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Changes on wet deposition of major organic and inorganic ions in subtropical region of Brazil

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ABSTRACT

Wet precipitation composition could be an indicator of air quality since it carries components such as strong and weak inorganic and organic acids. These originate from oxidation of compounds containing sulphur, nitrogen, and hydrocarbons, coming from biomass burning, fuel combustion and industrial processes, as well as agricultural and biogenic activities. Wet precipitation samples were obtained from May 2014 to May 2015 in the city of Londrina-Paraná, Brazil, with an automatic rain collector. Volume, pH, conductivity, acetate, format, chloride, nitrate, sulphate, and ammonium concentrations were determined. The pH results revealed slightly acidic rainfall in 41% of the samples. The Volume Weighted Mean (VWM) showed an average annual concentration of inorganic ions of 0.71, 0.55, 0.24 and 0.20 mg L^{-1} for nitrate, sulphate, chloride, and ammonium, respectively and for organic ions of 1.00 and 0.29 mg L^{-1} for acetate and format, respectively. In the spring, the highest concentrations of nitrate and chloride were observed, which were possibly influenced by long-distance transport from fires in the north and west regions. The VWM of inorganic ions decreased compared with previous work (1998-2002) carried out for the same place, with reductions of approximately 35% for nitrate and sulphate. Finally, the extensive use of fuel ethanol in Brazil contributes to the higher concentrations of acetate and format compared to other places in the world.

Keywords: rainfall, air pollution, majority ions, the trajectories of air masses

Mudanças na deposição úmida em relação aos principais íons orgânicos e inorgânicos em região subtropical do Brasil

RESUMO

A composição da precipitação úmida pode ser um indicador da qualidade do ar, uma vez que transporta componentes como ácidos inorgânicos e orgânicos fortes e fracos. Estes se originam da oxidação de compostos contendo enxofre, nitrogênio e hidrocarbonetos, provenientes da queima de biomassa, combustão de combustível e processos industriais, assim como atividades agrícolas e biogênicas. As amostras de precipitação úmida foram obtidas no período de maio de 2014 a maio de 2015 na cidade de Londrina-Paraná, Brasil, com um coletor de chuva automático. Foram determinados volume, pH, condutividade e as concentrações dos íons acetato, formato, cloreto, nitrato, sulfato e amônio. Os resultados de pH revelaram chuvas ligeiramente ácidas em 41% das amostras. A média ponderada pelo volume (MPV) mostrou a concentração média anual de íons inorgânicos de 0,71, 0,55, 0,24 e 0,20 mg L^{-1} para nitrato,sulfato, cloreto e amônio, respectivamente e para os íons orgânicos de 1,00 e 0,29 mg L^{-1} para acetato e fomato, respectivamente. Na primavera, foram observadas as maiores concentrações de nitrato e cloreto, que foram possivelmente influenciadas pelo transporte de longa distância dos incêndios nas regiões norte e oeste do país. O MPV de íons inorgânicos diminuiu em comparação com trabalhos anteriores (1998-2002) realizados no mesmo local, com reduções de aproximadamente 35% para nitrato e sulfato. O uso extensivo do etanol combustível no Brasil contribui para as maiores concentrações de acetato e formato em comparação com outros lugares do mundo.

Palavras-chave: precipitação, poluição do ar, íons majoritários, trajetórias de massas de ar

Introduction

Wet precipitation chemistry has been the target of several studies that have determined their soluble and insoluble components because they affect buildings, soil, water, and vegetation, when deposited. Precipitation dissolves and removes the constituents of atmospheric air, whose concentrations may suffer several influences depending on the origin of the air masses (Kawamura, Steinberg and Kaplan, 1996; Fornaro and Gutz, 2003; Migliavacca et al., 2005; Fornaro, 2006*;* Pelicho et al., 2006; Migliavacca, Teixeira and Rodriguez, 2012; Oliveira, Figueiredo and Cardoso, 2012; Fia, Frizzarim and Fia, 2013; Keresztesi et al., 2020a; Zeng et al., 2020; Kesereka et al., 2021).

The concentration of chemical species in wet precipitation are influenced by multiple factors, such as distribution ond type of matticulate matter, transport of chemical species and the scavenging processes (Keresztesi et al., 2020b).

The population growth and the industrialization of urban centres imposed large demand for energy generation. The fossil fuels burning have generated an increase in the emission of pollutants into the atmosphere that consequently have changed the natural chemical characteristics of precipitation (Pelicho et al., 2006; Migliavacca, Teixeira and Rodriguez, 2012; Fia, Frizzarim and Fia, 2013; Li et al., 2021).

The chemical species found in the atmosphere are present in particulate form and as trace gases, whose main pollutants involve compounds originating from sulphur, nitrogen, heavy metals, metal oxides, volatile organic compounds, and organic acids (Chebbi and Carlier, 1996; Wang et al., 2007; Domingos et al., 2012). It was noticed, for example, that carboxylic acids at high concentrations influence 40% on the acidity of precipitation in urban sites and 65% in remote places (Kawamura, Steinberg and Kaplan, 1996; Souza amd Carvalho, 2001; Fornaro amd Gutz, 2003).

Chemical reactions involving organic radicals, ozone-olefin reaction, isoprene oxidation, gas phase reaction of aldehydes, aromatic hydrocarbons and difunctional acids are the main processes responsible for in situ formation of organic acids in the gas/liquid phase and in the atmospheric aerosol (Zhang, Lee and Cao, 2011). Even in tropical Amazonian continental site, direct emission from vehicles, soil, vegetation, and biomass burning are important sources of these species (Honório, Horbe and Seyler, 2010).

