiquitous at these sites, followed by potassium that could also have come from biomass burning occurred in the vicinities.

Ammonium and sulfate often seem to be the most abundant species in other studies.[7,14]

In previous fog studies,[14] in California, ammonium (1066 μmol L^{-1}, 41%) was the most abundant ionic species followed by sulfate (22%), calcium (12%) and nitrate (7.7%). In China, fog samples collected in the Nanjing area, at a site close to pollution influenced by petrochemical factories, nitrogenous fertilizer plant, highways and other sources, presented concentration of 6969 μeq L^{-1} for sulfate and 6654 μeq L^{-1} for ammonium.[24] These two ions made up more than 60% of the total ion concentrations.

In the present study, ions concentrations are highly variable and differences can reach 2 orders of magnitude between two events at the same site.

Calcium has been one of the most abundant species in these samples. São Paulo City is 80 km far from the sea and atmospheric samples are often impacted by the sea salt. In addition, building construction can contribute to build up calcium. To check if the fog events might be affected by sea salt, non-sea salt calcium concentration was calculated (nss-Ca^{2+}) using the equation by Błaś *et al.*:[25]

$$[\text{nss-Ca}^{2+}] = [\text{Ca}^{2+}] - 0.0373[\text{Na}^+] \qquad (1)$$

where [nss-Ca^{2+}], [Na$^+$], [Ca^{2+}] are concentrations of the species.

At both sites, more than 95% of calcium origin appeared to be predominantly from soil resuspension.

Studies on fog composition are scarce in São Paulo. Yet, some studies occurred on rainwater composition. In the 80's, rainwater was collected on campus of the University of São Paulo during the dry and wet seasons. The major species were calcium, nitrate, sulfate and ammonium; the highest concentrations were found in the dry period due to meteorological conditions.[26]

In the same way, Oliveira *et al.*[13] collected rainwater samples at a sugarcane burning site (Araraquara City, 300 km from São Paulo) and observed the major ions were also calcium, ammonium and nitrate; they observed that the concentrations were influenced by seasonal variation due to the agricultural activities.

Other species were found in the fog water samples in lower concentrations at both sites: oxalate (2.5 and 6 μeq L^{-1}), fumarate (over 1.0 μeq L^{-1}), succinate (over 1.5 μeq L^{-1}), formate (from 0.4 to 6.0 μeq L^{-1}) and acetate (from 5.1 to 8 μeq L^{-1}).

Acetate and formate are ubiquitous in urban atmospheres. Their origin is mostly attributed to anthropogenic emissions and their concentrations can be increased due to photochemical reactions and vegetation contribution. Higher acetate concentrations rather than formate in the

atmosphere may indicate strong vehicular emissions influences. Previous studies in São Paulo City showed that approximately 98% of the total acetic and formic acids found in aerosols were in the gas-phase and the gas-aerosol equilibrium was influenced by high relative humidity.[27] In 2009, they were the most abundant organic acids followed by oxalate. Kawamura and Kaplan[28] mentioned reactions forming oxalate at urban sites, but vehicle emissions, biogenic activity and biomass burning have also been proposed. The main air pollution source in the metropolitan area of São Paulo has been attributed to vehicular emission. The addition of ethanol to motor vehicle fuels reduces carbon monoxide, but increases aldehyde emissions (especially acetaldehyde), inducing a unique photochemical smog problem. Besides these different fuels, biodiesel has been used and consequences in the air pollution has recently been studied.[29]

Succinic and fumaric acids presented low concentrations. Dicarboxylic acids are important since their hygroscopicity property can affect cloud formation and global radiation reaching the ground.[30]

Sulfate/nitrate average ratios ranged from 0.8 to 3.0. One sample presented this ratio equal 8.1. High ratios are found in atmospheric samples due to the nitrate volatilization that occurs under high temperatures.[31]

Concentrations of the acidic inputs (nitrate plus sulfate) were correlated with the sum of ammonium and calcium (coefficient of determination (R^2) = 0.8646) in the fog samples. It indicates that calcium was also important to neutralize nitrate and sulfate (Figure 1).

In fact, in all samples collected, only two samples presented higher concentration of ammonium than the sum of nitrate and sulfate. For these samples, organic acids must be important species for neutralization of the atmosphere.

Sulfate in fog water derives from aerosol scavenging or *in situ* oxidation of dissolved sulfur dioxide, and nitrate from both the scavenging of aerosol nitrate and the uptake of gaseous nitric acid.[2]

The average and range of the balance between total anions/total cations are the following: at CBR 2009 is 1.1 (1-1.3), RTR 2009 is 1.7 (0.7-2.7), at CBR 2010 is 0.54 (0.41-0.79) and at RTR 2010 is 0.67 (0.63-0.71). The 2009 samples presented higher ratios than 2010. Unmeasured organic acids contributed to these results.