Brazil has a unique vehicular emission in the world, since ethanol is used in large scale as fuel in its vehicles (Pérez-Martínez et al., 2014; Carvalho et al., 2015). Although each city has specific characteristics, light vehicles usually use hydrated ethanol (95% ethanol and 5% water) or gasohol (75% gasoline and 25% ethanol). A small fraction of light vehicles also uses compressed natural gas (Pinto et al., 2005; Andrade et al., 2012). Since 1975 with the National Alcohol Program (ProAlcool), Brazil has become the only area in the world to use fuel with a high ethanol content, and the program had as one of its objectives to improve air quality in urban areas. However, there is evidence that the use of fuels such as ethanol increases the levels of acetaldehyde in the atmosphere making the concentrations of this compound in Brazil higher than in other areas of the world (Brito et al., 2015; Nogueira et al., 2015).

In the metropolitan region of São Paulo, it was found that formaldehyde and acetaldehyde are the most abundant carbonyl compounds emitted by light vehicles, and that acetaldehyde emissions result from incomplete combustion of ethanol (Nogueira et al., 2015). In the atmosphere, ethanol forms acetaldehyde and peroxyacetyl nitrate by photo-oxidation and oxidation processes, so the use of ethanol as fuel or mixed with gasoline increases NOx concentrations in the atmosphere (Anderson, 2009; Andrade et al., 2017). Because of the intensive use of ethanol/gasoline fuel in Brazil, rainwater composition shows different constitution in comparison with other countries. Therefore, quantifying rainwater chemical composition can contribute to know how human activities have influenced the hydrological cycle (da Silva et al., 2020).

Studies about changes on wet deposition of organic and inorganic species is an adequate way to infer about the air quality in determined region. Soluble species in precipitation can show the influence of air masses and the impact on the environment.

In this direction, this study presents the quantification of water-soluble organic acids (WSOC) including formic and acetic, inorganic ions such as chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}), and ammonium (NH_4^+) in wet deposition. Wet deposition fluxes of nitrogen, sulphur and carboxylates were calculated and compared with data obtained in the same place (1998 to 2002) in Londrina, Brazil.

Materials and Methods

Sample site and collection of rainwater

Rainwater samples were collected on the campus of the State University of Londrina (Latitude: 23°19`37.71” S and Longitude: 51°12`02.15” W) located in the city of Londrina, state of Paraná, southern Brazil. The collection point is in a residential region, but close to agricultural areas, pasture, forest fragments and the Celso Garcia Cid highway, which has heavy traffic for light and heavy vehicles (Figure 1).

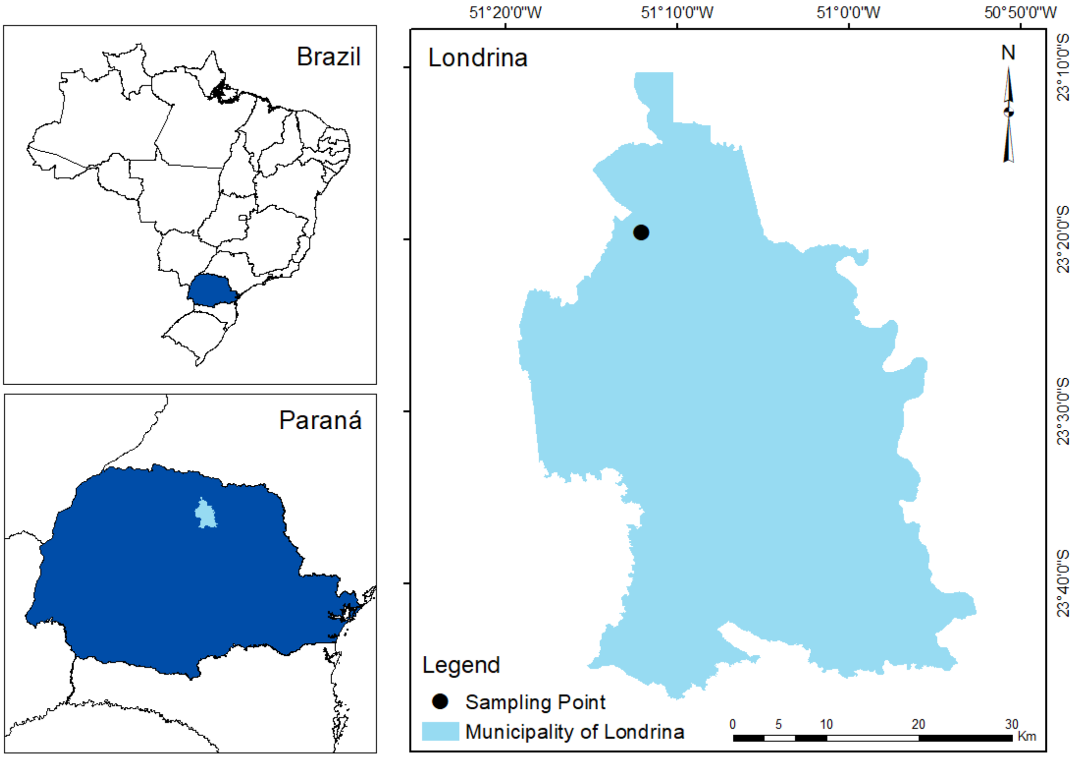

Figure 1. Geographical location of sampling site. Brazil, Paraná State and Municipality of Londrina.

Londrina has an estimated population of 569,733 inhabitants, with 97% residing in the urban area (IBGE, 2019; IPARDES, 2020) The municipality has a fleet of 398,424 vehicles (light and duty-vehicles), which are powered with gasoline (47%), ethanol/gasoline (38%), diesel (7%), hydrated ethanol (5%), and others (4%) (DENATRAN, 2018).

Sample collection was carried out continually from May 2014 to May 2015 (1 year of sampling during winter, spring, summer, and fall of 2014/2015) on an event basis with a wet-only collector integrated for 24 h. The rainfall samples were removed at a fixed time, around 12.30 p.m. local time after each event during the week, considering the integrated rainfall in 24 hours. The wet-only collector (Eigenbrodt-D-2III-Konigsmoor UNS 130) had a 503 cm^2 funnel and a 10 L polyethylene collecting flask. The collector had a lid that opened during rainfall and closed after rainfall had stopped. Standard operating procedures included routine checks and maintenance of the wet-only precipitation sampler. All sampler surfaces that were exposed to the rain were cleaned with deionized water between collections at the analytical laboratory.

Volumes of rainwater below 0.36 mm were not sufficient to carry out the subsequent chemical determination and, for this reason, were not used and recorded. Events that happened during the weekend (from 12:30 p.m. of Friday to 12:30 p.m. of Monday) were considered as one event. In total, 70 events (samples) were considered in the chemical analysis.

Climatologically there are around 86 days of precipitation annually in the region (WEATHERBASE, 2021).

Chemical analysis and calculations

During all sampling periods, after collection and weighing, an unfiltered aliquot of the sample was used to determine pH and conductivity immediately after collection. Measurement of pH was made using Tecnal TEC-2 pH meter with a combination glass electrode, calibrated before every measurement with standard buffer solutions of pH 4.00 and 7.00. A Hanna HI 8820N conductivity meter, calibrated with KCl standard solutions, was used for conductivity measurements (25 ºC).

The second aliquot of 110 mL was destined for determination of major ion concentrations. The samples were filtered through a 0.45-mm-membrane filter (Millipore) and preserved in a freezer (Freitas and Solci, 2009). Before analysis, they were defrozen at room temperature. Organic (acetate ($HCCOO^-$) and formate ($HCOO^-$) standard for IC – Fluka Analytical) and inorganic (chloride, nitrate, and sulphate standard for IC – SpecSol) anions were determined by ion chromatography using a Sykam liquid chromatograph (model S-1100) equipped with a Shimadzu CDD-6A conductivity detector. A Dionex Ionpac pre-column AG23 (4 x 50 mm) and a Dionex Ionpac HPIC-AS23 (4 x 250 mm) column were employed for ion separation and a Dionex AMMS 300 micro-membrane suppressor (4-mm) for eluent suppression. Elution was carried out with 10 mmol L^{-1} NaOH solution at flow rate of 1.0 mL min^{-1} and a suppressor solution of 9.0 mmol L^{-1} H_2SO_4 at 2.0 mL min^{-1}. The regenerant was transported through a silicone tube by a Minipuls 2-Abimed Gilson peristaltic pump. The volume of 50 µL was injected for standards and samples and the columns and conductivity cell were maintained at 35 °C. All solutions were prepared with deionized water supplied by a Milli-Q-Millipore system (Freitas and Solci, 2009).

Ammonium concentration was determined by the modified Berthelot method, employing a Genesys 10uv spectrophotometer with measurements at 694 nm. For calibration curves, solutions were added in the following order: 1.25% (w/v) sodium salicylate in 0.35 mol L^{-1} sodium hydroxide, 0.5% (w/v) sodium nitroprusside, 0.1% (w/v) sodium hypochlorite, ammonium nitrate (or sample) and 0.01 mol L^{-1} phosphoric acid (Pelicho et al, 2006).

The standard solution of anions and ammonium, as well as blank samples, were prepared with different concentrations and given random numbers among real samples. The quality assurance procedures included the routine running of blanks and control samples, besides triplicate samples (coefficient of variation of 2.5%). The linear correlation coefficients of calibration curves were between 0.998 and 0.999. The limits of quantification calculated as blank signal + 10 SD were: 1.4 µmol L^{-1} for Cl^-; 0.3 µmol L^{-1} for NO_3^-; 0.03 µmol L^{-1} for SO_4^{2-}; 1.1 µmol L^{-1} for $HCOO^-$; 0.8 µmol L^{-1} for $HCCOO^-$ and 1.4 µmol L^{-1} for NH_4^+. The concentration of H^+ was calculated from pH values.

The criterion for quality control of the rainfall samples based on the ionic balance was not applied because bivalent cations such as Ca and Mg were not analysed.

The neutralization of the rain acidity by ammonium was calculated by a neutralization factor (NF) with a cation ration over anions [$NH_4^+ / NO_3^- + SO_4^{2-}$] (Flues et al., 2002). Wet deposition fluxes (F) were estimated by multiplying the VWM concentrations (mg L^{-1}) by the climatological yearly rainfall amount for the region (1564.9 mm per year). F was expressed in mg m^{-2} yr^{-1}. The VWM [(Σ Ci x Vi)/ ΣVi. Ci is the ion concentration and Vi is the rainfall volume of the corresponding rain event sampled] was used in the calculations of seasonal and annual concentration averages.

The back trajectories, arriving every six hours at heights of 10, 100 and 500 m throughout the entire measurement period, were calculated for 96 h with the HYSPLIT model (Hybrid Single Particle Lagrangian Integrated Trajectory) (Steins *et al.*, 2015). Trajectories were calculated online at the website: http://ready.arl.noaa.gov (HYSPLIT.php).