Other correlations were also observed between sulfate and chloride and they were strong (correlation coefficient (R) $\geq$ 0.98) at both sites, except at RTR in 2010. Sulfate in São Paulo atmosphere is often attributed to fossil fuel burning and chloride, to landfill burning or marine plumes.[32]

As expected, calcium and magnesium, soil components also presented strong correlation (R $\geq$ 0.88) and sulfate and ammonium presented moderate correlation (R $\geq$ 0.55) in 2009; between sulfate and nitrate, the correlations were strong (R $\geq$ 0.99), except at CBR in 2009; ammonium and chloride presented good correlations (R $\geq$ 0.52), except at RTR in 2010. Chloride and potassium also presented strong correlations at both sites and campaigns (R $\geq$ 0.99). Potassium is a crustal species that can be found at sites with agricultural influences and on roads, suspended by vehicles. Fertilizers industries for soil liming in this region may enhance potassium chloride concentration in the fog samples. Nitrate and potassium presented good correlation (R ca. 0.96) at RTR (2009) and at CBR (2010) samples and it is likely that they have the same source.

Potassium in São Paulo atmosphere is often attributed to the contribution of sugarcane burning often observed in the state during wintertime,[18] mainly when it comes well correlated with levoglucosan.

In this work, levoglucosan and its isomers were found only in four samples in low levels (from 0.001 to 0.014 µeq L^{-1}). Table 2 presents the monosaccharides concentrations.

Other sugars were found in low concentration in some samples: arabitol (n = 6; 0.0002-0.0043 µeq L^{-1}), mannitol (n = 6; 0.0002-0.0046 µeq L^{-1}), trehalose (n = 2; 0.0002-0.0006 µeq L^{-1}), glucose (n = 6; 0.0002-0.0048 µeq L^{-1}), fructose (n = 1; 0.0013 µeq L^{-1}) and galactose (n = 1; 0.0002 µeq L^{-1}).

Bauer *et al.*[33] suggested that mannitol and arabitol concentrations are correlated to the fungal spore counts

Table 2. Average concentration of monosaccharides, OC and EC found in the fog samples collected in Castello Branco Road (CBR) and Raposo Tavares Road (RTR) in the years 2009 and 2010

	CBR-2009	RTR-2009	CBR-2010	RTR-2010
Levoglucosan / (µeq L^{-1})	0.328	0.597	BDL	BDL
Mannosan / (µeq L^{-1})	0.030	0.113	BDL	BDL
Galactosan / (µeq L^{-1})	0.020	0.010	BDL	BDL
OC / (µg mL^{-1})	2.6	4.9	2.3	1.5
EC / (µg mL^{-1})	0.4	0.5	0.45	0.1

BDL: below detection limit; OC: organic carbon; EC: elemental carbon.

in coarse particulate matter (PM_{10}). These polyols are common storage substances in fungal spores. Mannitol, common in fungi and abundant in algae, was detected in more than 70 plant families.[33,34] These alcohol sugars, glucose and trehalose are abundant in atmospheric coarse particulate matter. Likely, they are derived from primary biological particles.[35]

Organic carbon (OC) and elemental carbon (EC) were found in the samples ranging from 1.5 to 4.9 µg mL^{-1} and from 0.03 to 0.53 µg mL^{-1}, respectively (Table 2). In the atmosphere, the OC originates from both direct emissions of particles and atmospheric transformation of organic gases. Secondary OC is generated by the condensation of low vapor pressure products. On the other hand, EC is emitted directly to the atmosphere.[36] In Brazilian atmospheric samples, biomass burning can contribute to EC content. The contribution of OC was higher than EC in all samples; thus it can indicate the influences of local vehicular traffic. However, the relative contribution of EC associated to the presence of levoglucosan and its isomers may indicate long-range transport of air masses and influence of biomass burning.

Advection *vs.* radiation fog events

The data resolved by fog type shows substantial differences in the species concentrations (Figure 2). The pH observations are only available for advection fogs and ranged from 5.03 to 7.76.
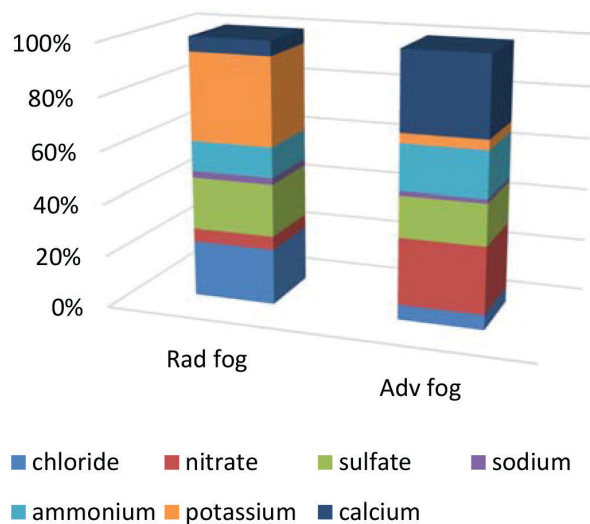

Figure 2. Composition of radiation (Rad) and advection (Adv) fogs of the samples collected in 2009.