Results and discussion

Measurements of pH and conductivity

Seventy rainwater samples were collected from May 2014 to May 2015 totalling a sample volume of 982.6 mm. The daily values of rainfall varied from 0.36 to 82.0 mm and the highest accumulated rainfall occurred in the summer, and the lowest was observed in the winter (Table 1).

The average pH value for the study period was 5.68 ± 0.43, a typical rainwater value (Coelho et al., 2011). The lowest pH value was recorded in the fall (pH 4.68), but values close to pH 5.0 were observed in all seasons, and the highest pH value was observed in the spring (Table 1). Figure 2 shows the pH frequency distribution (number of cases) where 66% of the samples presented pH between 5.4 to 6.1. Considered as acid rain, 15 events showed pH below 5.4 (21%).

In the same site, from 1998 to 2002, studies on the composition of rainfall showed that 35% of the samples collected in a wet collector were acid (Pelicho et al., 2006). The results then were obtained with a comparison of two types of collectors (bulk and wet-only) and showed different ionic compositions, revealing that the sources that cause precipitation acidity could be anthropic (agriculture, biomass burning, burning of fossil fuels, among others).

In southern Brazil, a study in Candiota/RS, identified the occurrence of slightly acidic precipitation in 42% of the samples analysed. In that case, two types of collectors were used (wet-only and bulk) and the wet-only were more acid than the bulk samples, due to the presence of carbonates and hydroxides that cause neutralization of rain (Migliavacca et al., 2005). In Porto Alegre/RS, also in south Brazil, 22% of the samples were characterized as acid and the remaining samples as slightly alkaline. According to the authors, this may not be related to the lack of precipitation acidity but to the process of neutralization by species such as NH_3 and HCO_3^- (Migliavacca, Teixeira, and Rodriguez, 2012). In Maçarambá/RS, the pH presented seasonal behavior with mean pH evaluated was 5.78. About 33% of the biweekly water samples presented pH values between 4.88 and 5.58 and 20% presented pH between 6 and 6.7 (Momolli et al., 2020).

Rainwater pH in Araraquara/SP, southeastern Brazil, ranged from 4.7 to 6.7 with an average pH of 5.5, and 43% of all samples showed pH below 5.6, which is the value expected for rainwater in clean atmosphere (Oliveira, Figueiredo and Cardoso, 2012). Also in southeastern Brazil, Ribeirão Preto/SP, wet depositions were sampled. The pH mean of the rainwater samples was 4.96 and 84% of the samples showed a pH below the value corresponding to equilibrium with atmospheric carbon dioxide (pH 5.6) (Coelho et al., 2011). In Lavras/MG the pH values ranged from 5.52 to 8.29, with an average of 5.92 and most deposition samples (~94%) were alkaline (pH > 5.6) (Pereira, Fornaro and Vieira-Filho, 2021).

Rainwater conductivity presented a variation from 4.0 to 36.0 µS cm^{-1} and an average of 11.4 ± 6.23 µS cm^{-1}. The highest conductivity occurred in September 2014, spring, and the lowest in July 2014, winter, (Table 1). The rainwater conductivity found in this work was close to that for rainfall samples from Araraquara/SP that ranged from 2.1 to 30.2 µS cm^{-1} (Oliveira, Figueiredo and Cardoso, 2012).

In Londrina (1998 to 2002), the conductivity values varied from 2.5 to 243 µS cm^{-1} with a mean of 24 µS cm^{-1} and showed that the high conductance was due to strong acids (Pelicho et al., 2006). In our study, the highest conductances were caused by alkaline species showing that it is not only the strong acids that influence the measured ionic conductance. The most acidic rains showed conductance in the range of the total mean of the samples identified that was 11.4 µS cm^{-1}.

Table 1. Volume of rainfall (mm), pH and conductivity (µS cm^{-1})

Period	Rainfall (mm)		pH		Conductivity (µS cm^{-1})		Samples number
	Accumulated	Range	Average±SD	Range	Average±SD	Range	
Fall	269	0.43 - 53.1	5.66±0.46	4.68 - 6.33	12.9±5.30	6.70 - 26.0	18
Winter	133	0.36 - 31.3	5.51±0.37	5.00 - 6.50	14.5±9.34	4.00 - 36.0	14
Spring	253	0.64 - 45.1	5.66±0.40	5.01 - 6.59	9.74±5.54	5.10 - 30.0	20
Summer	328	2.71 - 82.0	5.86±0.43	4.90 - 6.49	9.42±3.48	4.30 - 18.0	18
all	983	0.43 - 82.0	5.68±0.43	4.68 - 6.59	11.4±6.23	4.00 - 36.0	70

SD= Standard deviation

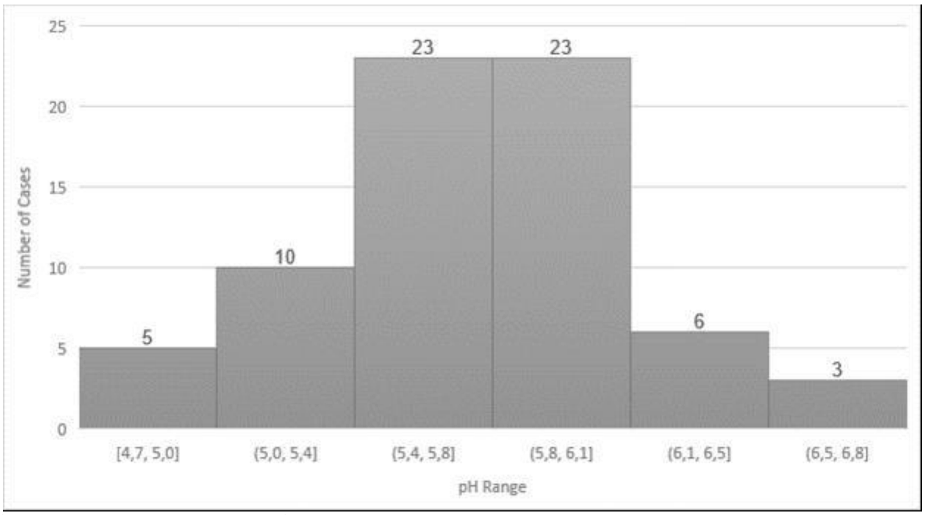

Figure 2. pH frequency distribution of wet deposition samples collected in Londrina, Brazil (May 2014 – May 2015). Source: Authors.

Concentration levels of inorganic and organic ions in rainwater

The VWM concentrations of wet-only rain samples were calculated, and the values obtained in mg L^{-1} were 1.00, 0.71, 0.55, 0.29, 0.24, and 0.20 for H_3CCOO^-, NO_3^-, SO_4^{2-}, $HCOO^-$, Cl^-, and NH_4^+, respectively. The VWM concentrations for the seasons (mg L^{-1}) can be seen in Figure 2. Nitrate was the inorganic ion with the highest concentration with maximum value of 5.44 mg L^{-1} (Winter – Table 2), and it was identified in 60 samples, while ammonium was quantified in 93% of samples analysed. Table 2 shows the mean and range concentration of ions present in the rainwater samples.

Formic and acetic acids are the most abundant carboxylic acids in the troposphere. They interact easily with the aqueous phase and, due to their solubility, they are removed from the atmosphere by rainfall (Pereira et al., 2021). Souza and Carvalho, 2001). Acetate was quantified in 37 of the samples (53% of the rainfall) with VWM highest concentration of 1.9 mg L^{-1}. Format with VWM concentration of 0.65 mg L^{-1} was identified in 19 of the samples, representing 27% of the wet precipitation.

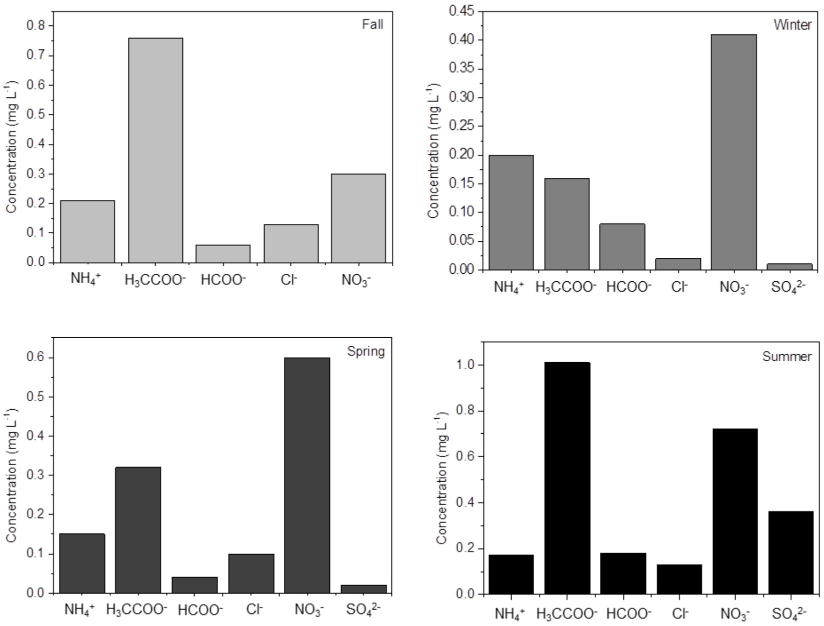

Figure 3. The Volume Weighted Mean (VWM) concentrations of ions (mg L^{-1}) for the seasons Fall, Winter, Spring, and Summer (2014 - 2015) in Londrina, Paraná, Brazil. Source: Authors.

Table 2. Number of samples (N), mean and range concentration of inorganic and organic ions (mg L^{-1}) present in rainwater samples collected in Londrina-Paraná, Brazil (2014 – 2015)

Ions	Fall	Winter	Spring	Summer
	Mean (range) (N)			
NH_4^+	0.21 (0.06 - 0.73) (18)	0.28 (<LD - 1.42) (14)	0.16 (<LD - 0.73) (18)	0.18 (<LD - 0.53) (17)
H_3CCOO^-	1.58 (<LD - 2.16) (8)	1.04 (<LD - 2.71) (4)	0.66 (<LD - 1.19) (9)	1.15 (<LD - 1.60) (16)
$HCOO^-$	0.27 (<LD - 0.45) (2)	0.54 (<LD - 1.60) (4)	0.18 (<LD - 0.30) (6)	0.38 (<LD - 0.83) (7)
Cl^-	0.43 (<LD - 1.42) (9)	0.22 (<LD - 0.37) (4)	0.19 (<LD - 0.49) (12)	0.25 (<LD - 0.34) (13)
NO_3^-	0.90 (<LD - 4.02) (15)	1.17 (<LD - 5.44) (10)	0.90 (<LD - 2.69) (18)	0.99 (<LD - 2.05) (17)
SO_4^{2-}	<LD	0.22 (1)	0.28 (<LD - 0.39) (2)	0.60 (<LD - 0.93) (11)

Detection limit (LD): 0.01 mg L^{-1}
N: number of samples that the species was quantified.
Source: Authors.