Some patterns emerge when considering the relative composition of the fog events based on average concentrations by fog type and location of samples collected in 2009. The

main ionic species in the radiation fog were K$^+$, Cl$^-$, and SO$_4^{2-}$. This fog composition is unusual, normally ammonium and nitrates are the dominant species in fog as reported elsewhere.[7,14] A previous work[37] on rainwater in São Paulo City, at a much-polluted site (center), showed the most abundant ions: ammonium, nitrate and acetate. On the other hand, advection fog presented Ca^{2+}, NO$_3^-$ and SO$_4^{2-}$. Ca^{2+} presence coupled to high pH might be the indication of a soil contribution (CaCO$_3$). An important contribution of soil could come from local unpaved roads as well as activities on the road (unpaved streets are common in the vicinities of roads).

Between the fog events, a large difference in the species concentrations is observed. The radiation fogs presented much higher concentrations of the ionic species (105952 µeq L^{-1}) than the advection fogs (1763 µeq L^{-1}). Monosaccharides were present only in two samples of radiation fog, in low concentrations.

Figures 3a and 3b present the air mass back trajectories calculated for the two days most polluted (May 1st and September 29th, 2009). In the Figure 3a, on May 1st, characterized by radiation fog, 96 h air masses came from Southwest Brazil, coming before from other South American countries (Argentina and Paraguay), while on September 29th, characterized by advection fog, the air masses came from the ocean, passing over polluted region where petrochemical derivatives are produced.

Conclusions

Fog water composition was investigated at two roadside sites in São Paulo State, where both sites experienced radiation as well as advection fog.

Two important events, for advection and radiation fog, are herein presented. The radiation fog occurred in 2009 at CBR, presented the highest concentration of pollutants comparing with all events. The most abundant species were potassium, chloride and sulfate. These species are associated with biomass landfill and fossil fuel burning. Air mass trajectory indicated air masses coming from the Southwestern Brazil and other countries. Locally, the region has a strong impact by the fertilizer industries and big vehicles traffic.

The second most polluted event, an advection fog also at CBR, presented higher concentration of calcium, nitrate and sulfate, species attributed to soil resuspension and anthropogenic emissions.

Levoglucosan and its isomers were present in few samples and is often attributed to biomass burning. Other sugars like arabitol, mannitol, trehalose, glucose, fructose and galactose indicated the presence of biogenic emissions.
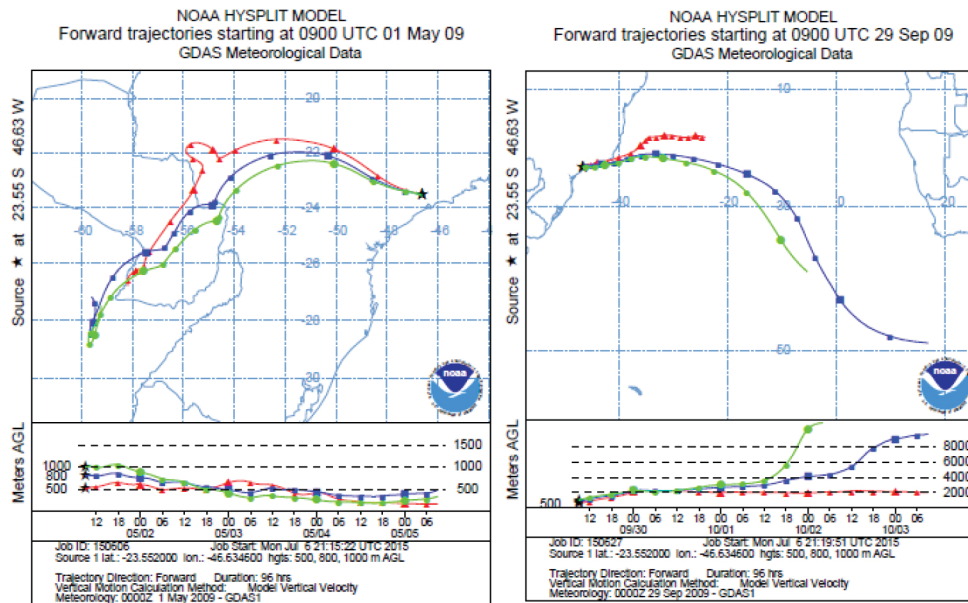
Figure 3. Air mass back trajectories calculated for the two most polluted days in 2009: (left) May 1st and, (right) September 29th, at CBR site.

The contribution of OC was higher than EC in all samples; it indicates the influences of local vehicular traffic. However, the relative contribution of EC associated to the presence of levoglucosan and its isomers may indicate long-range transport of air masses and influence of the incomplete biomass burning.

Summarizing, the results highlighted the fact that there is a concentration of pollutants, particularly hygroscopic species at both sites. The study of these species is important to monitor the local air quality and the fog formation in the atmosphere of important roads surrounding São Paulo City.

Acknowledgments

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