For ions (NH_4^+, $HCOO^-$, and NO_3^-) the highest average concentrations were recorded in winter, for H_3CCOO^- and Cl^-, in fall, and most samples where it was possible to quantify SO_4^{2-} ions, in summer (Figure 3 and Table 2). The occurrence of the highest average concentrations, for most ions, was in fall and especially in winter, possibly because they are seasons with lower rainfall volumes, resulting in differences in removal of these species in the atmosphere.

Pelicho et al. (2006) verified that NO_3^-, SO_4^{2-}, Cl^- and NH_4^+ represented about 90% of the investigated ions and their relative abundance, compared to other ions, suggested anthropogenic emissions of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3), associated mainly to vehicular and agricultural activities. Sulphate and nitrate can be present in rainwater mainly in neutralized form. The formation of ammonium salts, particulate material of secondary origin, implies the removal of ammonium and sulphur and nitrogen oxides from the atmosphere.

A study of atmospheric particulate matter carried out in Londrina showed that the possible source of sulphate/sulphur is vehicular, and chloride and nitrate would come from the burning of waste/biomass and industrial activities (Beal et al., 2017; Moreira et al., 2018). Farming activities, intense in the region of Londrina, are potential sources of NH_3 and NH_4^+ and could act as a neutralizing constituent. To verify the contribution of NH_4^+ to the neutralization of NO_3^- and SO_4^{2-}, the neutralizer factor (NF) was calculated through the ratio [$NH_4^+/NO_3^- + SO_4^{2-}$] (Kulshrestha et al., 1995; Flues et al., 2002). For the period 2014-2015, it was found the NF of 0.14 against the NF of 0.34 for the period 1998-2002, due to the decrease of anions compared to NH_4^+.

The presence of ammonium ions in the atmosphere has their origin in animal waste, and in the use of fertilizers in agricultural activities, among others (Coelho et al., 2011; Vieira-Filho et al., 2016; Beal et al., 2021). In addition, some studies have shown that the use of three-way catalysts emits ammonia due to the reduction of nitrous oxide (NO) that occurs when the air / fuel ratio in the combustion process is less than the stoichiometric value (Vieira-Filho et al., 2016). This source cannot be neglected since the study region is close to a highway with a large circulation of vehicles.

Carboxylic acids have photochemical transformations and primary emissions as their main sources. Format might originate from secondary transformations and acetate by different sources of primary emission (Wang et al., 2007). Therefore, format and acetate might originate from different emission sources and the acetate/format ratio can be an indicator of the relative importance of direct emissions (high proportion) and in situ formation by photochemical processes (low proportion). In this study, the acetate/format ratio was 2.62, which may be an indicator of the importance of direct emissions (high ratio) and in situ formation by photochemical processes in the gas phase (low ratio) (Wang et al., 2007; Freitas, Martins and Solci, 2012). Although fuel burning (vehicular) is an important source of acetate and format, the seasonality observed for organic ions indicates that other sources of these species, such as secondary emissions and direct emissions from agriculture, are also possible.

Wet deposition fluxes estimated, considering the climatological rainfall volume and the VWM, for each ion in descending values were: 1565 mg m^{-2} yr^{-1} of acetate, 1111 mg m^{-2} yr^{-1} of nitrate, 861 mg m^{-2} yr^{-1} of sulphate, 470 mg m^{-2} yr^{-1} of format, 376 mg m^{-2} yr^{-1} of chloride and 313 mg m^{-2} yr^{-1} of ammonium. The wet deposition flux of total N (as NH_4^+ and NO_3^-) is 1424 mg m^{-2} yr^{-1}. The presented deposition value for total N shows similar pattern to the value observed of 1440 mg m^{-2} yr^{-1} in the same place (Pelicho et al., 2006). Sulfur and nitrogen wet deposition was mainly from secondary inorganic aerosols (Zhang et al., 2020). The deposition flux for total N appeared to be influenced by potential continental sources as intensive agricultural activity (animal/fertilizer), and biomass and fossil fuel combustion.

Air masses trajectories

Analysing the air masses trajectories that arrived in Londrina, in 39 events the air masses had passed through the southeast and central-west regions (56%), more specifically Minas Gerais and Goiás states. In 43 events, air masses came from the ocean (61%), in 23 from the south (33%), more specifically Rio Grande do Sul and Santa Catarina states and neighbouring countries like Argentina and, in four others the masses showed to be in a steady state in the study region. In the cold months, the air masses at the height of 500 m passed close to the study region and the air masses at the height of 10 and 100 m travelled greater distances. In the warm months, starting in October, the air masses in 10, 100, and 500 m passed through the same regions. It was observed that in the four samples that presented pH below 4.9, the air masses trajectories had a stationary characteristic in the last 24 hours that preceded the rain event. Of the air masses that passed through the ocean that preceded the events and the collection of rain samples, fourteen samples had a pH above 6.1.

On March 27, autumn 2015, the highest concentration of NO_3^- for the season and one of the highest concentrations of Cl^- and H_3CCOO^- was observed (Table 2). In that occasion, the air masses that arrived in the study region came from the ocean (Figure 4). In the winter, more specifically on September 19, 2014, the highest concentrations of H_3CCOO^-, $HCOO^-$, NO_3^- and Cl^- ions were observed and the first three showed the highest concentrations throughout the sampling period (Table 2). On that date, the 10 and 100 m air masses that arrived in Londrina had passed through the coast of Uruguay and Rio Grande do Sul, while the masses in 500 m at 00:00 UTC had passed through northern Argentina, Paraguay, Mato Grosso do Sul and São Paulo states and the one at 12:00 UTC had passed through the southeast region (Figure 4B).

During the period of the air masses trajectories observed in Figures 4A and B, more than 8,200 fires were recorded throughout the country. The air masses that arrived on March 27, 2015, had passed through São Paulo and Paraná states, and had registered 4.5% and 3.6% of fires for the period between 23 and 27 March 2015, respectively (CPTEC/INPE, 2020).

The highest concentration of Cl^- and one of the highest of NO_3^- in the spring was observed on October 20, 2014, and the air masses that arrived in the region came from the ocean (10 and 100 m) and north and west (500 m) (Figure 4C). The higher altitude air masses may be bringing these species from the fires in the north and west, which represent 35% of the outbreaks recorded between 16 and 20 October 2014. Contributions of the fires from the north and west of the country in the composition of the atmospheric particulate matter in Londrina were also observed (CPTEC/INPE, 2020).

In the summer, the highest concentrations of $HCOO^-$ and one of the highest of H_3CCOO^- and Cl^- were observed in the sample collected on January 14, 2015, and the highest concentration of NO_3^- on January 15 of the same year. It can be observed in Figure 4D that the air masses that arrived on January 15 came from the eastern region (10 and 100 m) and northeast of Paraná State (500 m).

Comparison of pH and VWM concentrations of ionic and organic component in rainwater

As showed in Table 3, in Londrina the concentrations of all ions were lower in this study when compared to the values found for the same location in the period from 1998 to 2002. The decreases in SO_4^{2-} concentrations may be related to changes in the composition of the diesel used in Brazil, as in the 1980s the sulphur concentration was 13,000 ppm, decreasing to 500 ppm in 2009 and 10 ppm with S10 diesel in 2012 (ANP, 2014).

In 2016 the bus fleet in the city of Londrina was, on average, five and a half years old and used fuels such as S500 and S10 diesel (and mixed with 8% biodiesel), but the largest amount was S500 (Moreira et al., 2018).

Differences in sulphur concentration in diesel were also verified in studies of atmospheric particulate material carried out in São Paulo city (Bourotte et al., 2007, Vasconcellos et al., 2010; Souza, et al., 2014). In the metropolitan region of Porto Alegre city, there was a decrease in sulphate concentrations in rainwater samples and a decrease in the NO_3^-/SO_4^{2-} ratio in relation to the 1990s. The authors associated that to the use of metropolitan diesel in public transport, which has a lower sulphur content and encourages the use of vehicles powered by ethanol and natural gas (Migliavacca, Teixeira and Rodriguez, 2012).

The highest decreases in the MWM concentrations in this study concerning to previous are for Cl^-, NO_3^-, and SO_4^{2-}, with approximately 62%, 35%, and 35%, respectively. This behavior indicates a reduction in the wet deposition fluxes of N and S, which agrees with the decrease in the gas concentrations (NOx and SO_2) registered in Brazil (Andrade et al., 2017) due to the control of vehicular emissions.

The concentrations of NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} ions found in Londrina are lower than those found in other places like Singapore, Karachi, Zhejiang, Gwangju, Anshun and Newark. The concentrations of H_3CCOO^- and $HCOO^-$ in Londrina for the period 2014 to 2015 were higher in relation to places like Singapore, Karachi, Zhejiang, Anshun and Newark. The burning of biomass, biogenic emissions and direct emissions from vehicles are important sources that favour the emission of acetic acid over formic acid (Coelho et al., 2011). The higher concentration of H_3CCOO^- in relation to the $HCOO^-$ in Brazil is due to the extensive use of ethanol as fuel (Freitas, Martins and Solci, 2012). In this study, the H_3CCOO^- concentration is also higher than in other places (Table 3), possibly because ethanol is not used as fuel in these other places.

Conclusion

Changes on wet deposition of organic and inorganic species could be observed and used to infer about the air quality in Londrina region.

The analysis of the 70 rain events that took place in Londrina city between May 2014 and May 2015 showed an average value of pH 5.68, typical value for rainwater. However, 41% of the samples showed slightly acidic pH values (pH < 5.6), a higher percentage than that found in the same place and period from 1998 to 2002, which was 35%. The mean conductivity value (11.4 $\mu S\ cm^{-1}$) was approximately twice lower than that found for Londrina about 20 years ago.

The VWM concentrations of ionic species for the period were $H_3CCOO^- > NO_3^- > SO_4^{2-} > HCOO^- > Cl^- > NH_4^+$. The highest values of ionic concentration were recorded in the fall and in the winter, possibly because these are seasons with low rainfall volumes. In the spring, the highest concentrations of nitrate and chloride were observed, and could be influenced by the long-distance transport of the fires that occur every year in the north and west of the country.

Sulphate concentrations were lower in this study than those recorded between 1998 and 2002 due to the decrease in sulphur concentrations in the diesel used in the country, and which was also observed in other studies. The extensive use of ethanol as fuel in Brazil favours the emission of acetic acid in relation to formic acid and possibly this is the cause of this species presenting higher concentrations when compared to other places in the world.

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Author Contributions

Rain sampling e analysis were performed by students Carla E. Batista, Ismael R. Amador, Priscila Brugin and Bianca F. de Lima under orientation of Prof. M. C. Solci that participate in all stafe of the work, project administration, resources, validation and writed the original draft. Hysplit date and interpretation were performed by Prof. L. D. Martins and Dr. A. Beal, and writing review and editing.

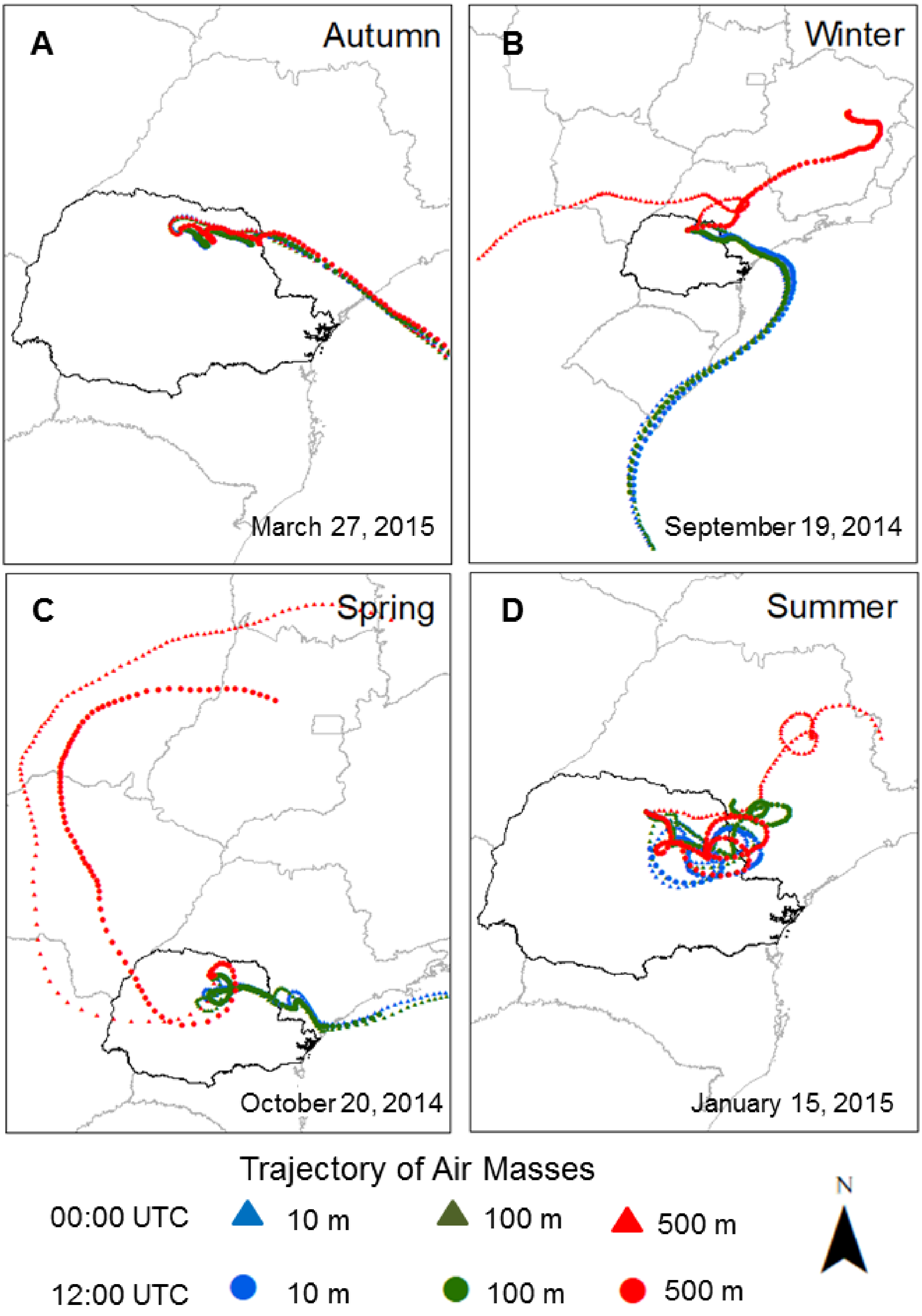

Figure 4. Air mass arrival trajectories (HYSPLIT) of 96 h referring to 00:00 and 12:00 UTC, for the days 27/03/2015 (A), 19/09/2014 (B), 20/10/2014 (C), and 15/01/2015 (D). Source: (HYSPLIT; ready.noaa.gov/HYSPLIT.php (2019).

Table 3. Comparison of pH and Volume-Weighted Mean (VWM) concentration of ionic and organic components of rainwater from different places in the world

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Site	pH	VWM (mg L^{-1})					
		NH_4^+	H_3CCOO^-	$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}
Londrina[a]	5.68	0.20	1.00	0.29	0.24	0.71	0.55
Londrina[b]	5.46	0.22	-	-	0.64	1.10	0.85
Singapore[c]	4.20	0.34	0.06	0.09	1.21	1.38	4.01
Karachi, Pakistan[d]	6.84	2.21	0.55	0.22	8.58	1.68	19.06
Zhejiang, China[e]	4.74	-	0.23	0.43	-	-	-
Gwangju, Korea[f]	5.78	1.13	-	-	4.38	2.28	4.41
Anshun, China[g]	5.34	-	0.41	0.39	-	-	-
Newark, USA[h]	4.57	0.44	0.21	0.20	0.38	0.89	1.83

[a]This study; [b](Pelicho et al., 2006); [c](Hu et al., 2003); [d](Masood et al., 2018); [e](Niu et al., 2018); [f](Chon et al., 2015); [g](Zhang et al., 2011); [h](Song & Gao, 2009). Source: Authors.

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